

AD721288

AD

TECHNICAL REPORT
71-33-PR

THE THERMAL CONDUCTIVITY
OF
NATURAL RUBBER FROM 134 TO 314°K

by

Malcolm N. Pilsworth, Jr.

Harold J. Hoge

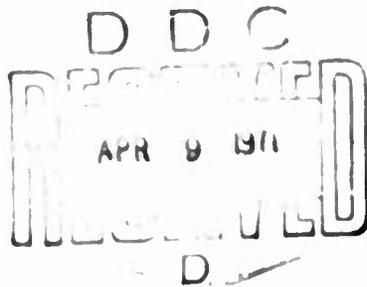
U.S. Army Natick Laboratories,
Natick, Mass.

and

Henry E. Robinson

National Bureau of Standards,
Washington, D.C.

January 1971

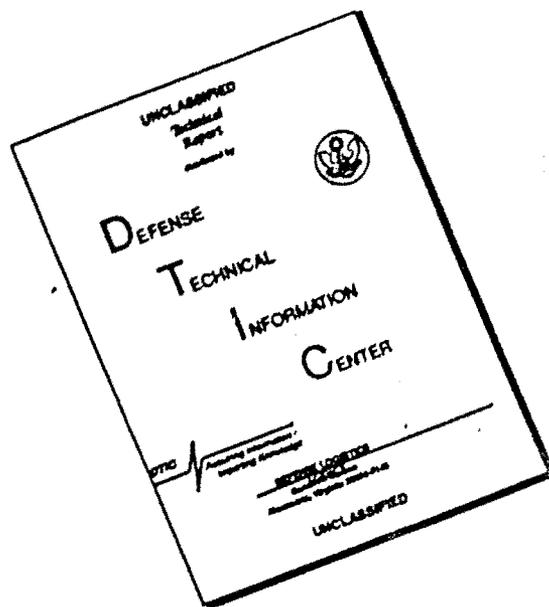


UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760.



Pioneering Research Laboratory

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

This document has been approved
for public release and sale; its
distribution is unlimited

AD _____

TECHNICAL REPORT
71-33-PR

THE THERMAL CONDUCTIVITY OF NATURAL RUBBER
FROM 134 TO 314°K

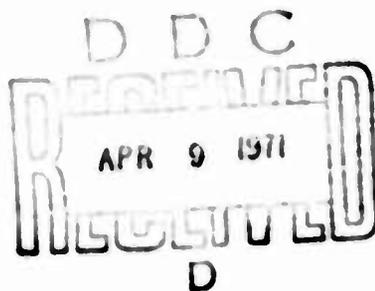
by

Malcolm N. Pilsworth, Jr.
Harold J. Hoge
U. S. Army Natick Laboratories

and

Henry E. Robinson
National Bureau of Standards, Washington, D.C.

Project Reference:
1T061102BLLA-07



January 1971

Pioneering Research Laboratory
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760.

Foreword

There are many compilations of numerical data for scientific and engineering use. The accuracy of these data is in many, perhaps most, cases adequate for technical applications. There are exceptions, however, and when one takes the trouble to look up the numerical data on some property it is surprising how often he finds that there is hardly any really good data, only a little of average quality, and much more that has almost no value at all. This was the case with natural rubber when one of the present authors took part in a critical survey of data on its thermal conductivity a few years ago. The present investigation is an attempt to improve the situation found at that time, and to confirm the behavior of the thermal conductivity in the neighborhood of the glass transition.

CONTENTS

	<u>Page</u>
List of Figures	iv
List of Tables	iv
Abstract	v
1. Introduction	1
2. Preparation of Samples; NBS Measurements	2
3. Thermal-Conductivity Apparatus (NLABS)	5
Test assembly	5
Test chamber	10
Auxiliary cold-plate assembly	10
Thermocouples and resistance thermometer	10
4. Measuring and Control Equipment (NLABS)	12
Power and temperature difference	12
Automatic guard-ring control	14
Top guard and spacer	16
Automatic cold-plate control	16
5. Experimental Procedures (NLABS)	17
Determination of λ	17
Determination of sample thickness	19
6. Results (NLABS); Discussion	20
7. Comparison with Previous Results	25
8. Acknowledgments	26
9. References	27

List of Figures

	page
Fig. 1. Thermal-conductivity apparatus used at NLABS.	6
Fig. 2. Details of test chamber and test assembly.	7
Fig. 3. Thermal conductivities determined in the present investigation (NLABS and NBS), with data of previous investigators for comparison.	23

List of Tables

Table 1. Thermal conductivity and related data for the two sets of samples. NBS measurements.	4
Table 2. Thermal conductivity of natural rubber. NLABS measurements.	21

Abstract

The thermal conductivity of soft natural rubber, compounded and vulcanized as specified in ASTM recipe 2A, has been measured over a range extending from well below the glass transition to above room temperature. The glass-transition temperature deduced from the thermal-conductivity measurements is 212°K (-78°F). Most of the measurements were made at the Natick Laboratories in a guarded-hot-plate apparatus, with silicone rubber pads on either side of the sample. The rest of the measurements were made at the National Bureau of Standards with apparatus and procedures that have been used for many years in reference-standard work. The thermal-conductivity data are believed to be accurate to 3% or better at room temperature and to about 6% at the glass transition and below.

1. Introduction

A number of investigations of the thermal conductivity of soft, vulcanized natural rubber have been published. The wide scattering of the data makes it evident at once that some of the published data are unreliable. The remaining data, which appear to be reasonably accurate, have two defects: (1) many investigations cover only a limited temperature range, and (2) the vulcanizing procedure and the compounding ingredients present in the rubber are often not fully specified. In many cases the missing information was probably not known to the investigator. Recently a critical survey [1] of the thermal conductivity (λ) of rubber was made at the U. S. Army Natick Laboratories (NLABS); this survey shows the situation that existed when the present work was undertaken. The only investigation showing the glass transition was that of Eiermann and Hellwege [2], who used a quasi-steady-state method in which the rate of temperature rise of a heat reservoir (copper block) was observed. Such an experimental arrangement is well suited to studying the changes in thermal conductivity that occur at the glass transition (T_g) but it cannot be expected to give as good accuracy as more conventional, slower, steady-state methods.

It was therefore decided to prepare rubber samples of known and controlled composition, and to have a few measurements of their thermal conductivity made at the National Bureau of Standards (NBS) for reference and standardizing purposes. A more extensive study of λ , especially of its temperature dependence was then to be carried out by NLABS. The investigation has now been completed. The present report contains the results of both studies with descriptions of the apparatus, procedures, and the preparation of the samples.

2. Preparation of Samples; NBS Measurements

Two sets of samples of rubber were prepared at NBS, the first (Batch 8849) in 1964 and the second (Batch 9791) in 1966, by G. W. Bullman of the Rubber Section. Both sets of samples were prepared according to recipe 2A of the American Society for Testing and Materials [3] and were cured as specified for that recipe. Dr. Lawrence A. Wood, consultant on rubber at NBS, recommended this choice after discussing the problem with us. The recipe yields a typical soft vulcanized natural rubber. We hope that others who wish to work with a rubber of this general type will, whenever possible, choose the same composition and vulcanizing procedure, as specified by the ASTM. If this is done, the comparison of data taken in different laboratories and on different specimens will become more meaningful.

Recipe 2A contains, in parts by weight

raw rubber	100
sulfur	2.5
benzothiazyl disulfide	1
zinc oxide	5
stearic acid	2
phenyl beta naphthylamine	1.

The specified vulcanizing conditions are 30 minutes at 140°C (284°F).

The first set of samples consisted of 6 pieces, each nominally 8 x 8 x 1/2 inch. They were assigned the numbers 1 to 6. The second set also consisted of 6 pieces, each nominally 8 x 8 x 1/4 inch. They were assigned the numbers I to VI. Measurements were made at NBS on various combinations of pieces 1 to 6. The results are given in Table 1. Each NBS measurement of λ requires two samples, one on each side of the hot plate. Normally each sample was a single piece 1/2 inch thick but in one run 2 pieces, each 1/2 inch thick, were used on each side

of the hot plate. After measurement, two pieces (3 and 4) were sent to NLABS. Only one run was made on the second set of samples, which were made up at a later time. The results are given in the last line of Table 1. As indicated in the table, 3 pieces, totaling a little less than 3/4 inch in thickness, were placed on each side of the hot plate. Pieces III and IV were sent to NLABS but were not measured there.

The thermal conductivities in Table 1 have been corrected for plate-rubber end-effects by simultaneous solution of the uncorrected data for 1/2-inch and 1-inch specimens. For the 1/2-inch specimens the corrected λ -values are 2.6% higher than the uncorrected; for the 1-inch specimens the corrected value is 1.2% higher than the uncorrected; for the 3/4-inch specimens the corrected value is 1.7% higher than the uncorrected.

The apparatus and procedures used in the NBS measurements are those that have been in use for more than 15 years for thermal-conductivity reference-standard measurements. They conform to ASTM Standard C177-63, paragraph 4. (h) for testing rigid specimens [4]. In all cases the actual thickness of the test specimen was determined as part of each measurement of λ . The thickness was measured with the sample in place in the apparatus, at the temperature of the test, and with the same pressure exerted on the sample as during the test. Discussion of the NBS results is given in Section 6.

Table 1. Thermal conductivity and related data for the two sets of samples. NBS measurements.

Pieces Tested	Mean Temperature		Thermal Conductivity		Temperature Gradient		Specimen Thickness		Density	
	°F	°K	Btu. in. hr ft ² °F	mw cm cm ² °K	°F in.	°K cm	in.	cm.	lb. ft ³	g cm ³
1 & 6	70.3	294.4	1.064	1.534	39.6	8.66	0.478	1.214	61.8	0.990
2 & 5	70.4	294.5	1.065	1.535	39.6	8.66	0.480	1.219	61.8	0.990
3 & 4	18.5	265.6	1.068	1.539	40.6	8.88	0.472	1.199	62.7	1.004
	69.7	294.1	1.066	1.536	40.8	8.92	0.478	1.214	61.9	0.992
2, 3 & 4, 5	129.8	327.5	1.059	1.526	41.2	9.01	0.487	1.237	60.8	0.974
	72.2	295.5	1.065	1.535	38.6	8.44	0.963	1.176	61.6	0.987
I, III, V & II, IV, VI	70.1	294.3	1.067	1.533	48.7	10.65	0.685	1.740	61.9	0.992

3. Thermal-Conductivity Apparatus (NLABS)

The thermal-conductivity apparatus used at NLABS is shown in Fig. 1. It consisted of a sealed cylindrical test chamber having a copper bottom that served as a cold plate. Below the cold plate was an auxiliary cold plate and equipment for maintaining both cold plates at the desired temperature for a test. The test chamber and the auxiliary cold plate assembly were bolted together as shown and placed inside an "immersion chamber" which in turn was placed inside a metal Dewar-flask. The space between the immersion chamber and the inner wall of the Dewar flask was filled to a suitable depth with liquid nitrogen. Usually a level about 2 inches above the bottom of the immersion chamber was convenient, but under some circumstances it was desirable to increase the 2-inch distance to about 6 inches.

Test Assembly. Inside the test chamber was the test assembly, which is indicated only schematically in Fig. 1. For details of the test chamber and test assembly see Fig. 2. Beginning at the cold plate and working upward, the test assembly is seen to comprise the lower pad, the sample, the upper pad, the hot-plate-guard-ring, the spacer, the insulating gap, the top guard, and finally the compressing springs. The compressing springs are not shown in Fig. 2; one of them is shown in Fig. 1.

The sample was a disk-shaped piece of rubber about 6.5 inches in diameter and about 1/2 inch thick. Pads were used on both sides of the sample to insure good thermal contact with it and to promote uniform heat flow. The use of pads is especially important near and just below the glass-transition, where the sample becomes hard but where the pads remain relatively soft. If the hardening is accompanied by any warping, an air layer could be formed that might cause serious error. Silicone rubber pads 1/8 inch thick were used in Run 450 and in all

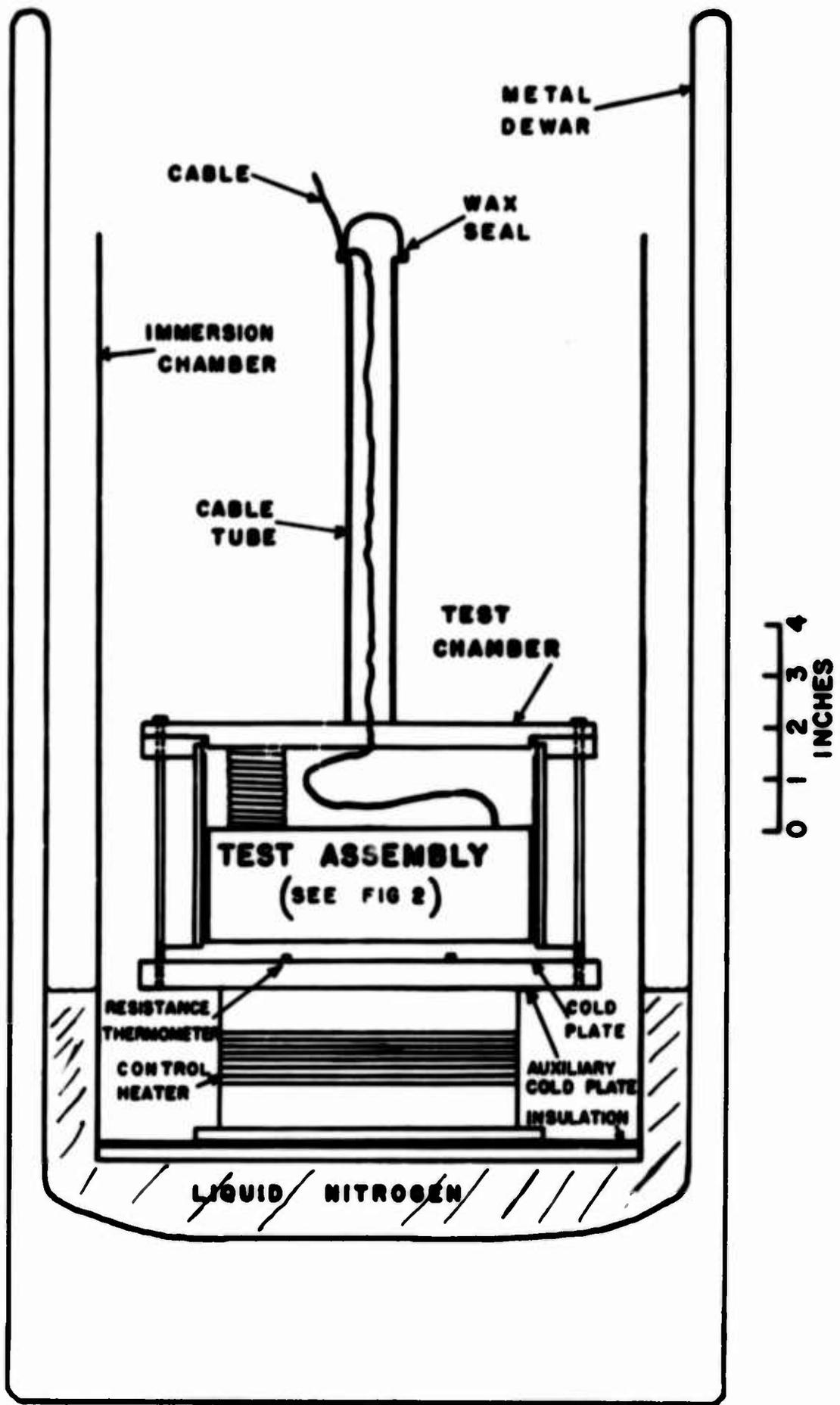


Fig. 1. Thermal-conductivity apparatus used at NLABS.

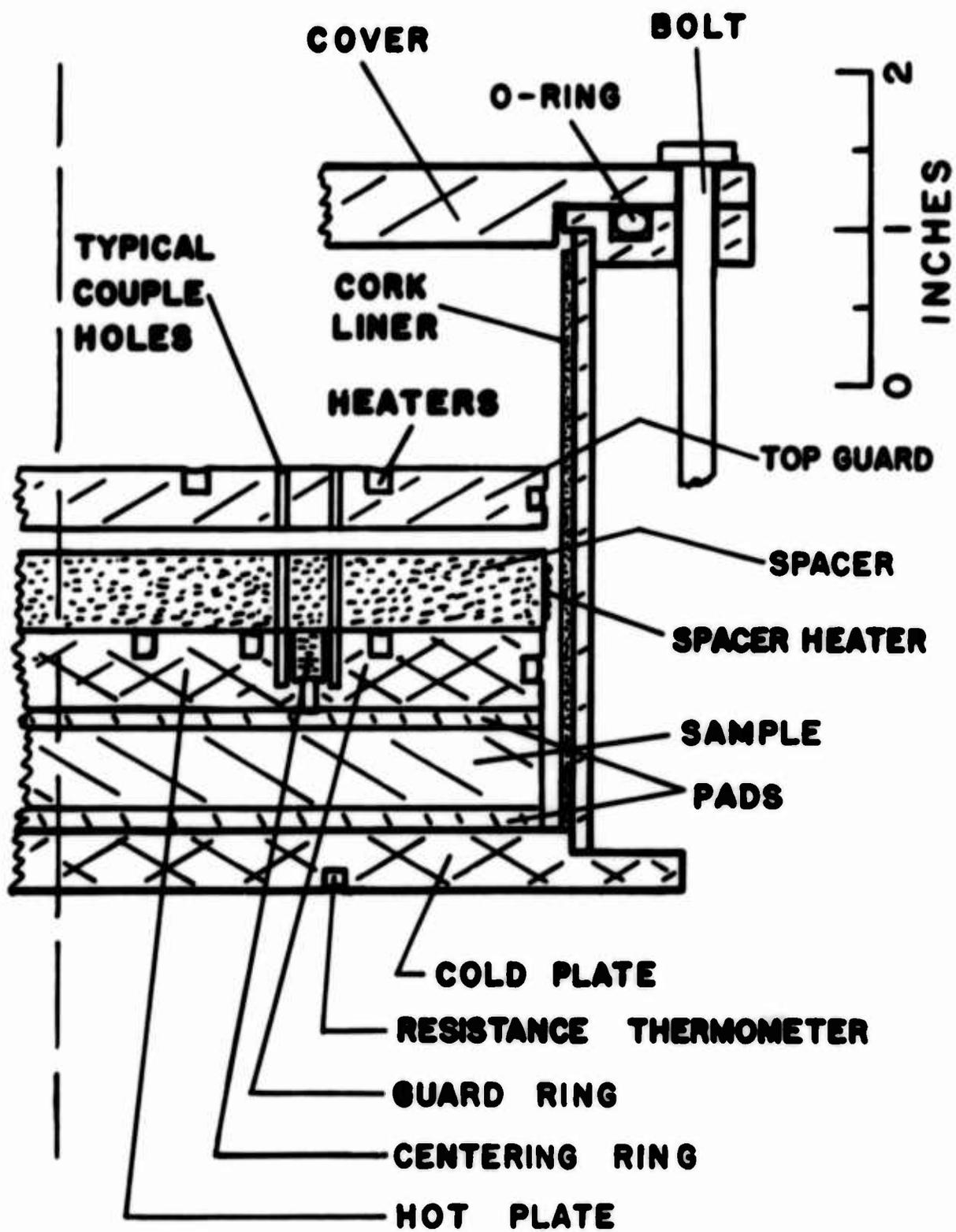


Fig. 2. Details of test chamber and test assembly.

subsequent runs. All of the runs below the glass transition and two of those above it were made with silicone-rubber pads. The 5 remaining runs were made before the silicone-rubber pads were obtained. In these runs the pads were of 1/8-inch rubber similar to the sample being measured. The silicone pads were Dow-Corning Silastic 651; this composition was chosen because of its low brittle temperature, which according to the manufacturer is -178°F (156°K). The glass-transition temperature may be expected to lie near or somewhat below the brittle temperature. Since the reported measurements extend down to 134°K there is a region of about 20°K in which the pads themselves (or at least the lower pad) may have been too hard to perform their function well.

The hot plate and its guard ring were of copper 0.481 inch thick. They were held in their proper relative positions by a bakelite centering ring. As shown in Fig. 2 this ring was flush with the upper surface of the hot plate and guard ring but did not extend to the lower surface. The empty slot below the centering ring served to minimize heat flow between the hot plate and the guard ring. It was 1/16 inch wide and 3/16 inch deep. In calculating λ , the effective area of the hot plate was assumed to extend to the middle of the slot. With this assumption the effective diameter of the hot plate was 3.375 inches (8.572 cm) and its effective area was 8.946 in^2 . (57.71 cm^2). The hot plate contained two circular heater grooves, each 0.125 inch wide x 0.188 inch deep and positioned as shown. The two constantan heater-windings were imbedded in epoxy resin; they were connected in series (47 ohms total) and had one current and one potential lead connected to each end of the combination. The guard ring also contained two circular grooves with heaters; it was similarly wired except that the potential leads were omitted (total guard heater resistance 35 ohms).

Above the hot-plate-guard-ring was a spacer disk of 1/2-inch bakelite. A heater of 84 ohms resistance was wound on the peripheral surface of the spacer. This heater was added after preliminary tests had shown that it was necessary if accurate results were to be obtained.

The insulating gap just above the spacer was about 0.150 inch wide. It was produced by washers placed on the screws that held the top guard to the spacer. The gap was partially filled with styrofoam to prevent convection. The gap was introduced to see if it would improve the data, but it had no noticeable effect and would be omitted if the apparatus were to be reconstructed.

The top guard was made from a sheet of 3/8-inch brass. As shown in Fig. 2 there were two heater grooves in the top surface and one in the peripheral surface. The three heaters were in series (total resistance 51 ohms).

The three compressing springs were placed between the top guard and the cover of the test chamber. From the measured constants of the springs and their estimated compression it was calculated that they together exerted a force of about 40 pounds on the top guard and the parts below it. Adding 4 pounds for the weight of the hot-plate-guard assembly, the pressure exerted on the sample was calculated to be about 1.3 psi.

The test assembly was put together in such a way as to avoid any path for metallic heat conduction between the top guard and the hot-plate-guard-ring. Each of these elements was fastened to the spacer disk by a separate set of machine screws. The screw heads were recessed when necessary to avoid metallic contact. In addition the tapped holes in the hot-plate-guard-ring did not go all the way thru, so there were no holes in the surface that contacted the upper pad.

Test chamber. The test chamber had a copper bottom 3/8-inch thick (the cold plate), a wall of 7-inch o.d. brass tubing, and a cover of brass 1/2-inch thick. A heavy brass flange soldered to the wall contained a groove with an O-ring; the O-ring gave a vacuum-tight seal for the test chamber at room temperature and down to about 215°K. Measurements in atmospheres of air and of helium were anticipated but were not made because the O-ring seal began to leak below about 215°K, presumably because it had become hard. Hence the test chamber contained air at atmospheric pressure during all of the measurements, altho there were a few occasions when measurements made in a helium atmosphere would have been helpful.

Auxiliary cold-plate assembly. The auxiliary cold-plate assembly consisted of two brass plates and a brass tube (6 inches o.d. x 1/16-inch wall x 3 inches long) soldered together as shown in Fig. 1. The brass tube served as a thermal resistance between the cold plates and the bottom of the immersion chamber, which was at the temperature of liquid nitrogen (77°K). Additional thermal resistance was supplied by underwear material (4 to 8 layers) that was located between the bottom of the immersion chamber and the lower brass plate. The brass tube carried a heater (270 ohms) with which the upper brass plate (the auxiliary cold plate) was maintained at the desired temperature.

Thermocouples and resistance thermometer. The temperature drop across the sample proper was measured with a 6-power copper-constantan thermopile with 6 junctions located between the sample and the lower pad and the remaining 6 located between the sample and the upper pad. The junctions were positioned, within the area covered by the hot plate, at varying distances from the center. The thermopile was of bare 5 mil wire (AWG 36). The various pieces of copper and constantan were threaded thru holes in the edges of the test specimen before they were soldered

together to make the junctions, so that the thermopile was firmly fixed to the test specimen. Small wire was used because of the possibility that the wires and their junctions would produce air pockets between the sample and the pads. By using the smallest practical wire size these pockets were kept small and any errors associated with them were minimized.

A second 6-power copper-constantan thermopile was used to indicate any difference between the temperature of the guard ring and that of the hot plate. Six of the junctions were sealed in holes in the hot plate and the remaining six were sealed in adjacent holes in the guard ring (Fig. 2 shows typical holes). The signal from this thermopile was used for automatic control of the guard-ring temperature, as will be described later.

A 3-power copper-constantan thermopile was used to indicate any difference between the temperature of the top guard and that of the guard ring. The junctions were cemented in holes in the two guards as described above.

The hot-plate and the cold-plate temperatures could each be determined independently. One and preferably both of these temperatures are needed to establish the mean temperature of a measurement. Hot-plate temperatures were measured by a 6-power copper-constantan thermopile with half its junctions in the hot plate and the other half in ice. Cold-plate temperatures were determined in the same way except that a single-power couple was used.

There was also a nickel resistance thermometer of 4 mil wire (AWG 38) mounted in a circular groove cut in the bottom of the cold plate. The thermometer consisted of about 150 turns imbedded in clear glyptal lacquer. It was calibrated against the thermocouple and the signal from it was used for automatic control of the cold-plate temperature. The thermometer had an ice-point resistance of about 392 ohms and appeared to be quite stable.

A single copper-constantan thermocouple was used to indicate any difference between the temperature of the spacer disk and that of the guard ring. One junction was placed in a hole drilled in the spacer disk, near the top, and about 3/8-inch from the surface where the spacer-heater was located. This junction was referred to one of the junctions of the top-guard-guard-ring system.

The wires leading to the various heaters, thermopiles, and thermocouples were collected into a cable that was coiled in the space directly above the top guard before it left the apparatus. The length of the coiled portion was about 5 feet. Thermocouples were imbedded in the cable, in the end near the test assembly, and a heater was wound on the cable. By using the heater and thermocouples, the cable could be brought quite close to the temperature of the hot-plate and its guards. However, tests showed that the values of λ obtained were not affected by the use or non-use of the cable-tempering system; hence the use of the tempering system was discontinued. The constantan wires in the cable were 0.010 inch in diameter. The copper wires were 0.008 inch in diameter except the current-carrying wires, which were 0.011 inch in diameter.

4. Measuring and Control Equipment (NLABS)

Power and temperature difference. The electrical quantities required in the determination of λ were all measured with a Leeds & Northrup Type K-3 potentiometer. The power supplied to the hot plate was found from the current in the heater and the voltage across it. Current was found from the voltage drop across a calibrated 1-ohm standard resistor. Voltage was measured on the potentiometer by using a 15,000-ohm volt box of 100 to 1 ratio, corrected to include the resistance of the potential leads that connected it to the hot-plate heater. In a selected typical set of measurement we observed:

$$E = 4.272V, I = 0.09068A, P = EI = 0.3874W.$$

The temperature of the hot plate was determined from the emf of the 6-power thermopile connected between it and the ice bath. The temperature of the cold plate was determined from the emf of the single-power thermocouple connected between it and the ice bath. Both emf's were read on the K-3 potentiometer. The mean temperature of the hot and cold plates was taken as the mean temperature of the sample. This assumes that the temperature drops across the upper and lower pads are equal. The accuracy with which the temperatures of the hot and cold plate were determined was adequate, but it was considerably less than the accuracy with which ΔT , the temperature drop across the sample, was determined. The drop ΔT was determined from the emf of the 6-power thermopile with junctions between the sample and the adjacent pads.

Power for the hot plate was supplied by a Sorensen Nobatron E28-5 power supply. This unit supplies up to 5 amperes dc at 28 volts. It is just as satisfactory as storage batteries and much more convenient altho a few minor troubles developed. The variable resistor (30 ohms, 4 watts) with which the output voltage could be adjusted between 26 and 30 volts became unsteady. Another resistor from a different manufacturer developed the same trouble. Hence, since voltage adjustment at this point was not required, the adjustable resistor was replaced by a fixed resistance of 16 ohms. This gave a steady output of about 28 volts. Some unsteadiness was also traced to the load-compensating resistor but this could be cured by scrubbing the brush of the resistor back and forth.

Regardless of the condition of the power supply, fluctuations in the hot-plate current will occur unless the controlling resistances are of the highest quality. Resistors with movable brushes are not sufficiently steady. A bank of highly stable control resistors was

made up from fixed power-resistors connected in series, and so arranged that any resistor could be shorted out by closing a copper knife-switch. The control bank consisted of 15 resistances totaling 1090 ohms, and permitting variation in steps of 1/8 ohm. A permanent protective resistance of 7.5 ohms was left in the circuit at all times. With the hot-plate heater resistance of 47 ohms, this limits heater current to about 1/2 ampere.

The hot-plate current was monitored continuously by a recorder, using the potential drop across the same 1-ohm resistor used in measuring I. Provision was made to disconnect the recorder whenever I was measured on the K-3 potentiometer, but the disconnecting was found to be unnecessary. To permit small fluctuations in I to be observed on the recorder chart, most of the signal was bucked out by a steady emf from a converted Rubicon Type B potentiometer. With this arrangement the full width of the 10-inch recorder-chart typically corresponded to a change of only 4% in the current.

A steady heating current is very important when accurate measurements of thermal conductivity are to be made. The use of a recorder to monitor the current substantially eliminated one possible source of error in our work. Usually the current was very steady but on some occasions (fortunately not often) the current would fluctuate badly, possibly as a result of fluctuations in line voltage. By observing the recorder it was usually possible to compensate for these changes manually and save a run that might otherwise have been wasted.

Automatic guard-ring control. The guard ring must be held at the temperature of the hot plate so that no heat will be exchanged between them. This was accomplished by adjusting the current supplied to the guard-ring heater, which was DC drawn from the Nobatron power supply. An automatic controller was used to maintain this current at the required average value.

The signal from the 6-power hot-plate-guard-ring thermopile was detected by a Honeywell 104 WIG null detector. The output of this detector, taken from its output meter circuit, was fed to a magnetic amplifier (Sigma 8205K3P-93270; 2500/2500 DA). This amplifier contained a relay that controlled the power supplied to the guard-ring heater. Control was effected by shorting out a small resistance connected in series with the heaters.

Proportional control based on the Gouy principle was obtained by applying a second input to the magnetic amplifier. The amplifier had two input windings, so that the two inputs could be kept electrically separate. The second input was a more or less sinusoidal voltage with a period of about 5 seconds, with an amplitude sufficient in normal, steady-state operation to override the error signal from the thermopile. In steady-state operation the relay opened and closed with the period of the sinusoidal voltage. Normally the open periods and the closed periods of the relay were about equal, but if the guard ring became too cold, the signal from the thermopile caused the closed periods to lengthen and the open periods to shorten until the guard-ring temperature was restored to the proper value. Without proportional control produced by superposition of the oscillatory signal the guard-ring temperature would have hunted above and below the hot-plate temperature with an unacceptably large amplitude.

The control system was quite satisfactory and saved a great deal of operator fatigue. A more complete description of it is given in reference [5]. It involves a Wien bridge oscillator circuit that could perhaps be replaced by a more sophisticated modern circuit such as the one described by Jewell [6]. Zero-stability of electronic devices is often a problem. In the present equipment the zero of the thermopile signal was monitored by a mechanical galvanometer of sensitivity 2.08 mm/ μ V, connected in parallel with the null detector. When the controller was in operation the periodic rise and fall in guard-ring

current caused a barely detectable oscillation of the galvanometer spot. However, zero-instability of the electronic equipment caused the spot to wander slightly and it was necessary to make an electrical adjustment every 10 minutes or so in order to keep the galvanometer spot within 2mm (1 μ V) of perfect balance. At mid-range of the data (225°K) a thermopile output of 1 μ V corresponds to a temperature difference of 5 mdeg between the hot plate and guard ring. Assuming an average difference of half this, the automatic controller does a considerably better job than a manual controller is likely to do.

Top guard and spacer. Manual control of the top guard and spacer temperatures was used. The output from the top-guard thermopile was continuously observable on a galvanometer of sensitivity about 2mm/ μ V. The output of the spacer couple was observed only about once an hour. Both outputs were kept at zero by manual adjustment of their appropriate heater currents. Power-line AC was used, stepped down by Variac transformers and with provision for fine control. Automatic control of the top guard would have been a convenience, but is much less important than automatic control of the guard ring.

Automatic cold-plate control. The resistance thermometer mounted in a groove in the cold plate (Fig. 1) formed part of a Wheatstone bridge. The (DC) unbalance signal from this bridge was applied to a Leeds & Northrup Speedomax G recorder fitted with controller contacts. Current to hold the cold plate near the desired operating temperature was supplied to the heater (Fig. 1) by a Variac transformer connected to the AC power line. As the temperature of the cold plate increased thru the control point, the current to the heater was given a step-wise reduction. As the cold-plate subsequently cooled, the opposite change in current was made. The result was a steady hunting of the cold plate above and below its mean temperature. Because of the considerable

thermal separation between the heater and the resistance thermometer the amplitude of the hunting was appreciable (± 20 millidegrees). However, the mean temperature was held constant within 10 mdeg during any one rating period (2 to 4 hours) and since the oscillations appeared to have no adverse effects on the data we did not bother to eliminate them.

The cold-plate temperature-control system was affected by the level of liquid nitrogen in the Dewar flask. To get good control it was necessary to add liquid nitrogen about every 30 minutes during a rating period.

In the measurements now being reported (mean temperatures from 134 to 314°K) the cold-plate automatic control system operated satisfactorily at temperatures ranging from 128 to 306°K. It appeared that this range could have been extended in both directions.

5. Experimental Procedures

Determination of λ . In making an experimental determination of thermal conductivity, the first step was to bring the cold plate to the desired temperature; usually this was done by putting liquid nitrogen in the lower part of the Dewar flask. The second step, which usually was begun somewhat before the cold plate had reached its operating temperature, was to bring the temperature drop from hot plate to cold plate to the desired value by adjusting the power supplied to the hot-plate and guard circuits. When these adjustments had been made and the rate of change of ΔT , the temperature drop across the sample, had become small, the rating period was begun.

During the rating period the power supplied to the hot plate was held constant and ΔT was allowed to seek the value corresponding to this power. At intervals of 30 minutes or less, readings were made of the hot-plate voltage and current and of ΔT . If the current had changed

appreciably from its previous reading it was brought back to the accepted value. Since the heater resistance remained constant this procedure kept the power constant. From each set of readings, λ was computed, using the equation

$$\lambda = \frac{P}{A} \frac{\Delta x}{\Delta T} \quad (1)$$

where P is the power to the hot plate, A is its effective area, and Δx is the sample thickness.

Our criterion for an acceptable rating period was that the successive measured values of k should change by less than 1% during a time of at least 3 hours. Usually the change during a rating period was considerably less than 1%. When the initial choice of P was such as to produce too large a drift, the value of P was sometimes readjusted, but the old rating period was abandoned and a new rating period was begun at the time of the adjustment. Our experience has indicated that a rating period of 3 hours is more than sufficient when all goes well; in a few instances measurements of λ based on shorter rating periods were accepted.

In a typical run (No.459) the hot-plate temperature was -46.82°C and the cold-plate temperature was -54.36°C , from which the mean temperature was -50.59°C (222.6°K). The output of the 6-power thermopile across the sample had an average value of $1036.3 \mu\text{V}$. Anticipating that ΔT would be about 5° , the emf table [7] was entered at -48 and -53°C ; for the interval between these two temperatures the thermo-electric power of copper-constantan was found to be $33.6 \mu\text{V}/^{\circ}\text{K}$. Hence ΔT was $1036.3 \div (6 \times 33.6) = 5.140^{\circ}\text{K}$. Note that the 5-degree interval for which the thermoelectric power was computed is the interval most nearly centered on the mean temperature of the run. Most of the measurements now being reported were made with $\Delta T = 5^{\circ}\text{K}$. A few measurements were made with $\Delta T = 10^{\circ}\text{K}$, but this value is too large in regions where λ may be changing

rapidly with temperature, as it does near T_g .

Note that in the above example the temperature drop from hot plate to cold plate was 7.54°K whereas ΔT was only 5.140°K . The difference between these two values, 2.40°K , is the temperature drop across the silicone-rubber pads. Since rough values of the thickness of the pads were available, we attempted to calculate λ for the pads. It appeared, however, that the overall drop from hot plate to cold plate was less accurately known than the drop across the sample, probably because of the roundabout way in which it was determined and the use of only a single couple on the cold plate. In any event, some preliminary data taken on natural-rubber pads appeared to be of relatively low accuracy so it was decided not to include our data on the silicone-rubber pads.

Determination of sample thickness. A set of separate experiments was made to determine sample thickness as a function of temperature. The sample (Piece No.4) was placed in the apparatus between the hot and cold plates without pads. The position of the hot-plate assembly was then determined by making depth-gage measurements at 3 holes in the cover of the test chamber. This made it possible to measure changes in sample thickness. The actual thickness of the sample at room temperature (taken as 298°K) was determined primarily from a number of measurements made with the sample outside the apparatus, with some weight given to thicknesses obtained by using calibrating blocks in place of the sample, between the hot and cold plates. The calibration readings made it possible to convert depth-gage readings directly into sample thicknesses.

The thickness at 298°K was found to be 0.482 inch (1.224 cm). Measurements in the apparatus were made at room temperature and also at 271 , 241 , and 217°K , from which the linear thermal expansion coefficient was found to be 0.00024 per $^\circ\text{K}$. Note that we made no measurements of thickness or expansion coefficient below the glass transition because

we feared that the sample might warp slightly as it was cooled thru T_g ; this would invalidate any data we might obtain. Bekkedahl [8] measured the volume-expansion coefficient of some rubbers similar to ours, both above and below T_g . The linear-expansion coefficients corresponding to his values are 0.000217 above T_g and 0.000073 below T_g . The **difference** between our value of 0.00024 and Bekkedahl's value of 0.000217 is within the experimental error of our measurements. This made it reasonable to accept Bekkedahl's value below T_g where we had no measurements. Having decided to use his expansion coefficient below T_g , we decided in view of the small difference mentioned above to use his expansion coefficient (rounded off) above T_g also. Thus we calculated thickness from the following equations:

$$\Delta x = 1.201 [1 + 0.00022(T - T_g)] \quad (2)$$

(above T_g)

$$\Delta x = 1.201 [1 + 0.00007(T - T_g)] \quad (3)$$

(below T_g)

where $T_g = 212^\circ\text{K}$ and Δx is in cm.

6. Results (NLABS); Discussion

The experimental data obtained at Natick Laboratories are given in Table 2. All of these measurements were made on a disk cut from piece No.4 of the first set of samples (see Table 1). In some preliminary measurements a disk cut from piece No.2 was measured, and a few measurements were made on both these disks together. The results are not reported because the apparatus was in its shake-down period at the time and the results were less accurate than those being reported. These measurements showed no evidence of differences in thermal conductivity between pieces 3 and 4. No primary NLABS measurements were made on any of the second set of samples, the set that were 1/4 inch thick.

Table 2. Thermal Conductivity of Natural Rubber. NLABS measurements.

Test No.	Mean Temperature		Thermal Conductivity		Temperature Gradient		Thickness	
	°F	°K	$\frac{\text{Btu in}}{\text{hr ft}^2 \text{°F}}$	$\frac{\text{mw cm}}{\text{cm}^2 \text{°K}}$	$\frac{\text{°F}}{\text{in}}$	$\frac{\text{°K}}{\text{cm}}$	in	cm
474	-217.7	134.5	0.961	1.386	20.0	4.37	.470	1.195
473	-200.7	143.9	0.975	1.406	20.0	4.38	.471	1.195
470	-183.5	153.5	0.996	1.435	19.8	4.33	.471	1.196
465	-170.1	160.9	1.024	1.476	20.7	4.52	.471	1.197
475	-164.6	164.0	1.016	1.464	19.5	4.26	.471	1.197
464	-151.6	171.2	1.039	1.497	20.7	4.54	.472	1.198
463	-151.6	171.2	1.033	1.488	20.6	4.50	.472	1.198
471	-144.6	175.1	1.024	1.475	19.4	4.25	.472	1.198
461	-137.0	179.3	1.061	1.530	20.0	4.37	.472	1.198
469	-121.0	188.2	1.060	1.528	19.9	4.34	.472	1.199
476	-120.8	188.3	1.048	1.511	19.9	4.35	.472	1.199
457	-118.1	189.8	1.064	1.533	20.4	4.46	.472	1.199
472	-114.2	192.0	1.037	1.495	19.6	4.28	.472	1.199
478	-107.7	195.6	1.052	1.516	19.8	4.34	.472	1.200
453	-105.0	197.1	1.058	1.525	19.4	4.25	.472	1.200
460	-102.5	198.5	1.062	1.530	19.6	4.29	.472	1.200
452	-95.6	202.3	1.072	1.545	20.7	4.52	.473	1.200
477	-90.2	205.3	1.070	1.542	19.9	4.35	.473	1.200
451	-86.6	207.3	1.076	1.551	20.2	4.42	.473	1.201
458	-78.7	211.7	1.084	1.563	19.6	4.29	.473	1.201
459	-59.1	222.6	1.075	1.550	19.5	4.27	.474	1.204
447	-38.7	233.9	1.055	1.521	38.8	8.50	.475	1.207
450	-21.5	243.5	1.057	1.524	39.7	8.68	.476	1.209
446	-2.7	253.9	1.054	1.520	38.8	8.50	.477	1.212
445	32.2	273.3	1.047	1.509	38.3	8.38	.479	1.217
448	68.7	293.6	1.038	1.496	37.8	8.28	.481	1.223
449	105.1	313.8	1.041	1.501	37.8	8.27	.483	1.228

The temperature given in Table 2 is the mean of the observed hot-plate and cold-plate temperatures. The temperature gradient is calculated for the sample proper, excluding the pads. Thermal conductivity of the sample is plotted versus temperature in Fig. 3. There is a clearly defined, rather sharp break in the curve at the glass transition, T_g . The peak in the curve comes at about 212°K and this has been accepted as the glass-transition temperature according to our measurements of λ . The value obtained by some other method, from the change in thermal-expansion coefficient for example, might of course differ slightly from our accepted value.

The NBS data are also shown in Fig. 3. There are 7 NBS points, as given in Table 1, but 5 of them (those with mean temperatures near 70°F) lie so near together that they are not fully distinguishable in the figure. The NBS data lie about 2% above the NLABS curve. The NBS values are believed to be more nearly correct. There are several reasons for assigning a somewhat lower accuracy to the NLABS data. Among them we note that NBS used larger samples, 8 x 8 inches, whereas circular samples 6.5 inch in diameter were used at NLABS. But most important, the apparatus and procedures used at NBS had been well tested over a period of many years; in contrast the NLABS apparatus was relatively new.

In preliminary measurements made at NLABS a number of thermocouple systems were mounted inside the sample chamber and on the sample in studies of temperature uniformity and ~~temperature~~ gradients. All these measurements indicated that the apparatus was working properly. A sample of fiber-glass insulating board, 1/2 inch thick, previously calibrated at NBS, was measured in the NLABS apparatus. At 293.8°K (69.0°F) the NBS value was 0.309 mw/cm°K and the NLABS value was 0.303, which is 2% lower. Thus the two laboratories differ in the same direction and by about the same amount in their results on the two substances. This is considered satisfactory agreement.

The cause of the discrepancy of 2% between the NBS and the NLABS values is not definitely known. Various possibilities have been considered

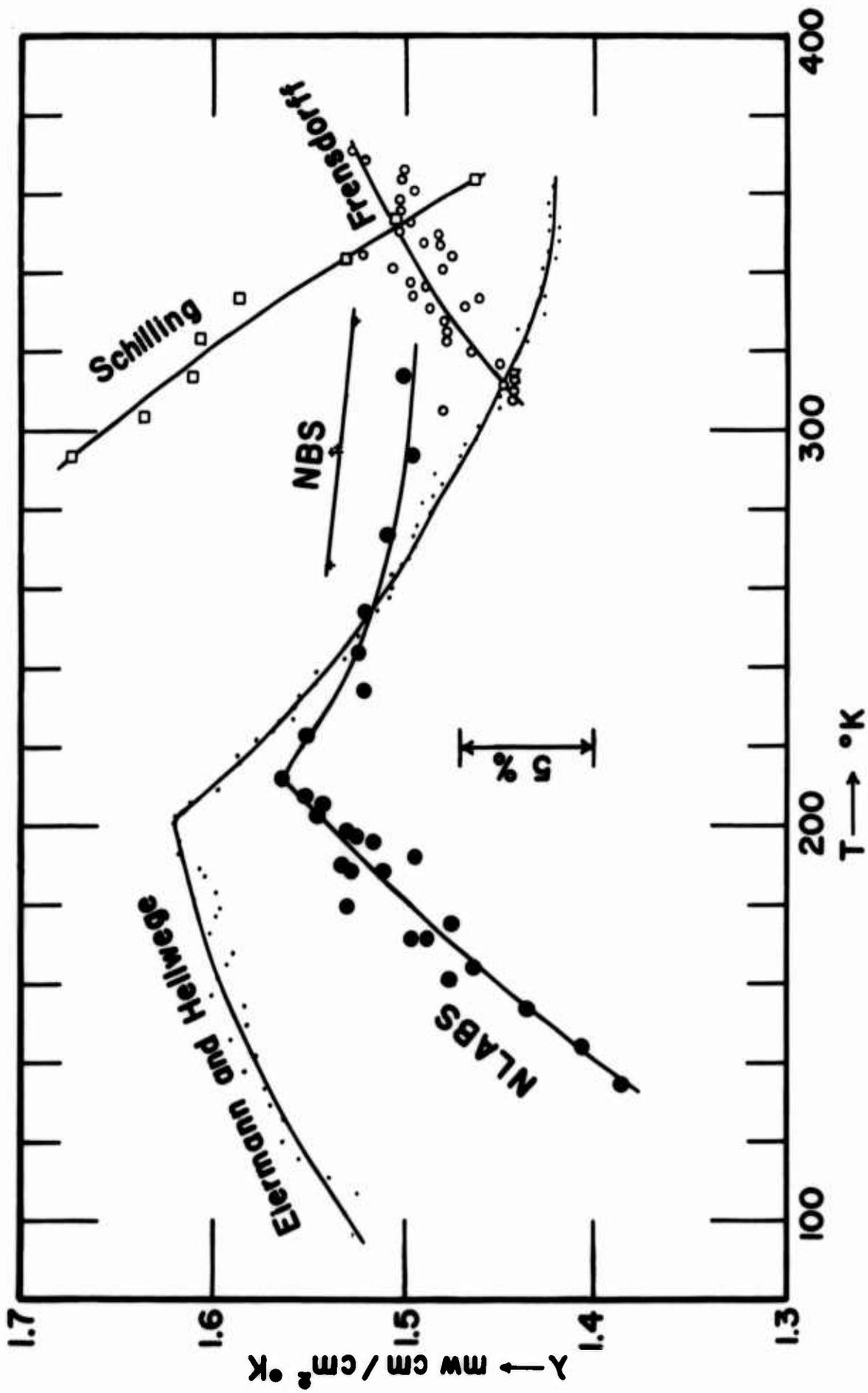


Fig. 3. Thermal conductivities determined in the present investigation (NLABS and NBS), with data of previous investigators for comparison.

but they are little more than conjectures. The data of the two laboratories could have been arbitrarily brought into agreement by raising the NLABS data by 2%, but this is a dubious procedure when applied to data taken at temperatures far below the lowest NBS measurement. Hence we have presented both sets of data without adjustment.

One feature of the NLABS measuring system that could possibly cause error is associated with the thermopile used to measure ΔT . Altho the wire was only 0.005 inch in diameter it would distort the sample and pad somewhat, producing small air pockets around the wires and the junctions. Air pockets could perhaps appreciably increase the total resistance to heat flow; this would lower the measured values of λ and thus could account for the NLABS results being lower than the NBS results.

The NLABS data taken below T_g show somewhat more scatter than those taken above T_g , as can be seen in Fig. 3. Slow cooling of the sample from somewhat above T_g to somewhat below it was desirable; values of λ measured after rapid cooling were often low. However, this was not always the case. It is possible that rapid cooling may cause the sample to warp at T_g and that the warping was somewhat variable and could not be entirely compensated by the pads. When a low value of λ had been obtained after rapid cooling the apparatus was sometimes held at dry-ice temperature (195°K) over night and a run made the next day. The λ -values found on the second and subsequent days after cooling were usually normal. This would tend to show that warping was not the cause of low points but that the sample was actually in a different state after rapid cooling. If the different state was metastable and gradually changed to a more stable state at 195°K, some of the observations could be explained. Our facilities for over-night control of temperature were not adequate to resolve the question of what caused the low values of λ . Since the low values scattered erratically, we felt justified in rejecting them.

7. Comparison with Previous Results

A critical survey of published data on the thermal conductivity of rubber was published by Carwile and Hoge [1]. The three best sets of data found at that time, excluding work in which measurements were made at only 1 or 2 temperatures, were those of Eiermann and Hellwege [2], Frensdorff [9], and Schilling [10]. A search of the literature since reference [1] was published did not reveal any new investigations. The three sets of data referred to have been included in Fig. 3.

The agreement of our data with the earlier data is fairly good from 250°K upward; the agreement with Frensdorff's data is the best. The results of Eiermann and Hellwege (EH) and the present results agree reasonably well down to the glass transition but below it the difference becomes as large as 15%. The cause of the discrepancy is not clear. One would not expect the rapid method used by EH to give as accurate results as the method used in the present investigation. Schilling's results appear to slope downward too steeply.

The glass transition of EH is at about 203°K, whereas our value is 212°K. The EH sample contained 2.0% of bound sulfur as compared with 2.5% in our sample. Ignoring possible effects of other compounding ingredients, the extra 0.5% of sulfur in our sample should raise its T_g by 2 or 3°K, accounting for only a third of the observed difference. A value of T_g that agrees better with our value can be derived from the measurements of shear-compliance made by Wood and Roth [11]. These authors found for several different rubbers a temperature T_a closely related to T_g ; they estimate that T_a is "probably not more than a few degrees above the glass transition as determined by volume-temperature relations". One of the rubbers they measured was ASTM formula 2A, the type of rubber used in the present measurements, and for it they found $T_a = 212^\circ\text{K}$.

We will interpret "a few degrees" as 3°, whence their data yield $T_g = 209^\circ\text{K}$, in reasonably good agreement with our value of 212°K . Other values from the literature could be quoted, some supporting the EH value and others agreeing better with our value of 212°K .

The glass-transition temperature of a small sample of our rubber was determined for us by differential thermal analysis, by Lt. Geoffrey R. Mariner and Dr. John H. Cornell of NLABS. The break in the DTA curve corresponding to T_g was found at 216°K . The temperature scale of the analyzer was calibrated by running a sample of n-octane; this material has a melting point of 216.7°K .

It is believed that the thermal-conductivity values found in the present investigation are correct within $\pm 3\%$ near room temperature. The NBS values are probably more accurate than this. The error in the NLABS data probably increases at lower temperatures. At the glass transition and below the error may be as large as 6%.

8. Acknowledgments

We wish to thank G. W. Bullman for preparing the samples of rubber used in this investigation and T. W. Watson for making the NBS measurements of λ .

Daniel R. Flynn took part in several discussions of the work. We are especially grateful to Dr. Lawrence A. Wood for arranging to have the samples prepared, and for numerous discussions of the data and the present report.

9. References

1. Lois C. K. Carwile and Harold J. Hoge, "Thermal Conductivity of Soft Vulcanized Natural Rubber: Selected Values", U. S. Army Natick Labs. Tech. Rept. 66-49-PR (June 1966) 26 p. The same paper is published in "Advances in Thermophysical Properties at Extreme Temperatures and Pressures" p 320-7, Am. Soc. Mech. Eng., New York (1965), also a shortened version is given in Rubber Chem. Technol. 39, 126-31 (Feb 1966).
2. Kurt Eiermann and K. H. Hellwege, "Thermal Conductivity of High Polymers from -180°C to 90°C", J. Polymer Sci. 57, 99-106 (1962).
3. American Society for Testing and Materials. "Standard D15-68a. Sample Preparation for Physical Testing of Rubber Products", 1969 Book of ASTM Standards, Part 28, p 14-33.
4. American Society for Testing and Materials. "Standard C 177-63 (Reapproved 1968). Thermal Conductivity of Materials by Means of the Guarded Hot Plate", 1969 Book of ASTM Standards, Part 14, p 17-28.
5. Michael J. Sacco, Francis W. Botsch, and Alan H. Woodcock, "An Automatic Guard-Ring Temperature Controller for Thermal-Conductivity Measurements", U. S. Army Quartermaster Res. Eng. Center, Natick, Mass., Tech. Rept. PR-7 (Oct. 1962), 13 p.
6. A. J. Jewell, "Converting On-Off Furnace Controllers to Proportional Operation", J. Sci. Instr. 44, 81-3 (Jan 1967).
7. H. Shenker, J. I. Lauritzen, R. J. Corruccini, and S. T. Lonberger, "Reference Tables for Thermocouples", Natl. Bur. Stds. Circular 561 (27 Apr 1955), 84 p.
8. Norman Bekkedahl, "Forms of Rubber as Indicated by Temperature-Volume Relationship", J. Research Natl. Bur. Stds. 13, 411-31 (Sep 1934).

9. H. K. Frensdorff, "The Thermal Diffusivity of Natural Rubber", J. Applied Polymer Sci. 6, Issue No. 23, p S28-9 (1962).
10. H. Schilling, "Thermal Conductivity of Elastomer-Filler Systems at 20 to 90°C", Kautschuk und Gummi 16, 84-7 (1963).
11. L. A. Wood and F. L. Roth, "Creep of Pure-Gum Rubber Vulcanizates from Indentation-Time Measurements", Proc. 4th Rubber Technology Conf., London (1962), p 328; Rubber Chem. Technol. 36, 611-20 (1963).

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Natick Laboratories Natick, Massachusetts 01760		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE The Thermal Conductivity of Natural Rubber from 134 to 314°K			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) Malcolm N. Pilsworth, Jr. Harold J. Hoge Henry E. Robinson			
6. REPORT DATE January 1971	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 11	
8a. CONTRACT OR GRANT NO. A. PROJECT NO. 1T061102B11A-07		8b. ORIGINATOR'S REPORT NUMBER(S) 71-33-PR	
c.		8c. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Natick Laboratories Natick, Massachusetts 01760	
13. ABSTRACT The thermal conductivity of soft natural rubber, compounded and vulcanized as specified in ASTM recipe 2A, has been measured over a range extending from well below the glass transition to above room temperature. The glass-transition temperature deduced from the thermal-conductivity measurements is 212°K (-78°F). Most of the measurements were made at the Natick Laboratories in a guarded-hot-plate apparatus, with silicone rubber pads on either side of the sample. The rest of the measurements were made at the National Bureau of Standards with apparatus and procedures that have been used for many years in reference-standard work. The thermal-conductivity data are believed to be accurate to 3% or better at room temperature and to about 6% at the glass transition and below.			

DD FORM 1473
1 NOV 66

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal conductivity	8					
Heat transfer	8					
Rubber	9					
Natural	0					
Hevea	0					
Transport properties	8					
Thermophysical properties	8					