INVESTIGATION OF THE RADIATIVE CONTRIBUTION
TO THE THERMAL CONDUCTIVITY
IN SODIUM CHLORIDE, DUNITE AND FUSED QUARTZ

by

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ABSTRACT

Submitted to the Department of Geology and Geophysics on May 13, 1961, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The purpose of this investigation is to measure the radiative contribution to the thermal conductivity at high temperatures.

The cylindrical envelope method for thermal conductivity measurements is employed. Measurements are conducted in the temperature range 50°C to 1150°C on pressed, natural and synthetic sodium chloride, clear fused quartz, and dunite rock composed essentially of the mineral olivine. Transmission measurements are also made in order that the observed radiative effect may be compared with theory using optically determined absorption coefficients.

The results on pressed sodium chloride powder show that the thermal resistivity is linear in temperature up to at least 650°C, in agreement with the theory of phonon or lattice wave conduction. The natural and transparent sodium chloride samples also show only phonon conductivity to 450°C. Fused quartz shows a strong increase in thermal conductivity above 300°C, increasing from $3.5 \times 10^{-5}$ (cal/cm sec °C) at 100°C to about $20 \times 10^{-5}$ (cal/cm sec °C) at 1136°C. The results on dunite show only phonon energy transport up to 400°C. Beyond this, grain boundary separations and dissociation of serpentine present on grain boundaries masked the lattice conductivity and whatever radiative transfer may have been present.

The enhanced conductivity of fused quartz beyond 300°C is equated to radiative transfer. It is smaller in
magnitude than that predicted by theory by a factor of 50, yet agrees exactly in temperature dependence. The discrepancy is sought in the effects of the boundaries. Existing theory treating boundary effects is shown inadequate to account for the measurements on quartz. It is proposed that the use of cylindrical geometry rather than parallel plane, or the independent analysis of the radiative contribution in the transparent and opaque regions of the spectrum of fused quartz may explain the measurements.

The absence of any observed radiative contribution to the thermal conductivity in either the pressed sodium chloride or the transparent synthetic salt is attributed to strong grain boundary and pore scattering in the former and to low surface emissivities in the latter.

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Dr. A. Hughes
Assistant Professor of Geophysics
MEASUREMENT OF THE THERMAL CONDUCTIVITY OF
SODIUM CHLORIDE AT HIGH TEMPERATURE

by

William Aeppli Schneider

THESIS SUMMARY PAPER

The thermal conductivity of single crystal, and polycrystalline pressed and natural sodium chloride is measured in the temperature range 60 °C to 750 °C. The results show that phonon energy transport is the dominant thermal conductivity mechanism up to the highest temperatures measured in the various materials.

I. Introduction

The cylindrical envelope method (Loeb, 1951) for conductivity measurements was used in this investigation. The envelope methods are particularly suitable for high temperature thermal conductivity measurements because they minimize stray heat losses.

In the cylindrical method, the sample is in the shape of a cylinder with a hole along the axis for an internal heater, and thermocouple holes at two different radii parallel to the axis. The conductivity may then be related...
to the power input per unit length $P$, and the temperature difference at the two different radii by (Carslaw and Jaeger, 1947)

$$K = \frac{1}{2\pi} \ln\left(\frac{R_2}{R_1}\right) \frac{P}{(T_1-T_2)}.$$  \hspace{1cm} (1)

This equation is derived for an infinite cylinder, but will give results within 1 percent of the actual solution if the length to diameter ratio is greater than 4:1. The author investigated the case for a ratio of 3.5:1, the geometry used here, and found agreement within about 4 percent.

II. Experimental

Apparatus -- The apparatus used in this investigation, Figure 2, consists essentially of a tube furnace to control the ambient temperature. The sample is located in the center of the furnace isolated from the ends by ceramic baffles to prevent convection. The sample compartment was found to have a uniform longitudinal and transverse temperature distribution. Temperatures were measured thermo-electrically using chromel-alumel thermocouples, and the power was determined by measuring the voltage across the center part of the heater and the current in the winding.
Sample Preparation and Description -- The pressed sodium chloride samples were fabricated in the pressure vessel shown in Figure 3. They were pressed at about 17 tons per square inch and then annealed at 700°C for a day. They were then machined and drilled for the heater and thermocouples. The resulting samples were white, opaque, and had porosities of about 10 percent. It was later found the porosity could be reduced to 5 percent by pressing at elevated temperatures.

The natural samples were coarsely crystalline, dense, impure, and of varying transparency. The grain size ranged from 1/8 inch to 1 inch. The impurities were in the form of thin black shaley layers that controlled the transparency of the samples.

The synthetic samples were optical quality single crystal salt in the form of cylindrical blanks 1 3/8 inch in diameter and 1 and 2 inches long. Several of these were put together to get the desired length to diameter ratio. Great care was exercised in drilling so as not to fracture or cleave the blanks.

III. Results

The results on the pressed powder are shown in Figures 8 through 11. They are in good agreement with
the theory of phonon or lattice thermal conductivity which predicts that (Joffé, 1956)

\[ K \propto \frac{1}{Q_D} \quad \text{for } T > Q_D \]  

(2)

where \( Q_D \) is the Debye temperature. As the figures show, the thermal resistivity is quite linear in temperature up to about 500°C, above which there is some scatter. Sample 2C, however, shows linearity up to 650°C.

The natural and synthetic samples, Figures 12 and 13, agree almost exactly over the temperature range investigated, and show no departure from linearity up to 450°C. The intercepts give values of \( Q_D \) from 288°K to 325°K. The actual value for sodium chloride is 281°K (Dekker, 1957).

The measurements are compared with those in the literature in Figure 25. The results on natural and synthetic salt agree with those of Bucken (1928) on artificial salt when extrapolated to the axis. The results of Birch and Clark (1940) are in agreement with pressed powder sample 2C reported here; nonetheless, direct comparison appears to be of little value in view of the variation in the literature.

The variation of the conductivity among the pressed samples reported here, and its low value compared to the
natural or synthetic salt samples, cannot be explained in terms of the porosity correction of Loeb (1954). However, the results can be accounted for in terms of a grain boundary phase of lower conductivity.

Neither the opaque pressed samples nor the transparent synthetic salt revealed a radiative contribution to the conductivity at high temperatures. In the former, the radiative contribution is given by (Van der Held, 1952; Clark, 1957)

\[ K_R = \frac{16 n^2 \sigma T^3}{3 \varepsilon} \]  

(3)

where \( n \) is the index of refraction, \( \sigma \) the Stefan-Boltzmann constant, and \( \varepsilon \) the sum of the absorption and scattering coefficients. In the latter, the radiative contribution is simply that of direct transfer between the heater and the enclosing metal sleeve.

Infrared transmission measurements on the pressed powder indicate that the scattering coefficient (absorption being negligible) is large enough so that equation (3) would not have been observed. The actual determination of the scattering coefficient is uncertain because it is not simply related to the transmission measurements as is the absorption coefficient.

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The calculated direct radiant flux in the synthetic salt for assumed emissivities gives a contribution to the conductivity of less than 2 percent of the total conductivity. This is within the uncertainty of the measurements.

IV. Conclusions

1. The cylindrical envelope method of thermal conductivity tests provides a simple, rapid, accurate method for high temperature conductivity measurements.

2. Pressed sodium chloride powders, natural polycrystalline rocksalt, and optical quality single crystal salt show thermal conductivity at elevated temperatures in agreement with the theory of phonon conductivity.

3. The absence of a radiative contribution to the thermal conductivity at elevated temperatures is attributed to strong scattering of thermal radiation in the case of the pressed powders, and to low surface emissivities in the case of transparent synthetic sodium chloride.
ACKNOWLEDGEMENTS

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The use of the infrared spectrometer was made possible by Dr. A. Smith of the Electrical Engineering Department, M.I.T.

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CHAPTEJ I
INTRODUCTION

A. The Problem

In recent years there has been an interest in the role of radiative energy transfer in the mantle of the Earth. This mechanism of heat transfer is characterized by the emission and absorption of photons within the solid material. In the presence of a temperature gradient, there is a net flux of photons in the direction of the gradient as there are more photons created in the hot regions than in the cool. This diffusion current of photons carries energy which contributes to the total energy flux, thus giving rise to the term radiative thermal conductivity. The effectiveness of the mechanism in transporting energy in a given material depends on its absorption and scattering properties in relation to electromagnetic radiation. The attempt to evaluate the effectiveness of this mechanism in the Earth involves determining the variation of these parameters with temperature, pressure and composition, and substituting into the appropriate theoretical relationship. An alternate procedure is to measure the radiative conductivity directly; this latter approach is the one taken in this investigation.
B. The Plan of this Investigation

In this investigation only the temperature dependence of the radiative heat transfer is examined experimentally. The total thermal Conductivity is measured as a function of temperature. From this the radiative contribution is obtained by knowing the temperature dependence of the lattice conductivity.

In addition, infrared transmission measurements are obtained to determine the absorption coefficient of the materials tested, thus providing a test of the theoretical radiative conductivity equation.
CHAPTER II
EXPERIMENTAL

A. Measurement of Thermal Conductivity

1. General

The inherent difficulty in thermal conductivity measurements stems from the fact that only five orders of magnitude separate the best and worst conductors. In practice, however, there is usually less than one order of magnitude difference between the thermal conductivity of the various parts of the apparatus and the specimen, for non-metals. Therefore, in conducting heat flow measurements, great care must be taken to insure that the flow is properly channelled and that stray losses are kept to a minimum. Measurements at high temperatures are further complicated by radiation losses as well as convection and conduction losses.

The envelope methods of thermal conductivity tests (Loeb, 1951) offer distinct advantages over more conventional methods, particularly at high temperatures. In the envelope method, the heater is completely or almost completely enclosed by the material in which the conductivity is to be measured, thereby eliminating most stray losses. If the geometries are such that the coordinates used to
describe the particular shape also represent isotherms and flow lines, then simple expressions can be given for the conductivity in terms of the power input and a temperature difference in the direction of the temperature gradient.

The cylindrical envelope method was selected for this investigation because of its adaptability to a larger class of materials. In general, the major drawback of the envelope methods is sample fabrication. The geometries involved are complex, and the placement of thermocouples and heater is critical. Therefore, unless the materials can be cast, pressed, or easily machined, the envelope methods are impractical with the exception of the cylindrical method, where diamond core drills and saws can be conveniently used.

In this method, a heater delivering uniform power per unit length is placed along the axis of the sample. The temperature is measured at two different radii, and the conductivity is given by (Carslaw and Jaeger, 1947)

\[ K = \frac{1}{2\pi} \ln\left(\frac{r_2}{r_1}\right) \frac{P}{(T_1 - T_2)} \]  

(2.1)
where \( r_1 \) and \( r_2 \) are the radii at which \( T_1 \) and \( T_2 \) are measured. \( P \) is the power per unit length. This equation is derived for an infinite cylinder with conductivity independent of temperature. If the length to diameter ratio is greater than four to one, the error in using equation (2.1) to represent the conductivity of the finite cylinder at its center is often reported to be less than 1 percent. In Appendix B, a ratio of 3.6 is considered, and the resulting error is about 4 percent. If the thermal conductivity depends on temperature as it does for most materials, equation (2.1) must be modified to

\[
K_{\text{ave}} = \frac{T_2}{(T_1 - T_2)} \left[ \frac{1}{2\pi} \ln \left( \frac{r_2}{r_1} \right) \right] \quad (2.2)
\]

where now \( K_{\text{ave}} \) is the average value of \( K \) over the temperature interval \( T_1 \) to \( T_2 \).

2. **Apparatus I**

Figure 1 shows the arrangement of apparatus I. It consists of the cylindrical specimen with an axial heater hole and two thermocouple holes parallel to the axis, one near the inner wall and the other near the outer wall. The thermocouples are placed on opposite sides of the heater so that any disturbance of the
temperature field created by the inner thermocouple will not be seen by the outer one. An alumina tube and transite end pieces enclose the specimen, and the intervening space is packed with Sil-O-Cel powder insulation.

The heater consists of a length of two hole alumina or mullite insulating tubing 5/32 inch in diameter on which is uniformly wound .008 inch diameter platinum wire. The leads are run through the holes and brought out at slots cut in the tube where the winding starts and finishes. In order to obtain an accurate measure of the power generated in the center section of the sample where the radial gradient is measured, two additional leads are brought in through the tube and out through slots where they join the winding. These leads enable the voltage to be measured over the center half where the temperature is constant and therefore the power per unit length uniform. Near the ends the winding runs cooler, and because of the large temperature coefficient of resistance of platinum, the power generated per unit length is less than in the center.

The current in the winding was determined by measuring the voltage across a known resistor in series with the winding. These voltages were measured with a
Simpson meter calibrated against a vacuum tube volt meter in the experiments on apparatus I, described below.

Temperatures were measured thermo-electrically using chromel-alumel thermocouples and a Leeds and Northrup No. 8667 Potentiometer. The cold junction was kept at the temperature of melting ice. Power to the winding was supplied by a variac controlled manually. During the progress of a run, the power was taken up in steps and temperature and voltage readings were made at each power setting. Approximately one half hour was required for the establishment of steady conditions at each setting.

A number of preliminary runs were made on apparatus I using sodium chloride samples. These data are included in this work to provide a comparison with the results on apparatus II as well as to point out the general features of the measurements on sodium chloride.

Certain features of apparatus I made it inadequate for this investigation. The major drawback arose from having to use the heater to provide the temperature gradient as well as raise the mean temperature of the sample. At high powers and consequently high temperatures, very large gradients existed in the sample. For example, in a typical run on sodium chloride at 100°C, the temperature difference was about 4°C or 11.7°C per inch as the
thermocouple separation was .34 inch, and the power input per unit length was about 1.84 watts. At 650°C the temperature gradient was approximately 350°C per inch and the power input per unit length about 17.3 watts. Large gradients such as this are undesirable in polycrystalline materials since the resulting thermal stresses cause fracturing and grain boundary separations and fissures. In addition, apparatus I has no provision for controlling the atmosphere in which the tests are run. Certain of the materials tested required special atmospheres so that alteration of the sample would not result during the progress of the run. This also prohibits large temperature differences across the sample, because if a buffer is used, the temperature of the buffer and the sample should be the same.

3. **Apparatus II**

For these reasons the apparatus shown in Figure 2 was constructed. The heater, thermocouple implantment, and cylindrical specimen remain unchanged. However, the alumina tube and insulation were replaced by a tube furnace in which the ambient temperature may be controlled. The furnace itself consists of a mullite
APPARATUS II

BRASS VACUUM COUPLING

REFRACTORY CEMENT

THERMOCOUPLES

HEATER

KANTHAL-A WINDING

SIL-O-CEL INSULATION

TRANSITE

STAINLESS STEEL TUBE

CERAMIC INSULATING TUBE

CERAMIC BAFFLE

METAL SLEEVE

BRASS BUSHING

RUBBER BUSHING

HOSE CONNECTION

SCALE IN INCHES

FIGURE 2
refractory tube 1 1/2 inches inside diameter and 24 inches long. The tube is gas tight and according to specification furnished by the manufacturer, McDanel Refractory Porcelain Co., is capable of maintaining a vacuum of $10^{-5}$ mm. Hg. pressure up to 1450°C. The center 12 inches is wound with .04 inch Kanthal-A wire.

The insulating shell enclosing the winding consists of a stainless steel tube 4 inches in diameter, transite end supports, and Sil-O-Cel insulation. The ends of the tube extend 5 1/2 inches beyond the ends of the furnace, thereby remaining cool even at the highest temperatures. They are sealed off with brass vacuum couplings. The four leads from each end of the specimen are brought out through the coupling in a 1/8 inch, 4 hole insulating tube. The final seal is effected by running the 4 hole tube into a rubber hose, one end connected to the coupling and the other end clamped down over the bare leads. If a controlled atmosphere is required, gas may be passed through the system via glass tees simply inserted in the length of the rubber hose.

To prevent convection between the center and ends of the tube, baffles were employed on either side of the sample. These consist of two alumina disks
connected by a tube through which the leads were passed. The disks fit snugly in the furnace tube and effectively prevent any convective transfer between the center section and the ends. An additional measure to prevent convective losses from the heater involved packing very fine alumina cement between the heater and the walls of the heater hole in the sample. The ends of the hole were sealed by tamping damp cement in around the heater. It is felt that this prevented any convective loss from the heater. This, however, was not done in experiments on apparatus I.

The sample was centered in the furnace by a metal sleeve which fit snugly over the sample and inside the furnace. Since the metal sleeve had a higher conductivity than the furnace tube or sample, it tended to flatten out any longitudinal gradients that existed in the center section.

The center 5 inches of the furnace, the sample compartment, had a rather uniform temperature distribution at all temperatures. The worst longitudinal gradients were found to be 2-3°C per inch, and the worst transverse gradients observed were less than 1°C per inch. These latter, however, were not negligible compared to the radial gradients produced by the heater and had to be corrected.
to gain a precision of a few percent. This was accomplished by recording the temperature difference between the two thermocouples at each new setting of the variac which controlled the external furnace power while the power to the internal heater was off. Then the heater was turned on, and after steady conditions were reached, the temperature gradient was again measured. The difference between the two gradients was used to determine the conductivity. The correction was small, usually of the order of 1°C per inch or less compared to a total gradient of approximately 20°C per inch.

Voltage measurements on apparatus II were made with a Hewlett Packard Model 400H VTVM which has an accuracy of 1 percent of full scale. The thermocouples were not calibrated against any absolute standard except at the boiling point of water, where differences were found of the order of .25°C or less. An absolute calibration was not necessary as only the difference in readings of the two thermocouples was critical and, as explained above, this was checked at each reading throughout the run. Certainly part of the temperature difference that existed with the heater off was due to thermocouple error and not gradients in the furnace, but whatever the
cause, it was corrected by keeping a running calibration between the two thermocouples.

4. **Sample Description, Fabrication and Preparation**

a. **Sodium Chloride**

Measurements on sodium chloride constituted a major portion of the work because of its low intrinsic absorption in the infrared and its ease of fabrication into the desired shape.

The materials tested consisted of pressed sodium chloride powder, polycrystalline natural rocksalt from a mine in Kansas and furnished by the United States Geological Survey, and artificial single crystal samples obtained from Harshaw Chemical Co. in Cleveland, Ohio. The three types of samples, though of the same chemical composition, differ markedly in their microstructure and appearance.

i. **Pressed Powder** - The pressed samples were formed by first grinding granular sodium chloride in a mortar and then pressing the powder in a stainless steel container which is shown in Figure 3. The container consisted of a cylinder, sample chamber, and end screw cap.
PRESSURE VESSEL FOR MAKING SALT CYLINDERS

STAINLESS STEEL

CONICAL SAMPLE CHAMBER

END SCREW CAP

PISTON

FIGURE 3

SCALE IN INCHES
In the preparation of a sample, the sample chamber and part of the cylinder were filled with powdered salt. A piston was then inserted in the cylinder and force was applied to the piston with a 30 ton hydraulic jack. The sample was extracted by partially unscrewing the base and reapplying a slight force to the piston. The conically shaped sample would break contact with the wall at all points at the same time thereby preventing fracture due to partial unloading such as would result if it were pushed out of a cylindrical chamber. The sample was then annealed at 650-700°C for 24 hours or more to relieve stresses and promote crystal growth prior to machining.

The initial specimens prepared in this manner resulted in fine grained, homogeneous bodies of rather high porosity and low transparency. The grain size was quite uniform throughout a sample and ranged from .1 mm. to .4 mm. depending on the temperature and length of annealing.

The porosity was determined from the density, which was calculated from the weight and dimensions of the sample. Since the sample was machined, these could be determined quite accurately. The average porosity was high, ranging from 10-15 percent. This,
however, was not uniform throughout the specimen. The piston end of the sample for approximately 1 inch was considerably denser than the rest. The measurements, however, were carried out in the center of the specimen where the porosity was certainly as high as the average.

The high porosity resulted in white opaque bodies. If held up to a bright light, some transmission was evident but it was exceedingly small.

A further reduction in porosity seemed desirable if enhanced transmission was to be obtained from the pressed material. Ford and Wilkinson (1955) found that, in order to get optical quality disks from pressed alkali halide powders, they needed in excess of 65 tons/(in)$^2$ for sodium chloride. The hydraulic pump and piston used here could only give a maximum of 17 tons/(in)$^2$, considerably less than that needed for optical quality material. A further reduction in porosity, however, was obtained by pressing the salt at elevated temperatures.

A heating jacket consisting of sheet asbestos and heater wire were wrapped around the steel container prior to pressing the salt. The temperature was brought up to 275-300$^\circ$C and then the salt was pressed as before. It was found that the strength of the salt
was reduced markedly and creep enhanced resulting in denser samples with no increase in load. The average porosity was reduced to 5 percent and all but the bottom inch of the sample appeared dense. It is felt that the last inch accounted for most of the 5 percent porosity. Nevertheless, no significant optical advantage was gained by the reduction in porosity. After annealing, the grain size was significantly larger, ranging from .2 mm. to 5 mm., but as before, the sample appeared translucent at best and the overall transparency did not appear to have improved much.

ii. Natural - The natural samples were coarsely crystalline, dense, impure, and of varying transparency. The crystal size ranged from 1/8 inch to 1 inch with considerable development of incipient parting along cleavage planes. This latter was probably introduced during the machining of the samples. The porosity was estimated to be considerably less than 1 percent from microscopic examination, the only contribution coming from imperfect meshing of the crystals themselves. The individual crystal domains revealed no porosity. The samples contained rather large amounts of impurities in the form of thin black shaley layers. These layers ran
roughly perpendicular to the cylinder axis and seemed to follow grain boundaries forming an extremely irregular surface. The transparency of the specimens was controlled entirely by these finely dispersed layers. The various natural samples differed in transparency by at least a factor of two.

iii. Artificial - The artificial samples were optical quality monocrystalline cylindrical blanks approximately 1 and 2 inches in length. They were furnished with the correct diameter so that the only machining necessary involved drilling the heater and thermocouple holes. Great care was taken in the drilling operation so as not to develop cleavage in the cylindrical segments. The segments were then cemented together with Sauereisen's Insa-lute No. 1 to form a cylinder 4.5 inches long, the center 2 inches being one continuous piece.

The mechanical properties of the pressed cylinders were superior to those of the coarsely crystalline natural ones due to their homogeneity. The most critical operation in preparing the samples involved drilling the thermocouple holes. As the samples were 4.5 inches long, it was found that the smallest practical
hole that could be drilled straight was about .04 inch in the pressed salt. However, in the natural material, it was not possible to drill a straight hole of that size over 1 inch to 1 1/2 inches. Therefore, rather than go to a larger diameter hole, the sample was sectioned into three 1 1/2 inch lengths, drilled, and cemented together again using Sauereisen's No. 1 high temperature cement.

b. Fused Quartz

i. Description - A sample of clear fused quartz was obtained from Syncore Products Inc. in Malden, Massachusetts. The dimensions of the sample are 1 inch outside diameter by 4 1/2 inches length. It is commercial quality fused quartz and contains no macroscopic imperfections or porosity.

ii. Preparation - In order to prepare the sample for the conductivity measurement, the quartz rod was sawed in half lengthwise with a .019 inch diamond saw. Thermocouple groves .019 inch wide were then cut in the halves parallel to the axis at different radii and the heater hole was drilled with a 3/16 inch diamond core drill while the two halves were clamped together. The saw cut resulted in the rod being out of round by about 1 percent, but no attempt was made to account for the effect of this perturbation of the geometry. It is
felt that the resulting error is well within the accuracy of the measurements. During the run the sample was held in a nickel-chromium alloy sleeve which centered the sample in the furnace and enabled the two halves to be held firmly together by set screws in the sleeve.

c. Dunite

i. Description - The sample of dunite was furnished by Dr. E. C. Robertson of the U. S. Geological Survey, Theoretical Geophysics Branch. The sample was originally obtained from the Webster-Addie ultramafic ring in Jackson County, North Carolina, the source region of most domestic dunite rock.

The rock is massive, medium grained, homogeneous, light green, showing some alteration. It is composed of about 90 percent olivine present in equant grains with polygonal outlines ranging in size from 1/2 to 2 mm. in diameter. Chromite octahedra are scattered throughout the sample comprising about 2-3 percent of it. They range from 1/4 to 1 mm. in diameter. This sample, along with several others, is described by Miller (1953). He reported that the olivine has a beta refractive index of 1.666 and a molecular $Fe_2SiO_4$ content of 7 percent. In addition, he observed that serpentinization is present.
in the dunite in varying amounts up to 40 percent. Although he did not report the amount of alteration in this sample, it is thought to be of the order of 10-20 percent. The serpentinization begins along grain boundaries, cleavage traces, and fractures in the olivine grains. The contacts between the fresh dunite and serpentine alteration products are very sharp.

ii. Preparation - The sample dimensions are 1 inch outside diameter and 4 1/2 inches length. The thermocouple slits were prepared as with the fused quartz sample, that is by sawing the sample in two and cutting grooves parallel to the axis with a .019 inch diamond saw. In order to prevent any contamination of the thermocouple junction at high temperatures by the dunite, the thermocouple was embedded in Sauereisen Insa-lute No. 1 high temperature ceramic cement in the groove. This also provided good thermal contact.

5. Buffer

The use of a buffer to control the partial pressure of the oxygen in the furnace was necessary during the run on dunite. The olivine, belonging to the solid-solution series \((\text{Mg, Fe})_2\text{SiO}_4\), has the
approximate composition 90 percent $\text{Mg}_2\text{SiO}_4$ and 10 percent $\text{Fe}_2\text{SiO}_4$. Since the iron is in the ferrous oxidation state, it can either oxidize to the ferric state or reduce to metallic iron during heating depending upon the partial pressure of the oxygen in the atmosphere. The work of Eugster (1956, 1957) shows that a buffer of wüstite (FeO) composition will prevent alteration of ferrous silicates by controlling the $P_{\text{O}_2}$ at a level where neither oxidation nor reduction of the ferrous iron will take place.

Since FeO is unstable at room temperature, a mixture of Fe and $\text{Fe}_3\text{O}_4$ was used in the approximate proportions to give an FeO composition buffer. The actual composition is not critical so long as Fe and $\text{Fe}_3\text{O}_4$ are always present. At low to moderate temperatures, the $P_{\text{O}_2}$ is controlled by the oxidation of Fe or the reduction of $\text{Fe}_3\text{O}_4$ in the buffer rather than the oxidation or reduction of the ferrous iron in the olivine. At higher temperatures the reactions are more involved and have been considered in detail by Uhri (1961) using free energy data. He finds that it is always energetically more favorable for the buffer, rather than for the ferrous iron in the mineral, to be oxidized or reduced.
The buffer mixture was placed in nickel containers at both ends of the sample. Nickel is stable at the $P_{O_2}$ determined by the buffer over the entire temperature range. Approximately seven grams of buffer were used during a run. The furnace was flushed initially with argon to lower the $P_{O_2}$ to a reasonable level before calling on the buffer to reduce it further.

B. Transmission Measurements

1. General

The infinite space solution for the radiative conductivity given by equation (A.23), Appendix A, contains two material parameters, the index of refraction $n$, and the average extinction coefficient $\bar{c}$. If $n$ is assumed constant, as is done in the derivation, then the measurement of the radiative conductivity furnishes the temperature variation of $\bar{c}$. If absorption is the dominant mechanism in limiting the photon mean free path, then an independent determination of $\bar{c}$ can be made using spectral transmission data, for

$$\varepsilon_{\lambda} \approx \alpha_{\lambda} + \sigma_{\lambda}$$

$$\varepsilon_{\lambda} \approx \alpha_{\lambda} \quad \text{if} \quad \alpha_{\lambda} \gg \sigma_{\lambda}$$
where $\varepsilon_\lambda$, $\alpha_\lambda$, and $\sigma_\lambda$ are respectively the spectral extinction, absorption, and scattering coefficients. The average extinction coefficient $\overline{\varepsilon}$ can then be determined by appropriately averaging $\varepsilon_\lambda$ or $\alpha_\lambda$ over the spectrum at a given temperature according to equation (A.24) of Appendix A.

The absorption coefficient is related to the transmission of incoherent light through a plate of material with parallel optically flat surfaces by

$$T = \frac{I_t}{I_0} = \frac{(1-R)^2 e^{-\alpha_\lambda d}}{1 - R^2 e^{-2\alpha_\lambda d}}$$

(2.4)

where $I_t$ is the transmitted intensity, $I_0$ the incident intensity, $R$ the reflection coefficient for normal incidence, and $d$ the thickness of the plate. The reflection coefficient for normal incidence is given by the usual formula,

$$R = \frac{(n-1)^2 + n^2 k^2}{(n+1)^2 + n^2 k^2}$$

(2.5)

where $k$ is related to the complex index of refraction $n'$ by
\[ n' = n(1 + ik) \quad (2.6) \]

The transmission formula has a simple interpretation. The numerator represents the incident intensity reduced by \(1 - R\) for each reflection and by \(e^{-\alpha_z d}\) for absorption of the intervening matter. The absorbed radiation is removed from the radiation field and appears as other forms of energy, even radiation at different wave lengths. The denominator represents the contribution to the transmitted intensity due to multiple internal reflections.

In insulators \(k\) is small and can be neglected in the above formulas. In addition, the term in the denominator involving \(R^2\) is generally negligible compared to 1 so that the equations reduce to

\[ \frac{I}{I_0} = (1 - R)^2 e^{-\alpha_z d} \quad (2.7) \]

and

\[ R = \left( \frac{\mu - 1}{\mu + 1} \right)^2 \quad (2.8) \]

These equations may be used to solve for \(\alpha_z\) only if the surfaces are specular. In practice, it is difficult to obtain specular surfaces on polycrystalline materials with a few percent porosity and there usually results
additional surface losses due to diffuse reflection. In this case, the absorption coefficient may be obtained approximately by using two thicknesses of material to eliminate the unknown surface losses. The extinction coefficient is then given by:

\[
\frac{T_1}{T_2} = \frac{I_{t1}/I_o}{I_{t2}/I_o} e^{-(\text{Total Surface Losses})} e^{-\alpha_d d_1} (\text{Total Surface Losses}) = e^{-\alpha_d d_2}
\]

or

\[
\alpha_d = \frac{1}{(d_1 - d_2)} \ln \left( \frac{I_{t1}}{I_{t2}} \right)
\]

(2.9)

(2.10)

in the approximation that the diffuse internal reflections do not contribute significantly to the transmitted intensity. Of course, in this latter method, the surfaces of the two thicknesses must be polished to the same degree for the losses to cancel out even though diffuse.

In the transmission measurements made here two thicknesses of material were used to determine the absorption coefficient.

If scattering is the dominant mechanism for limiting the photon mean free path, the above equations cannot be used to determine the scattering coefficient \(\sigma_s\).
with any degree of accuracy. The reason is that the scattered radiation is not lost from the radiation field. The transmitted intensity consists of two parts: the reduced incident intensity (that part of the incident intensity that has not been scattered at all); and, the diffuse intensity which depends on the incident intensity, scattering coefficient, thickness, law of scattering, and direction. The most complete treatment of diffuse radiation problems is given by S. Chandrasekhar (1960) who has developed much of the mathematics peculiar to this branch of physics. Exact solutions exist for only a few of the simplest cases. The problem of interest here is the diffuse transmission through a finite thickness plate.

The basic equations of the problem of diffuse reflection and transmission by a parallel plane material scattering radiation isotropically with an albedo \( \widetilde{\omega} < 1 \), where \( \widetilde{\omega} = \frac{\sigma_t}{\varepsilon_x} \), are given by

\[
I_d(0, \mu) = \frac{1}{4\pi\mu} S(\tau_1; \mu, \mu_0) \] reflected (2.11)

\[
I_d(\tau_1, -\mu) = \frac{1}{4\pi\mu} T(\tau_1; \mu, \mu_0) \] transmitted (2.12)
where \( I_d(O,\mu) \) and \( I_d(\tau_1, -\mu) \) are the diffusely scattered and transmitted intensities, \( \mu = \cos \Theta \) is the angle between the normal to the plate and the direction in which the intensity is viewed, \( -\mu_o \) being the direction of the incident intensity, \( \tau_1 = \varepsilon_1 d_1 \) is the optical thickness of the plate, and \( S(\tau_1; \mu, \mu_o) \) and \( T(\tau_1; \mu, \mu_o) \) are the scattering and transmission functions respectively. They involve the scattering coefficient in a complicated manner, and it cannot be solved for simply by making transmission measurements as with the absorption coefficient.

The solution for the finite thickness plate of isotropically scattering material may be expressed as

\[
I_d(O,\mu) = \frac{1}{4\pi} \oint_0 \frac{\mu_o}{\mu + \mu_o} \left[ X(\mu, \tau_1)Y(\mu_o \tau_1) - Y(\mu \tau_1)X(\mu_o \tau_1) \right] \tag{2.13}
\]

\[
I_d(\tau_1, -\mu) = \frac{1}{4\pi} \oint_0 \frac{\mu_o}{\mu - \mu_o} \left[ X(\mu, \tau_1)Y(\mu_o \tau_1) - X(\mu, \tau_1)Y(\mu_o, \tau_1) \right] \tag{2.14}
\]

where the \( X \) and \( Y \) functions must be evaluated numerically. Unfortunately, at the time of printing of Chandrasekhar's book, these functions had not been tabulated. He does,
However, present some curves of the transmitted and reflected intensity for certain values of the parameters that enable one to draw some conclusions about the transmitted intensity as a function of $\mu$, $\tau$, and $\mu_o$.

Shown in Table I is the ratio of the diffusely transmitted intensity to the incident intensity for various values of $\mu$, $\tau$, and $\mu_o$.

**TABLE I**

<table>
<thead>
<tr>
<th>$\frac{I_d}{I_0}$</th>
<th>Optical Thickness</th>
<th>Direction of Transmitted Intensity $\mu = \cos \Theta$</th>
<th>Direction of Incident Intensity $\mu_0 = \cos \Theta$</th>
<th>Albedo $\hat{\omega}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0076</td>
<td>.25</td>
<td>$0^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.0725</td>
<td>.25</td>
<td>$90^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.051</td>
<td>.5</td>
<td>$90^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.061</td>
<td>.5</td>
<td>$90^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.055</td>
<td>1.0</td>
<td>$0^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.048</td>
<td>1.0</td>
<td>$90^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.067</td>
<td>2.0</td>
<td>$0^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
<tr>
<td>.032</td>
<td>2.0</td>
<td>$90^\circ$</td>
<td>$53^\circ$</td>
<td>1</td>
</tr>
</tbody>
</table>

The table shows that for small optical thickness, the diffuse intensity at $90^\circ$ to the surface normal is about ten times that parallel to the normal. As the optical thickness increases, the forward scattering
becomes predominant and at $\tau = 2$ the forward diffuse intensity is about twice that at right angles. Of course, it is the forward diffuse intensity that is of interest here as only a small slit of light in the normal direction is recorded in the spectrometer. The results presented in Table I cannot be applied directly to the problem at hand because they are for an incident intensity in the direction of $53^\circ$ to the normal and in the spectrometer the direction of the incident intensity is normal to the surface of the plate. For $\mu_0 = 1$, the results would show approximately the same dependence on $\tau$ but the magnitude of $I_t/I_0$ would be somewhat different. The result of central importance here is that the diffusely transmitted intensity in the forward direction increases with optical thickness, at least for the range of $\tau$ investigated. The total transmitted intensity is then given by

$$I_{t_1}(\tau_1, -\mu) = I_0 e^{-\tau_1} + I_0 \frac{1}{4\pi\mu} T(\tau_1; \mu, \mu_0) \quad (2.15)$$

where the first term decreases and the second increases with $\tau = \epsilon_2 d$. 

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Therefore, any attempt to use the ratio of the transmitted intensities of two thicknesses of scattering material to determine the scattering coefficients according to equation (2.10) will result in an effective scattering coefficient that is smaller than the true one. This can best be seen by a simple example. Let the material have a scattering coefficient of \( \sigma_2 = 100 \text{ cm}^{-1} \) and the thickness \( d_2 = 0.01 \text{ cm}, d_1 = 0.02 \text{ cm} \). Then the ratio of the total transmitted intensities according to equation (2.15) and Table I is

\[
\frac{I_{t_1}}{I_{t_2}} = \frac{I_0(e^{-2} + 0.067)}{I_0(e^{-1} + 0.055)} = 0.48
\]  

(2.16)

Now calculating the scattering coefficient by use of equation (2.10) gives

\[
\sigma_2 = \frac{-1}{d_1 - d_2} \ln(0.48) = 73 \text{ cm}^{-1}
\]  

(2.17)

resulting in a value 27 percent lower than the true scattering coefficient. As is also evident, the percent error increases with increasing \( \sigma_2 \) for the exponentials decay rapidly and the ratio of total intensities tends to the ratio of diffuse intensities which approaches
unity for large \( \tau \). Therefore, unless the total transmitted intensity is large, or equivalently the optical distance \( \tau \ll 1 \), the use of equation (2.10) to calculate the scattering coefficient will result in a serious underestimation of it.

2. **Apparatus**

The spectrometer used in the transmission measurements was made available to me by Professor Arthur Smith of the Electrical Engineering Department at M.I.T. This instrument is a Perkin-Elmer Model 12 single beam infrared spectrometer with a sodium chloride prism. The measurements were made in the spectral range of one micron to the long wavelength cut off due to lattice absorption. The range of the instrument with sodium chloride optics is from 1-15 microns.

Since it is a single beam instrument, it is necessary to record a background or \( I_0 \) spectra separately and then divide the spectra of the various samples at enough different wavelengths to get the transmission curve, \( T = \frac{I_t}{I_0} \) as a function of wavelength. For opaque samples with small transmission, however, it was more accurate to work with \( I_{t_1} \) and \( I_{t_2} \) directly to determine the absorption coefficient as then the gain
and slit width on the instrument could be adjusted to give full scale deflection for $I_{t_1}$ and $I_{t_2}$ rather than $I_o$.

3. Sample Preparation

Inasmuch as two thicknesses of each material were used in the transmission measurements, it was not necessary to produce optical surfaces. The thin sections were ground to the desired thickness with coarse abrasives and then brought up to a reasonable polish with finer and finer abrasives, finishing with Linde A on a dry paper lap. The fused quartz samples took a fine polish and appeared to have no diffuse losses, at least in the visible. The other samples did not polish as well.
CHAPTER III

RESULTS

A. Thermal Conductivity

1. Sodium Chloride

The results presented here have been corrected for porosity according to the equation derived by Loeb (1954)

\[ K_s = \frac{K_m}{(1-P_v)} \]  \hspace{1cm} (3.1)

where \( K_s \) is the conductivity of the solid with zero porosity, \( K_m \) is the measured conductivity, and \( P_v \) is the volume pore fraction. This relationship is valid under the following conditions: (1) that the pores are isometric, or if anisometric, randomly oriented; (2) that the solid phase is continuous; (3) that the passage of energy across the pore by direct radiation is neglected; and, (4) that the volume pore fraction is not too great. Franel and Kingery (1954) found the relationship to hold up to 50 percent porosity, the highest they investigated. The relationship has been thoroughly tested and proven by Kingery and his co-workers on ceramic oxides when the above restrictions are met.
The properties of the samples tested are listed in Table II.

The A and B series were prepared by pressing at room temperature and resulted in relatively high porosity. The stated grain size is representative for a particular group as all the samples were annealed at the same temperature for the same length of time, with the exception of 2B' which had a different annealing history. The two samples of the C series were pressed at elevated temperature resulting in a reduction of porosity of better than 50 percent over the A and B samples.

The shape of the intergranular pores depended on annealing time and temperature. Sample 2B', for instance, showed well isolated, smoothly contoured, elongate pores. The B series, however, generally showed angular pores indicating less sintering had occurred.

**Sample 3A** -- The conductivity and resistivity measurements for 3A are shown in Figure 4. The resistivity vs. temperature plot shows a linear increase with temperature, in accordance with the theory of lattice conductivity summarized in Appendix A, up to 200°C where a second linear relationship holds up to 350°C. Above 350°C the resistivity departs from linearity increasing slower than T. The kink in the line in the vicinity of 200°C is characteristic of
# TABLE II

## PROPERTIES AND MICROSTRUCTURE OF PRESSURED AND NATURAL SODIUM CHLORIDE SAMPLES

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Apparatus</th>
<th>Annealing Temp. and Time</th>
<th>Average Grain Size</th>
<th>Average Pore Size</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>I</td>
<td>700 °C 50 hours</td>
<td>10.0</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>1B</td>
<td>I</td>
<td>700 °C 12 hours</td>
<td>11.1</td>
<td>1-.4mm</td>
<td>.1mm</td>
</tr>
<tr>
<td>3B</td>
<td>I</td>
<td>700 °C 12 hours</td>
<td>9.7</td>
<td>1-.4mm</td>
<td>.1mm</td>
</tr>
<tr>
<td>4B</td>
<td>I</td>
<td>700 °C 12 hours</td>
<td>10.6</td>
<td>1-.4mm</td>
<td>.1mm</td>
</tr>
<tr>
<td>5B</td>
<td>II</td>
<td>700 °C 12 hours</td>
<td>17.1</td>
<td>1-.4mm</td>
<td>N.D.</td>
</tr>
<tr>
<td>2B'</td>
<td>II</td>
<td>775-800 °C 6 hours</td>
<td>12.5</td>
<td>2-.5mm</td>
<td>.1mm</td>
</tr>
<tr>
<td>1C</td>
<td>II</td>
<td>650-700 °C 24 hours</td>
<td>5.0</td>
<td>2-5mm</td>
<td>.05-1.5mm</td>
</tr>
<tr>
<td>2C</td>
<td>II</td>
<td>650-700 °C 24 hours</td>
<td>5.0</td>
<td>2-5mm</td>
<td>.05-1.5mm</td>
</tr>
<tr>
<td>1N</td>
<td>I</td>
<td>--</td>
<td>&lt;1.0</td>
<td>1/8-1 in.</td>
<td>--</td>
</tr>
<tr>
<td>3N</td>
<td>II</td>
<td>--</td>
<td>&lt;1.0</td>
<td>1/8-1 in.</td>
<td>--</td>
</tr>
<tr>
<td>1S</td>
<td>II</td>
<td>--</td>
<td>0.0</td>
<td>Single Crystal</td>
<td>--</td>
</tr>
</tbody>
</table>

*The pore size given here represents that part of the total porosity resulting from imperfect meshing of the grains and not the bubble pores in the grains which had diameters of a few tens of microns on the average.*
almost all the runs on apparatus I including those not reported in this investigation.

**Sample 1B** -- The measurements on 1B are shown in Figure 5. The results again show the increase in slope of the resistivity vs. temperature curve near 200°C and a departure from linearity in this case above 450°C. The magnitude of the conductivity of sample 3A is approximately 17 percent higher than that of 1B; however, 3A was annealed four times as long.

**Sample 3B** -- The conductivity and resistivity of 3B are shown in Figure 6. The results are practically identical with those of 1B, differing by only 6 percent at 75°C and 2 percent at 400°C. This is to be expected as the samples had similar porosities and identical annealing. Sample 3B departs from linearity above 400°C as is evident from Figure 6.

**Sample 4B** -- The measurements on sample 4B shown in Figure 7 are significantly different from the rest of the B series. Figure 10 shows that the resistivity is linear in T up to 400°C with no discontinuity in the slope of the line at about 200°C. In addition, the magnitude of the conductivity of sample 4B is lower.
FIGURE 4
Sample -- 3A
Porosity 10%
Apparatus I

- Conductivity
- Resistivity

Temperature °C

K (cal cm⁻¹ sec⁻¹ °C⁻¹) * 10⁻⁵
FIGURE 5
Sample --- 1B
Porosity 11.1%
Apparatus I
FIGURE 6
Sample -- 3B
Porosity 9.7%
Apparatus I
than the conductivity of 1B and 3B by about 20 percent at 100°C and 12 percent at 500°C. This particular sample, though of similar porosity and annealing history as 1B and 3B, had been used in a number of test runs wherein it was cycled through large temperature ranges several times as well as having moderate temperature gradients in it. It is interesting to note that the slope of the resistivity curve of 4B is exactly parallel to the slopes of 1B and 3B above 200°C. It appears, therefore, that in the vicinity of 200°C on apparatus I, the temperature gradient in the sample has exceeded some threshold gradient required to introduce some irreversible temperature effect. A similar phenomenon was noted on other rerun samples that had originally been run on apparatus I with large temperature gradients.

Sample 5B -- The results for 5B are shown in Figure 8. These data were taken on apparatus II. A running calibration between the two thermocouples, however, was not kept, possibly accounting for the scatter in the data above 500°C. Inasmuch as the temperature difference was kept small, of the order of 10°C, the results on apparatus II should not show the kink in the resistivity vs. temperature plot that occurs at about
FIGURE 8
Sample -- 5B
Porosity 17%
Apparatus II

* Conductivity
* Resistivity
200°C in the measurements on apparatus I. Figure 8 verifies this conjecture. The resistivity is quite linear up to 500°C. Above this, not much can be said because of the scatter in the data. However, it is noteworthy that the departures from linearity above 500°C are toward the side of higher resistivity, directly opposite to the behavior at high temperatures on apparatus I. The magnitude of the conductivity of sample 5B is lower than that of 1B and 3B by 27 percent at 125°C and 23 percent at 500°C. As this sample had not been previously run, the only explanation for the large discrepancy between this and the other members of the B series is its large 17 percent porosity.

Sample 2B — The results of the measurements on 2B are presented in Figure 9. Reference to the figure reveals no kink in the data at 200°C. As with sample 5B, a running calibration between the two thermocouples was not kept, probably accounting for the scatter. The data is linear up to 500°C with departures above 500°C toward the side of higher resistivity. These, however, show no regularity and are probably not significant. Sample 2B was not a member of the B series, but was the sole survivor
FIGURE 9
Sample -- 2B'
Porosity 12.5%
Apparatus II

$K_{(\text{cal cm}^{-1} \text{sec}^{-1} \text{°C}^{-1})} \times 10^{-5}$

- $\bigcirc$ -- Conductivity
- $\bullet$ -- Resistivity

Temperature °C
of a group of five samples that had melted or partially melted during annealing. It is estimated that it was at a temperature slightly below the melting point 800°C for a few hours. Previous to this, it had annealed at 700°C for 12 hours. The magnitude of the conductivity is greater than 1B and 3B by 24 percent at 100°C and 26 percent at 500°C. It is also a few percent greater than the conductivity of 3A which had a long annealing time but at 700°C. It appears that the annealing process plays a critical role in the conductivity of the pressed samples.

Sample 1C -- The results for 1C are given in Figure 10. Thermocouple calibration was kept during the entire progress of the run as described in the Experimental Section. The data shows linearity up to 600°C with little scatter. Between 150°C and 600°C, the points fall within 1/2 percent of the solid line. Above 600°C a sharp decline in resistivity occurs. The last two points both at 752°C were taken within several minutes of one another, the lower point last. The conductivity was apparently increasing rapidly. From previous results and the results on sample 2C, it is felt that the sharp decline in resistivity above 600°C may have been due to thermocouple
FIGURE 10
Sample -- 1C
Porosity 5%
Apparatus II
difficulties. The magnitude of the result is greater than that of 1B and 3B by 9 percent at 180°C and 17 percent at 500°C. A direct comparison is of little value in view of the differences in porosity and annealing time. It appears that the reduction in porosity of 1C may have been in part compensated by lower annealing temperature.

**Sample 2C** -- Figure 11 shows the conductivity and resistivity of sample 2C. This sample and the previous one were formed under as nearly identical conditions as possible. Their porosities were identical as well as the annealing time and temperature. The results agree so closely that the same straight line fits the resistivity data in both cases. Between 150°C and 600°C, the data for 2C deviate from a straight line by less than 1 percent with the exception of one point, which deviates by 2 percent. The solid circles represent the original run in which measurements were taken while heating up. At 618°C the emf. from one of the thermocouples was fluctuating slightly indicating a bad connection. At the next power setting, one of the thermocouple leads broke, and it was necessary to shut down the furnace, remove the sample, and repair the connection. In the process, care was taken not to disturb the heater or thermocouples.
The open circles were taken during reheating and fall within 1/2 percent of the line determined by the original run up to 550°C. At 700°C a series of readings were taken at 15 minute intervals as this is the temperature region where departures were usually observed. The first reading was low, the next high and with each subsequent reading, the resistivity apparently decreased rather uniformly. How far the decrease would have continued is not known. Two additional readings were taken on cooling to determine if any irreversible changes had taken place at 700°C. These are represented by the open triangles; clearly no such changes occurred.

The data on samples 1C and 2C demonstrate the reproducibility of the measurements from sample to sample when it is known that the samples have identical micro-structure. Sample 2C demonstrates the reproducibility of the measurements on a particular sample when the gradient is kept small, and it is known that no irreversible temperature effects have been introduced by previous runs. All the measurements on apparatus II demonstrate the linear increase of thermal resistance with temperature, and in particular, sample 2C demonstrates that this relationship holds up to at least 650°C, perhaps the most important result of all as concerns radiative transfer.

-50-
FIGURE 11
Sample -- 2C
Porosity 5%
Apparatus II

Original run
Rerun (heating)
Rerun (cooling)
Samples 1N and 3N -- The data on the natural samples 1N and 3N are shown in Figure 12. The open circles represent 1N and the solid circles 3N. Figure 12 shows the linearity of the data up to 300°C, the highest temperatures obtainable with the natural material. The data on 1N were taken on apparatus I. At about 300°C, the sample suffered a rather forceful disintegration attended by a loud report. It was felt that the gradient in the sample was responsible for the breakup because of thermal stresses in the large grains. Therefore, further tests on the natural material were put off until apparatus II was constructed. Sample 3N is one of several attempts to make a run on the second apparatus. It too had an explosive end at almost exactly the same temperature; yet the gradient was kept well below that which had caused 1N to disintegrate. One of the natural samples was placed in the furnace without any heater and the temperature increased. It too burst apart at approximately 300°C. Since the furnace gradients were extremely small, the only explanation that seemed to offer itself was that internal forces other than thermal stress must have been operative. A re-examination of the natural samples under the microscope revealed a remarkable phenomenon.
Distributed uniformly on all the grain boundaries were isolated, nearly spherical pores a few tens of microns in diameter. As the pore pressure increased with temperature, there was a net force acting to separate the grains due to the pores being localized on the grain boundaries. This agrees with the observation that the fractures occurred along grain boundaries and not across the grains.

In spite of the failure to get measurements above 300°C on the natural salt, the data do provide a valuable comparison between apparatus I and II. At low temperatures and consequently low gradients, the results should be identical as they are. The temperature difference involved in apparatus I was of the order of 12°C at the highest reading which is comparable with that in apparatus II. The conductivity of the natural samples is 36 percent greater than that of the C series in the region of overlap. This gives some indication of the failing of the porosity correction applied to the pressed cylinders. If it was valid for these materials, samples 1C and 2C should differ from the dense natural material by only 5 percent.
Sample 18 -- The results on the synthetic sodium chloride are shown in Figure 13. As usual, the thermocouples were calibrated throughout the run at each reading. The thermal resistivity shows a linear increase up to 450°C. Above this, and continuing to 700°C, the thermal resistivity decreased in an erratic manner, only the point at 534°C being shown. The cause of the irregular behavior above 450°C is not known. The thermocouples and heater appeared to be functioning properly, and upon disassembly, the sample was intact and had not fractured or otherwise altered to cause the spurious behavior.

The results on 18 agree within 3 percent of those on the natural salt, samples 1N and 3N. This was to be expected considering the grain size of the natural samples. Their shaley impurities would affect the conductivity only at low temperatures.

2. Fused Quarts

The thermal conductivity measurements on fused quarts were made in apparatus II over the temperature range of 65°C to 1135°C. The results from 150°C to the highest temperature are shown in Figure 14. During the
FIGURE 13
Sample -- 1S
Apparatus II

○ -- Conductivity  
● -- Resistivity

$E$ (cal cm$^{-1}$ sec$^{-1}$ °C$^{-1}$) $\times 10^{-3}$ vs. Temperature °C
entire run the results were corrected for extraneous
temperature differences between the thermocouples as
described previously. The points form a smooth curve
with a strong upswing beyond 300°C, there being a 6.5
fold increase in conductivity between 65°C and 1135°C.

After the completion of the run, the conduc-
tivity was again measured at 65°C and found to agree
within 1 percent of the original determination, indi-
cating the reproducibility of the results as well as
the lack of any deterioration of the thermocouples at
the high temperatures.

3. Dunite

The thermal conductivity measurements on
dunite were made in apparatus II over the temperature
range 100°C to 1100°C. The results are shown in
Figure 15 along with those of Birch and Clark (1940).
As before, a running calibration between the thermo-
couples was kept. In order to control the partial
pressure of oxygen, approximately seven grams of
wustite composition buffer was placed in the furnace
in nickel dishes on either side of the sample, and
the furnace was flushed with argon.
FIGURE 14

THERMAL CONDUCTIVITY OF FUSED QUARTZ
The original run, represented by solid circles, shows a temperature dependence proportional to $1/(T-88^\circ K)$ up to $400^\circ C$. Above this, the conductivity decreased faster. No measurements were obtained above $500^\circ C$ because of a break in one of the leads in the furnace, but the sample was actually heated to about $650^\circ C$ on the original run. Above $400^\circ C$, it was noted that considerable gas was being expelled from the furnace, and upon disassembly, a rather large quantity of water was found condensed on the cool ends of the furnace. The sample appeared not to have altered except for some darkening, though a detailed examination was not made. After fixing the lead, the sample was run again. These results, represented by the open circles, show an almost constant conductivity to $400^\circ C$ with a slight decrease at higher temperatures. The low temperature value is about one third that of the original run. As before at temperatures above $400-500^\circ C$ and continuing to $700-800^\circ C$, much gas was expelled from the furnace, and there was considerable condensed water on the inside of the ends of the furnace tube.

Detailed examination of the sample after the second run revealed that: (1) the sample was extremely
FIGURE 15
THERMAL CONDUCTIVITY OF DUNITE

- Original Run
- Rerun
- Dunite 2 Birch + Clark (1940)
- Dunite 3 Birch + Clark (1940)
- Dunite 1 Birch + Clark (1940)

Temperature °C

K (cal cm⁻¹ sec⁻¹ °C⁻¹) · 10⁻³
friable and could be broken up into individual grains in
the hand; (2) the individual grains of olivine were still
light green in color and preserved their transparency,
indicating the success of the buffer in preventing oxida-
tion or reduction of the ferrous iron silicate; and,
(3) a thick grain boundary phase was present consisting
of an opaque light gray material.

B. Transmission Measurements

The data presented here are smoothed data obtained
from the measured transmitted intensity $I_t$ by dividing
it by the background spectra $I_o$ at enough different wave-
lengths to delineate the curve and by drawing the best
smooth curve through the points.

1. Sodium Chloride

The transmission spectra of two thicknesses
of the pressed sodium chloride powder are shown in
Figure 16. The samples were prepared from one of the
B series and had microstructure representative of all
the pressed samples. The surfaces of the two samples
were prepared identically. They admitted a reasonably
good polish considering the porosity, but were by no
FIGURE 16
INFRARED TRANSMISSION OF PRESSED SODIUM CHLORIDE

% Transmission ($I/I_o$) vs. Wavelength (microns)

Thickness = 0.324 mm

Thickness = 0.497 mm
means specular. However, the reflected light did have a strong specular component. The transmission was small and constant over the range investigated -- 1.5 to 8 microns. Since sodium chloride is transparent in the range 1 to 15 microns, the reduction in transmission observed here is due entirely to scattering by pores and grain boundaries, and it shows no wavelength dependence over the region investigated.

2. **Fused Quartz**

The transmission spectra of two thicknesses of fused quartz are shown in Figure 17. These samples were obtained from the quartz rod on which the thermal conductivity measurements were made. Their surfaces were polished to a high degree, and appeared to have no diffuse losses in the visible. The transmission was measured from 1 micron to 5 microns where the intensity was too low to be recorded. Lattice absorption starts at about 2.5 microns and becomes very strong above 3.5 microns. These data agree very well with that available in the literature on fused quartz. The short wavelength cutoff is below .2 micron.
FIGURE 17

INFRARED TRANSMISSION OF FUSED SILICA

% Transmission ($I/I_0$)

Wavelength (microns)

Thickness = 2.62 mm

Thickness = 8.9 mm
3. **Dunite**

The transmission measurements on dunite are shown in Figure 18. The samples were prepared from excess material not used in the conductivity measurement. The surfaces obtained a good polish, but because of grain boundaries and pores, some diffuse losses resulted. The measurements show a transmission window from about 2 microns to 4.5 microns with a smaller window between 6 and 7 microns. Beyond 8 microns, only a few percent transmission was recorded. The absorption below 1.5 microns is part of an absorption band centered about 1 micron and is attributed to absorption by the Fe$^{++}$ ion (Clark, 1957). The measurements of Hughes (1953) on single crystal peridot (gem variety olivine) are in substantial agreement with those reported here except that the absorption band at 3 microns does not appear. The absorption beyond 5 microns is attributed to lattice absorption of the silicate structure. The absorption at 3 microns is believed due to water in the hydrous alteration mineral serpentine present in the sample. Comparison with Coblentz's (1906) measurements on serpentine shows similar spectra but with a much stronger water absorption at 3 microns. In fact, the 3 micron
band is characteristic of the absorption spectra of all hydrous minerals (Coblentz, 1906).
FIGURE 18
INFRARED TRANSMISSION OF DUNITE

Wavelength in Microns

% Transmission (I/I₀)

Thickness = 0.465 mm

Thickness = 0.673 mm

Wavelength in Microns
CHAPTER IV
DISCUSSION OF RESULTS

A. Fused Quartz

1. Phonon Conductivity

The low temperature conductivity measurements on fused quartz reported here are found to be in excel-

lent agreement with values in the literature, Figure 19. The open circles were taken on heating and the solid
circle was taken after the entire run to 1150°C. The solid curve represents smoothed data compiled by
Devyamkova, Pemrov, Smirnov and Moishes (1960) from their own measurements on fused quartz using three
methods, and the measurements of Berman (1951), Kingery (1955), and Ratcliffe (1959). The agreement establishes
the accuracy of the method used in this investigation when proper care is taken in preparing the sample and
implacing the thermocouples and heater.

The strong upswing in the conductivity above 300°C, Figure 14, is unexplainable in terms of the lat-
tice conductivity \( K_\mu \) alone, for \( K_\mu \) may be written in a simplified form as

\[
K_\mu = \frac{1}{2} C_v \nu L_{ph}
\]

(4.1)
FIGURE 19
COMPARISON OF VARIOUS THERMAL CONDUCTIVITY DATA ON FUSED QUARTZ

\[ K(\text{cal cm}^{-2} \text{sec}^{-1} \text{C}^{-1}) \times 10^{-5} \]

- Standard Curve for Thermal Conductivity of Fused Quartz
- ○ This Investigation
- ● Rerun

Temperature °C
where $C_v$ is the specific heat at constant volume, $\nu$ is the velocity of elastic waves or phonons, and $L_{ph}$ is their mean free path. In crystalline solids, $L_{ph}$ is proportional to $1/T$ at high temperatures (Appendix A), but in glasses, the phonon mean free path is limited by the short range order of the structure and equals about 8 angstroms, the size of a silicon dioxide tetrahedron (Kittel, 1957). The phonon velocity $\nu$ is temperature independent. The specific heat $C_v$ is strongly temperature dependent for $T < \Theta_D$ but approaches the classical Dulong and Petit value of 6 calories per mole degree for $T > \Theta_D$ where $\Theta_D$ is the Debye temperature. Therefore, the lattice thermal conductivity $K_\mu$ will show the same temperature dependence as $C_v$, becoming constant for $T >> \Theta_D$.

The extra conductivity is then the result of other mechanisms being operative above 300°C. Since the electronic and excitation mechanisms (Appendix A) must be discounted in fused quartz, the extra conductivity is equated to radiative transfer.

2. **Photon Conductivity**

In order that the observed radiative contribution to the conductivity may be compared with theory,
equation (A.23), the mean extinction coefficient \( \bar{\varepsilon} \) or in this case \( \bar{\alpha} \), since there is no scattering, was computed from equation (A.24),

\[
\frac{1}{\alpha} = \frac{1}{\varepsilon} = \frac{15}{4} \int_0^\infty \frac{1}{\alpha(\lambda)} \frac{x^4 e^{-x}}{(e^x - 1)^2} \, dx
\]

where \( x = \frac{hc}{\lambda kT} \). The spectral absorption coefficient \( \alpha_\lambda \) was determined from the transmission data, Figure 17, and equation (2.10). Its reciprocal, \( L_\lambda \), the spectral photon mean free path, is shown in Figure 20. The integrated photon mean free path above depends on temperature implicitly through the integral, Figure 21, and explicitly through any temperature dependence of \( \alpha_\lambda \).

The temperature dependence of \( \alpha_\lambda \) was not investigated here, but Lee (1958) conducted infrared transmission measurements on fused quartz and other insulators up to 1200°C and found little dependence of \( \alpha_\lambda \) on temperature in the infrared. He found the transmission was reduced several percent at the highest temperatures and the lattice absorption cutoff moved toward shorter wavelengths with increasing temperature.

The integral for \( 1/\bar{\alpha} \) was evaluated numerically for several temperatures and put into the radiative conductivity formula.
FIGURE 20
PHOTON SPECTRAL MEAN FREE PATH IN FUSED SILICA

Wavelength (microns)

$L_{\lambda} = \frac{1}{\lambda}$ (cm)
FIGURE 21

WEIGHTING FUNCTION $f(x)$

$$f(x) = \frac{x^2e^x}{(e^x-1)^2}$$

$$x = \frac{h\nu}{\lambda kT}$$

$\lambda$ in Microns

1500°K 1000°K 750°K 500°K
\[ K_R = \frac{16 \pi^2 \sigma T^3}{3\alpha} \]  

(4.3)

to determine the contribution predicted by theory. The results are shown in Figure 22. The solid circles show the computed radiative conductivity, and the open circles show the observed radiative contribution obtained by subtracting \( K \) from the total measured conductivity. The observed values are one fiftieth of the calculated values over the range of temperature investigated. The remarkable thing is that the temperature dependence of the two curves is identical. This can best be seen in Figure 23 where the logarithm of the observed and calculated radiative conductivity is plotted against the logarithm of the temperature. The vertical scales have been shifted so that the curves may be compared. The agreement is well within the uncertainty of the numerical integration. The slope of the curve gives the exponent in \( T \) in the radiative formula (4.3), which varies from 7 at 380°C to 3.7 at 1136°C.

The failure of equation (A.23) or (4.3) to properly account for the magnitude of the observed result is undoubtedly related to the fact that it is derived in the approximation that the boundaries do not contribute
FIGURE 22
COMPARISON OF OBERSVED AND COMPUTED $K_R$

$K_R$ [cal cm$^{-1}$ sec$^{-1}$ °C$^{-1}$]

Temperature °K

- Computed $K_R$
- Observed $K_R$
FIGURE 25

COMPARISON OF THE TEMPERATURE
DEPENDENCE OF THE COMPUTED AND OBSERVED $K_R$
to the radiation field. It represents the infinite space solution and can be expected to hold if the sample dimensions are several times the mean free path for photons. In the case at hand, the integrated or weighted photon mean free path, equation (4.2), is at best equal to the radius of the quartz rod and at the highest temperatures, it is about twenty times the sample radius. Therefore, the simple theory, equation (4.3), cannot be applied. Equations (A.21) and (A.16) must be solved retaining the boundary term and specifying the appropriate boundary conditions.

3. Investigation of the Boundary Effects

In that which follows, the effects of the boundaries will be analyzed in terms of existing theory in an attempt to explain (1) the discrepancy in magnitude of the observed and the calculated radiative conductivity, and (2) the agreement in temperature dependence of the observed and calculated radiative contribution. As will be shown, existing theory does not properly account for (1) and (2). Several alternative mechanisms are proposed, though not proven, that may explain the observed results.
The presence of reflecting and radiating boundaries complicates the problem considerably. So far as the author knows, the only attempts to treat the problem of radiative transfer in a bounded medium characterized by an absorption, scattering, and emission coefficient have been carried out in parallel plane geometry. There exist extensive treatments of radiative transfer between surfaces of arbitrary geometry in non-absorbing media (Jakob, 1957), but these results cannot be applied here except in the limit of no interaction between the radiation field and the intervening matter.

The works of Hamaker (1947) and Kellett (1952) treat the radiation field as one dimensional, thereby reducing the fundamental equation of transfer (A.12) from an integro-differential equation to a differential equation. The equation is further simplified by linearizing $\eta(\lambda, T)$, the emission coefficient. Solutions are then readily available for various boundary conditions, and they predict qualitatively correct results in the limit of transparent or opaque material. The work of Van der Held (1954) will be discussed in detail since he retains the three dimensional nature of the radiation field, and it represents a more accurate formulation of the problem.
Van der Held (1954) considers the problem of two infinite parallel plane radiators separated by a distance $d$. The radiators are described by their temperatures $T_1$, $T_2$, and emissivities $\varepsilon_1$, $\varepsilon_2$, while the material between the plates is characterized by an absorption coefficient $\alpha_\lambda$, scattering coefficient $\sigma_\lambda$, thermal conductivity $K$, and emission coefficient $n^2\alpha_\lambda B(\lambda, T)$, where $n$ is the index of refraction and $B(\lambda, T)$ is Planck's radiation function. For simplicity, he assumes $\alpha_\lambda$ and $\sigma_\lambda$ wavelength independent and takes $n^2 = 1$. If the material between the plates is perfectly diathermanous, there will be direct radiative transfer between the surfaces, each surface radiating according to Kirchhoff's law the energy flux $\varepsilon_\lambda B(\lambda, T)$ in the wavelength interval $(\lambda, \lambda + d\lambda)$. Taking into account multiple reflections and conduction, the total heat flux is then given by

$$
\frac{\dot{Q}}{A} = -K \frac{dT}{dx} + \int_0^\infty \frac{B(\lambda, T_1) - B(\lambda, T_2)}{\varepsilon_1 + \varepsilon_2 - 1} d\lambda \quad (4.4)
$$

or if the emissivities are independent of wavelength
\[
\begin{align*}
\frac{d}{dt} = -K \frac{dT}{dx} + \frac{\sigma_o (T_1^4 - T_2^4)}{\frac{1}{e_1} + \frac{1}{e_2} - 1} \quad (4.5)
\end{align*}
\]

Therefore, an effective conductivity may be defined as

\[
K_{\text{eff}} = K + \frac{d}{(T_1 - T_2)} \frac{\sigma_o (T_1^4 - T_2^4)}{\frac{1}{e_1} + \frac{1}{e_2} - 1} \quad (4.6)
\]

or representing the last term by \(a_r\) gives \(K_{\text{eff}} = K + da_r\). On the other hand, if the separation of the plates is large and the extinction coefficient, \(\epsilon = \sigma + \alpha\), is also large, the effective conductivity must be given by equation (4.3)

\[
K_{\text{eff}} = K + \frac{16}{3} \frac{\sigma_o T_3^3}{\epsilon}
\]

or calling \(4\sigma_o T_3^3 = a_s\) gives \(K_{\text{eff}} = K + \frac{4}{3} \frac{a_s}{\epsilon}\). As is evident, \(a_r = a_s\) for small \(\Delta T = [T_1 - T_2]\) and \(e_1 = e_2 = 1\).

Thus, Van der Held (1954) writes the effective conductivity for intermediate cases as

\[
K_{\text{eff}} = K + \frac{4}{3} \frac{a_s}{\epsilon}\psi \quad (4.7)
\]
with $\psi < 1$. Since $K_{\text{eff}}$ cannot exceed $K + \frac{4}{3} \frac{a_r}{a_s}$ nor $K + da_s$, $\psi$ cannot exceed 1 nor $3/4$ ed. It can, however, exceed $\frac{3}{4} \frac{a_r}{a_s}$ ed if $a_r \ll a_s$ as Van der Held shows. The calculation of the effective conductivity proceeds as follows. Let $g_1$ be the radiant flux reaching surface 1 and $g_2$ the radiant flux reaching surface 2, then their difference $g = g_2 - g_1$ is the net radiant flux. The total heat flux is then

$$
\frac{Q}{\Lambda} = -K \frac{dT}{dx} + g = -K_{\text{eff}} \frac{dT}{dx} .
$$

(4.8)

From this and the relation $\psi = \frac{4}{3} \left( \frac{a_r}{a_s} \right) (K_{\text{eff}} - K)$, $\psi$ may be determined. The fluxes $g_1$ and $g_2$ are calculated using equation (A.13) and (A.11) but integrating over only the hemisphere in the latter. The problem is linearized by expanding Planck's function as

$$
B(\lambda, T) = B(\lambda, T_0) + \frac{\partial B}{\partial T} \bigg|_{T=T_0} (T-T_0) .
$$

(4.9)

The calculations and resulting expressions are messy and will not be presented here. However, Figure 24 shows a plot of $\psi$ vs. $D = \text{ed}$, the optical thickness, utilizing some of the data presented by Van der Held (1954). These results have been obtained under the assumptions (1) that
FIGURE 24

RATIO OF THE APPARENT TO THE MAXIMUM CONTRIBUTION OF RADIATION TO THE THERMAL CONDUCTIVITY
\( e_1 = e_2 = e \), (2) that \( \alpha, \sigma \) and \( e \) are wavelength independent, and (3) that the reflected intensity is diffuse. From the figure, \( \Psi \) goes to zero as \( D \) does and approaches unity for large \( D \). The details depend upon the emissivity \( e \), the fraction absorbed \( \varphi = \frac{\alpha}{\varepsilon} \), and the parameter \( \frac{K_\varepsilon}{\alpha_s} \), though the latter's influence is quite small. The influence of \( \varphi \) is large at small \( e \) and small at large \( e \). As is evident, \( \Psi \) is bounded by the line \( \frac{3}{4} D \) on the left and by unity from above. The data in Figure 24 are incomplete but give some indication of the behavior of \( \Psi \) with \( D, e \) and \( \varphi \) for the approximations made. Van der Held (1954) gives explicit solutions for \( \Psi \) only in the cases where \( \varphi = 0 \), that is, for a purely scattering material. This turns out to be the least difficult case. For \( \varphi \neq 0 \), he outlines the steps to the solution and presents numerical data for some variation of the parameters. The results shown, however, clearly indicate that for small \( D, D \ll 1 \), the function \( \Psi \) is proportional to \( D \). Reference to equation (4.7) shows that in this case the \( \varepsilon \) in the denominator of the second term will cancel with the \( \varepsilon \) in \( D = \varepsilon d \), and \( (K_{\text{eff}} - K) \), the radiative contribution, will be independent of \( \varepsilon \) for small \( D \).
As stated previously, the observed radiative contribution in fused quartz may be expressed as

\[(K_{\text{eff}} - K) = \frac{4}{3} \frac{\xi}{\varepsilon} \left( \frac{1}{20} \right) \]  \hspace{1cm} (4.10)

or \( \Psi = \frac{1}{20} \) over the temperature range 379°C to 1136°C.

In this range, the mean extinction coefficient \( \bar{\varepsilon} \) calculated from equation (4.2) varies between .247 cm\(^{-1}\) at 379°C and .054 cm\(^{-1}\) at 1136°C. The sample thickness \( d \), or in this case the difference in radii of the inner and outer walls, is 1.03 cm, giving an optical distance \( D = \bar{\varepsilon}d \) that varies from .255 at 379°C to .056 at 1136°C.

For these values of \( D \), Van der Held's theory predicts that the radiative contribution is independent of \( \bar{\varepsilon} \) and is given essentially by equation (4.6), simply the direct transmission of energy between the surfaces with negligible interaction between photons and intervening matter. The measurements, however, indicate that the absorption coefficient is still coming in to the first order, for the temperature dependence of the calculated and observed results agree so closely.

It is possible, of course, that the agreement is fortuitous, the actual contribution being given by equation (4.6) with emissivities whose temperature
dependence is such that the temperature dependence of
the whole term is the same as that calculated using \( \varepsilon \)
in equation (4.3). This, however, is a rather remote
possibility considering the large variation in the
exponent of \( T \) in the radiative term. It decreases from
\( T^7 \) at 380°C to \( T^{3.7} \) at 1136°C. Furthermore, the
radiative contribution predicted by equation (4.6)
is inadequate to account for the measurements with
the emissivities involved, as will presently be shown.
Rather than use equation (4.5), however, a more mean-
ingful result will be obtained using the equivalent formula
for coaxial cylindrical radiators with a diathermanous
medium of conductivity \( K \) enclosed within. Let the
inner infinite cylinder have radius \( r_1 \), temperature \( T_1 \),
and emissivity \( e_1 \), and the outer cylinder have radius
\( r_2 \), temperature \( T_2 \), and emissivity \( e_2 \). The total heat
flux is then given

\[
Q = 2\pi LK \frac{(T_1 - T_2)}{r_2} + \frac{2\pi r_1 L e_2 (T_1^4 - T_2^4)}{\ln\left(\frac{r_2}{r_1}\right) \left(\frac{1}{e_1} + \frac{r_1}{r_2} \left(\frac{e_1}{e_2} - 1\right)\right)}
\]  

(4.11)

for emissivities independent of wavelength. This may
be written as
\[
Q = \frac{2\pi L (T_1 - T_2)}{\ln \left( \frac{r_2}{r_1} \right)} K_{\text{eff}}
\]

where

\[
K_{\text{eff}} = \left[ K + r_1 \ln \left( \frac{r_2}{r_1} \right) \frac{4\sigma T^3}{e_1 + \frac{r_1}{r_2} (e_2 - 1)} \right]
\]

is the effective conductivity. In order to evaluate equation (4.13), the emissivities must be estimated. The heater consisted of a platinum winding on a ceramic tube. The emissivity of platinum filament varies from about 0.06 at 350°C to 0.18 at 1100°C. Since the heater had a composite surface, twice these values are taken for \(e_1\) to allow for emission by the tube. The nickel sleeve surrounding the sample was shiny but not polished; also it remained unoxidized during the run. The values appropriate to polished nickel are slightly higher than for platinum, but as the formula (4.13) shows, \(e_2\) has little influence so it will be taken equal to \(e_1\). Table III shows a comparison of the calculated and observed radiative contribution, \((K_{\text{eff}} - K)\), obtained from equation (4.13) and Figure 22, along with the emissivities used in the calculations.
As is evident, direct radiative transfer can account for only about 10 percent of the observed radiative effect with the emissivities involved. Even with black body radiation, $e=1$, the direct transfer is less than that observed except at the lowest temperature where it exceeds the observed result. Therefore, it appears that only a small fraction of the observed radiative transfer is due to direct radiation from one boundary to the other as is predicted by Van der Held’s theory for small $D$, the optical thickness.

The failure of Van der Held’s theory to account for the measurements may be due in part to (1) the use of cylindrical geometry rather than parallel plane, (2) the assumption of absorption coefficient...
being wavelength independent, or (3) an incorrect formulation of the problem. These will be discussed in the following in an attempt to reconcile the measurements with theory.

(1) A modest attempt was made to evaluate the integrals, equations (A.13) and (A.11), in cylindrical geometry. However, they appeared not to be expressible in terms of known or tabulated functions, and the calculations were not pursued. Nonetheless, the cylindrical geometry may produce a significant change in the results. The radiation reflected at the outer boundary may traverse the sample many times before intercepting the inner one, thereby effectively increasing the optical distance and the chance for absorption. In the parallel plane case, of course, each traversal of the sample encounters the opposite boundary.

(2) The assumption of the wavelength independence of the absorption coefficient is certainly not justified in the case of fused quartz, Figure 20. The effect this may have on Van der Held's (1954) solution is discussed below.

It is clear from the figure that the spectral photon mean free path in quartz shows two distinct regions. Photons with wavelengths below about 3.5 microns
"see" a very transparent material and can travel on the average 25 cm without being absorbed by the material. On the other hand, photons with wavelengths greater than 3.5 microns "see" an opaque material and are absorbed within a fraction of a centimeter. Therefore, it appears reasonable to analyze the radiative contribution in the two distinct regions of the spectrum independently. To do this, a cutoff wavelength $\lambda_c$ is defined such that the spectral mean free path $L_{\lambda_c}$ equals $d$, the thickness of the sample.

In the part of the spectrum for $\lambda < \lambda_c$, the optical distance decreases rapidly from $l$ to $0.04l$. Assuming Van der Held's theory holds here because $L_{\lambda}$ is reasonably constant, the only contribution of radiation to the heat flux is that of direct radiation from the boundaries, equation (4.11). And as is shown in Table III, this contribution is small for the emissivities involved. In fact, it is even smaller than calculated there because only photons with $\lambda < \lambda_c$ contribute. Those at longer wavelengths are absorbed within several mean free paths contributing little to the direct flux. This is particularly true at the
lower temperatures where the spectral energy distribution is further in the infrared.

In the part of the spectrum beyond \( \lambda_0 \), the optical distance increases rapidly from 1 to about 6 at the longest wavelengths measured. Direct transmission is negligible, but volume emission now becomes important. The contribution to the conductivity is approximately given by the infinite space solution, equation (4.3), except only those photons with \( \lambda > \lambda_0 \) would appear to be important in contributing to the energy flux by absorption and emission. Their integrated mean free path is then

\[
\bar{L} = \frac{15}{4\pi^4} \int_0^{\lambda_0} \frac{\hbar c}{\lambda^3} \frac{1}{\alpha(\lambda)} \frac{x^4}{(e^x - 1)^2} \, dx \tag{4.14}
\]

The validity of this mechanism, of course, depends on its success in explaining the magnitude and temperature dependence of the observed results. Unfortunately, sufficient transmission data were not obtained to evaluate the integral. The cutoff wavelength \( \lambda_0 \) is about 3.7 microns for \( \lambda_0 = d \), and the data extend only to 4.5 microns. The magnitude of the integral does appear to be of the correct order, for at 650°K the observed value of \( \bar{L} \) is .081 cm, increasing to .37 cm at the highest temperature 1409°K. These values are in accord with the
magnitude of the spectral mean free path in the region beyond 3.5 microns, Figure 20, and the temperature dependence of the weighting function, Figure 21. The definition of \( \lambda_c \) separating the spectrum into two distinct regions is an approximation to the actual situation that would hold exactly if the spectral mean free path had a discontinuity at \( \lambda_c \), the values on one side being much greater than \( d \), and those on the other side being much less than \( d \). This condition is reasonably well fulfilled by fused quartz, Figure 20.

Therefore, if these conditions on \( L \lambda \) are met, the total effective conductivity should be given approximately by

\[
\begin{align*}
K_{\text{eff}} &= K + r_1 \ln \left( \frac{r_2}{r_1} \right) \frac{1}{r_2} + \frac{r_1}{r_2} \left( \frac{1}{e_1} - 1 \right) \int_0^{\lambda_c} \left[ B(\lambda, T_1) - B(\lambda, T_2) \right] d\lambda \\
&+ \frac{16n^2 \sigma_0}{3} T^3 \int_0^{\lambda_c} \frac{\lambda_0 k T}{4 \pi} \frac{1}{\alpha(\lambda)} \frac{4 e^x}{(e^x - 1)^2} dx
\end{align*}
\]

(4.15)

where the first term is the lattice conductivity, the second represents the contribution of direct radiation from the boundaries in the transparent part of the spectrum, and the third term represents the contribution
from volume emission and absorption in the opaque part of the spectrum.

(3) Van der Held's (1954) formulation of the problem appears correct for the absorption coefficient not equal to zero, the case of interest here. It does appear though that his solution for pure scattering is incorrect. It reduces to the infinite space solution, equation (4.3), for large D. Clearly if \( \alpha \rho = 0 \), the matter neither absorbs nor emits radiation, and the radiation field is not related to the temperature of the scattering material. Detailed analysis of the radiative transfer in a scattering medium can be found in Chandrasekhar (1960).

In summary then, it has been shown that the observed radiative conductivity in fused quartz and that calculated from the infinite space solution, equation (4.3), differ in magnitude by a factor of fifty, yet agree exactly in their temperature dependence. The explanation of this discrepancy is sought in the effect of the boundaries. The existing theory is found inadequate to explain the measurements, and it is proposed that the use of cylindrical geometry rather than parallel plane, or the analysis of the radiation field in two distinct parts of the spectrum, may account for the observed measurements.
B. Sodium Chloride

1. Phonon Conductivity

The investigation of sodium chloride constituted a major part of the experimental work, because of its low intrinsic absorption, ease of fabrication, and availability. The results in Figures 4 through 13 are in excellent agreement with the theory of phonon conductivity (Appendix A), especially on apparatus II. The data on apparatus II show a linear increase in the thermal resistivity with temperature up to 650°C on the pressed salt. The differences in the measured conductivity between the various samples is large, even after the porosity correction of Loeb (1954) was applied. The conclusion must be drawn that some aspect of the microstructure of the pressed samples violates the conditions under which the porosity correction may be used. It is possible, of course, that the variation from run to run is the result of large systematic errors, except that agreement was excellent when it should have been, for example, between 1C and 2C, and between 1N, 3N and 1S.

Microscopic examination of the samples before and after a run revealed no obvious reason why the
porosity correction should fail. Certainly the grain size can have no effect. The phonon mean free path in sodium chloride at room temperature resulting from thermal scattering is of the order of 20-30 angstroms, whereas the grain size is of the order of \(10^6\) angstroms; therefore, grain boundaries cannot possibly limit the mean free path at room temperature and even less at higher temperatures. It is postulated, however, that the grain boundaries represent a second phase of lower thermal conductivity that must be accounted for. In order to do this, the following model is proposed. The heat path from the inner to the outer radius consists of alternate grains and grain boundaries. These are replaced by alternate concentric cylinders representing grains and grain boundaries respectively. Let the conductivity of the grains be \(K_s\) and that of the boundaries be \(K_b\). Let \(r_1\) be the inner radius of the first concentric cylinder, \(r_2\) the outer radius of the first cylinder and the inner radius of the second cylinder, etc. The heat flux is then given by

\[
\dot{Q} = \frac{2\pi L(T_1 - T_2N)}{\frac{1}{K_s} \ln \frac{r_2}{r_1} + \frac{1}{K_b} \ln \frac{r_3}{r_2} + \frac{1}{K_s} \ln \frac{r_4}{r_2} + \cdots + \frac{1}{K_s} \ln \frac{r_{2N}}{r_{2N-1}}}
\]
where \( N \) is the number of grains. This may be rewritten as

\[
\frac{Q}{2\pi L(T_1-T_{2N})} \ln \left( \frac{r_{2N}}{r_1} \right) = K_{\text{eff}}
\]

where

\[
K_{\text{eff}} = \frac{K_S}{\ln \frac{r_{2N}}{r_1}} = \frac{K_S}{\ln \frac{r_2}{r_1}} \frac{r_2 r_4 \ldots r_{2N}}{r_1 r_3 \ldots r_{2N-1}} + \frac{K_S}{K_B} \frac{K_S}{\ln \frac{r_{3r_5} \ldots r_{2N-1}}{r_2 r_4 \ldots r_{2N-2}}} \ln \frac{r_{2N}}{r_1} \frac{r_{2N}}{r_1}
\]

As is evident, if the grain boundary thickness goes to zero then \( r_2 = r_3, r_4 = r_5, \ldots, r_{2N-1} = r_{2N-2} \), and \( K_{\text{eff}} = K_S \) as it should. This relationship, although correct for the model proposed, is clumsy to work with because of the logarithms; therefore, the corresponding relationship in parallel plane geometry will be used. The results will not differ significantly but are considerably easier to get and will serve for this analysis. In the parallel plane case, then, the total heat flux is

\[
Q = A \left( \frac{T_1-T_{2N}}{L} \right) \frac{K_S}{L_S} \frac{L_B}{K_B \frac{L_B}{L}} + \frac{K_S}{L_S} \frac{L_B}{K_B \frac{L_B}{L}}
\]
or

\[
K_{\text{eff}} = \frac{K_S}{L} \frac{L_B}{L} + \frac{K_B}{L}
\]

where \( L \) is the thickness of the composite slab, \( L_S \) is the total thickness of grains, and \( L_B \) is the total thickness of boundaries. To evaluate the relationship requires an estimate of \( K_B \) and \( L_B \), \( K_S \) being the conductivity of the salt. Since the grain boundaries were in evidence only by their light reflecting properties under the microscope, it is assumed that their thickness is less than that which could be delineated by visible light, that is <.5 microns. It is further assumed that the grain boundary layer consists of entrapped air except for points of contact, since the samples were not pressed under a vacuum. With these assumptions then, the ratio of \( K_{\text{eff}}/K_S \) is shown in Table IV. These values of \( K_{\text{eff}} \) are more than sufficient to explain the variation of the observed conductivity of the pressed samples. For example, sample 20 has a conductivity 73 percent of either the natural or artificial samples at all temperatures.

In order to establish the accuracy of the results on sodium chloride, they are compared with values
TABLE IV

RATIO OF THE EFFECTIVE TO THE ACTUAL CONDUCTIVITY
IN A MATERIAL WITH A GRAIN BOUNDARY PHASE

<table>
<thead>
<tr>
<th>$K_S$ (cal/cm/sec °C)</th>
<th>$K_B$ (cal/cm/sec °C)</th>
<th>Grain Boundary Thickness (microns)</th>
<th>Grain Thickness (mm)</th>
<th>$L_B/L$</th>
<th>$K_{eff}/K_S \cdot 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-5}$</td>
<td>.5</td>
<td>.1</td>
<td>$5 \times 10^{-3}$</td>
<td>50 %</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-5}$</td>
<td>.4</td>
<td>.1</td>
<td>$4 \times 10^{-3}$</td>
<td>55.5 %</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-5}$</td>
<td>.3</td>
<td>.1</td>
<td>$3 \times 10^{-3}$</td>
<td>62.5 %</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-5}$</td>
<td>.2</td>
<td>.1</td>
<td>$2 \times 10^{-3}$</td>
<td>71.5 %</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-5}$</td>
<td>.1</td>
<td>.1</td>
<td>$10^{-3}$</td>
<td>83.5 %</td>
</tr>
</tbody>
</table>

in the literature in Figure 25. Here only 1S, 1N and 2C are shown as being representative of the synthetic, natural and pressed materials.

As is evident, there is considerable spread in the literature on the conductivity of sodium chloride. The data on 1S and 1N agree almost exactly, and when extrapolated to the temperature axis, agree with Eucken’s (1928) data on synthetic salt from a melt. They lie above Benfield’s (1933) result on rocksalt and Eucken’s result on single crystal natural salt. Birch and Clark’s (1940) result lies about in the middle of the pressed salt data, agreeing exactly with 2C. Eucken’s (1928) result on pressed salt is considerably higher than that reported.
FIGURE 25

COMPARISON OF VARIOUS THERMAL CONDUCTIVITY DATA ON SODIUM CHLORIDE

- 1S Single Crystal Artificial from Melt
- 1N Polycrystalline Natural Salt (Rocksalt)
- 2C Pressed Powder
- Single Crystal Natural Salt (Birch + Clark, 1940)
- Single Crystal Natural Salt (Eucken, 1911)
- Rocksalt (Benfield, 1933)
- Pressed Powder (Eucken, 1928)
- Single Crystal Artificial from Melt (Eucken, 1928)
- Single Crystal Artificial from Solution (Eucken, 1928)
here, but his sample was pressed at 8,000 atmospheres or 60 tons per square inch, which is of the order required to produce optical quality material (Wilkinson and Ford, 1955). It is interesting to note that his pressed sample gives a conductivity lower than his single crystal artificial materials in spite of its high pressure formation. At those pressures, Wilkinson and Ford (1955) found their pressed disks to have less than 1/2 percent porosity; therefore, Loeb's (1954) porosity correction does not apply to Bucken's measurements either.

Since the literature contains such a range of values for the conductivity, a direct comparison is of little help in deciding which are correct. Equation (A.6), however, does provide a further test since it predicts that the thermal resistivity should intercept the axis at $T = \theta_D / 3$ for $T > \theta_D$, where $\theta_D$ is the Debye temperature. For sodium chloride, the Debye temperature at high temperatures equals $\theta_D = 281^\circ K$ (Dekker, 1957). Figure 26 shows a plot of the thermal resistivity vs. temperature for all the samples investigated here. The intercepts fall between -162 and -177°C, a spread of 15°C. This itself is remarkable in view of the
variation of the conductivity from sample to sample. These intercepts give Debye temperatures from 288 to 333°K; in particular, sample 18 is the single crystal artificial salt gives 288°K. Birch and Clark’s (1940) measurements give a Debye temperature of 198°K, and Bucken’s (1911) work gives a value of 144°K.

Inasmuch as measuring the phonon contribution to the thermal conductivity is not the primary experimental objective of this research, a systematic investigation of the effect of porosity, grain size, and annealing time and temperature was not carried out. Therefore, a quantitative discussion of the interrelatedness of these various parameters cannot be given. However, certain qualitative observations are evident from the data.

a. Lower porosity, higher annealing temperature, longer annealing time, and any combination of these results in higher conductivities. The exact relative importance of these effects is indeterminate from the data since the parameters were not varied independently, but it appears that high annealing temperature is a critical factor. This is in agreement with the proposed model for the grain boundary conductivity.
FIGURE 26

THERMAL RESISTIVITY OF SODIUM CHLORIDE

1/\kappa (cal\textpm1 cm\textpm1 sec\textpm1 °C) \cdot 10^2

Temperature °C

0  100  200  300  400

-200 -100  0

1A, 3N

2A

5B

4B

1B

5A

3A

2C

1S

1M, 3N

3.6  3.2  2.8  2.4  2.0  1.6  1.2  0.8  0.4  0.0
At higher temperatures and consequently more complete sintering, the entrapped air layer would presumably be reduced to a smooth walled pore.

b. Pressed samples show irreversible changes in conductivity when the temperature gradient exceeds a limiting value.

The latter effect is observed on apparatus I where above 200°C the thermal resistivity increases faster than below. The gradients that exist in the sample at 200°C are of the order of 40°C per inch and increase to about 350°C per inch at 650°C in apparatus I. The corresponding gradients in apparatus II were always kept below 20°C per inch. Since the only difference in the experiments on the two apparatus is the gradient that exists in the sample, both the increase in resistivity above 200°C and the departure from linearity above 450°C observed with apparatus I must be attributed to the large gradient. It is suggested that the increase in the resistivity above 200°C may be due to grain boundary separations resulting from the large temperature gradient. Reference to Table IV shows that a few percent change in the conductivity can be accomplished with an exceedingly small increase in the
thickness of the grain boundary. This same explanation would not apply, however, to the high temperature departure from linearity toward lower resistivity.

2. **Photon Conductivity**

All the results on apparatus I showed smooth departures from linearity in the resistivity plots above 400-450°C. These, however, are attributed to the large gradients that exist in apparatus I at those temperatures. The results on apparatus II show no smooth departures from linearity above 450°C. Where departures do exist, they are erratic and toward higher resistivity. The data on 2C shows linearity up to 650°C implying that whatever radiative conductivity exists at that temperature is within the uncertainty of the measurements.

The transmission measurements on the pressed powder, Figure 16, yield a scattering coefficient of \( \sigma = 52 \text{ cm}^{-1} \) using equation (2.10). The absorption in this part of the spectrum by sodium chloride is negligible. Figure 27 shows the expected departure from linearity for various values of \( \bar{\varepsilon} \), the extinction coefficient. The straight line represents the resistivity of the 0 samples. From the figure, it appears
FIGURE 27

THERMAL RESISTIVITY OF SAMPLE 1C FOR VARIOUS VALUES OF $\bar{\epsilon}$

Temperature °C

$\frac{1}{K} (\text{cal}^{-1} \text{ cm sec}^{-1} \text{ °C}) \cdot 10^{2}$

$\bar{\epsilon} = 100 \text{ cm}^{-1}$

$\bar{\epsilon} = 50 \text{ cm}^{-1}$

$\bar{\epsilon} = 25 \text{ cm}^{-1}$

$\bar{\epsilon} = 10 \text{ cm}^{-1}$
that the extinction coefficient of the pressed samples is greater than 100 cm\(^{-1}\). The use of equation (2.10) to calculate the scattering coefficient in this case is clearly not justified. It was found that unless the optical thickness \( \tau = \sigma d \) is much less than 1, the use of equation (2.10) to calculate the scattering coefficient will result in a serious underestimation of it. For the sample thicknesses used, \( \tau \) is given by \( \tau_1 = 52 \cdot 0.324 = 1.68 \), and \( \tau_2 = 52 \cdot 0.497 = 2.58 \). Therefore, the calculated \( \sigma \) is smaller than the true one, by an unknown amount. The measurements indicate the true scattering coefficient may be twice as large.

The results on synthetic sodium chloride, Figure 13, show no radiative effect up to 450\(^{\circ}\)C, in spite of its extreme transparency. This may be understood in terms of the position of the lattice absorption edge. The absorption spectra of optical quality sodium chloride is well known (Kremers, 1940). It is uniformly transparent from about 2 to 15 microns. In the transparent region, the mean free path is estimated from Kaufmann's (1960) data as 200 cm. The cutoff wavelength in this case is about 18 microns, beyond which the absorption becomes very strong.
The contributions to the radiative effect are estimated using equation (4.15). Replacing $\lambda_c$ by $\infty$ and using emissivities $e = e_1 = e_2 = 1.2$, the second term gives a direct radiative contribution of $0.093 \cdot 10^{-3}$ (cal/cm sec °C) at 450°C. This is about 1.5 percent of the total measured conductivity at that temperature, and is within the precision of the measurements. The third term, giving the contribution from volume emission, also appears to be negligible, for in the opaque region beyond $\lambda_c$ the absorption coefficient is large, and only the tail of the weighting function contributes to the integral, Figure 21. Therefore, it is not too surprising that the effective conductivity $K_{\text{eff}}$ equals the lattice conductivity up to 450°C.

The measurements on fused quartz and synthetic sodium chloride both had the same boundary conditions. The direct contribution from the boundaries is shown to be small, yet fused quartz shows a radiative contribution of about $0.8 \cdot 10^{-3}$ (cal/cm sec °C) at 450°C and the salt shows none. The difference in the position of the lattice absorption edge appears to account for the contribution in the case of quartz and its absence in synthetic salt.

-106-
C. Dunite

1. Phonon Conductivity

Reference to Figure 15 reveals that the lattice thermal conductivity of dunite at low to moderate temperatures agrees with the theory of phonon conductivity (Appendix A). The agreement with other values in the literature is satisfactory considering the materials are not identical, even though they are from the same source area. Above 450°C irreversible temperature effects occur, masking the lattice conductivity. The temperature independence of the conductivity on the rerun (open circles) is believed due to the partial structural breakdown on grain boundaries of the hydrous alteration mineral serpentine, and the subsequent development of an amorphous grain boundary phase of low, temperature independent conductivity. Grain boundary separations due to the anisotropic thermal expansion of olivine undoubtedly contributed as well.

2. Photon Conductivity

No radiative effect was observed even at the highest temperature 1100°C. This is unexpected in view of the transmission properties of the dunite. Figure 28 shows the spectral absorption coefficient $\alpha_{\lambda}$ computed
FIGURE 28
SPECTRAL ABSORPTION COEFFICIENT OF DUNITE

\[ \alpha(\lambda) \text{ (cm}^{-1}) \]

Wavelength in Microns
from equation (2.10). In the range $\lambda = 1.5$ to 5 microns, the material is fairly transparent except for the water absorption at 3 microns due to the serpentine. The spectral mean free path $L_\varepsilon$ is of the order of .06 cm there; $\bar{L}$ would be somewhat less. Even so, the radiative contribution, equation (A.23), would be observable at 1100°C. Two factors, however, must be considered before applying equation (A.23) directly. First of all, the sample altered during the run. Even though the grains themselves retained their transparency and appeared unaffected, the formation of the thick, gray, opaque grain boundary phase obviously changed the transmission properties of the sample. After the run, the sample resembled a piece of concrete in color and appeared about as transparent, though no transmission measurements were attempted because of its friability. Secondly, because of the known electrical conductivity of olivine at high temperatures (Hughes, 1953; Uhri, 1961), there is the possibility that electronic absorption will drastically change the absorption spectra at higher temperatures.

In general, a solid may absorb radiation by (1) excitation of lattice vibrations in the infrared,
(2) excitation of bound electrons to higher levels in the valence band, (3) excitation of electrons from the valence band to various levels in the energy gap (exciton absorption), (4) excitation of electrons into the conduction band usually in the visible and ultraviolet, and (5) absorption by free charge carries in the conduction band. Mechanisms (1) and (4) determine the limits of transmission of a given solid and (5) will affect the transmission in the pass band. Of course, mechanisms (1) through (4) may be excited thermally as well as optically.

In insulators where the energy gap is large, of the order of 8 ev. in sodium chloride for example, there are few thermally excited electrons in the conduction band and the free carrier absorption is negligible up to the melting temperature. In elemental semiconductors, on the other hand, the gaps are small, of the order of 1 ev. or less, and free carrier absorption at moderate temperatures may approach that in metals.

The absorption by free carriers is related to their electrical conductivity as (Moss, 1959)

\[ \alpha_\lambda = \frac{120\pi\sigma(w)}{n} \]  

(4.16)
where \( n \) is the index of refraction. The electrical conductivity \( \sigma(w) \) at the frequency \( w = 2\pi C/\lambda \) is given by

\[
\sigma(w) = \frac{\sigma_0}{[1 + (w\tau)^2]}
\]

where \( \tau \) is the relaxation time, and \( \sigma_0 \) is the low frequency conductivity.

Clark (1957), and Lawson and Jamieson (1958) have discussed the radiative conductivity in the Earth using equation (4.16) in conjunction with the observed electrical conductivity in the mantle, estimation of the energy gap of the material there, and room temperature absorption spectra of olivine and other silicates. Their analyses, though different, indicate that the effect may well be large. The uncertainties involved are also large, and in fact prompted this investigation. The studies to date on the electrical conductivity of the silicates (Hughes, 1953; Uhri, 1961) indicate that the conductivity mechanism is complicated. Furthermore, it is not certain whether electronic conductivity, ionic conductivity, or a combination of both is operative at a particular temperature. The use of equation (4.16), of
course, depends on the knowledge of the type of charge carriers present.

The measurements presented here show no radiative conductivity at the highest temperatures. This, however, is felt not significant in light of the alteration of the sample during the run.

In spite of the failure to get meaningful measurements on dunite, the author feels that the measurement technique used here has general applicability for high temperature thermal conductivity measurements on natural geological materials. With slight modifications, the furnace could be run to about 1600°C using a platinum winding. Small heat losses are insured in the cylindrical envelope method and the sample fabrication is not a major drawback. A further advantage is that the method is quite fast for a steady state technique when compared to more conventional methods where elaborate heat guards are used and painstaking adjustments are required to establish the appropriate temperature gradients. Generally, an hour was required for a measurement on apparatus II, whereas Birch and Clark’s (1940) method required a day for each measurement.
A. Summary and Conclusions

The thermal conductivity of polycrystalline and single crystal sodium chloride, fused quartz, and polycrystalline dunite rock is investigated in the temperature range 50 °C to 1150 °C. The total conductivity is interpreted in terms of phonon and photon energy transfer. The microstructure of the polycrystalline materials and the infrared transmission spectra are investigated to assist in interpreting the measurements. Analysis of the results leads to the following conclusions:

1. Phonon energy transport is the dominant conductivity mechanism in the pressed sodium chloride powders up to at least 650 °C.

2. The photon mean free path is limited by grain boundary and pore scattering in the pressed powder.

3. The variation in magnitude of the conductivity of the pressed salt is the result of a grain boundary phase of low thermal conductivity.

4. The "effective" radiative conductivity in the transparent materials, synthetic sodium chloride, and
fused quartz is controlled by the boundaries only when the material is uniformly transparent over that region of the spectrum where the spectral energy distribution is important, as in sodium chloride. Fused quartz, on the other hand, is transparent for only part of the distribution. It is proposed that volume emission in the opaque region accounts for the major part of the observed radiative conductivity in quartz.

5. Meaningful high temperature thermal conductivity measurements on natural geological materials can be obtained only if

   a. oxidation or reduction is prevented by use of a suitable atmosphere,

   b. the material contains only a small percent of hydrous alteration products, and

   c. the grains are prevented from separating due to anisotropic thermal expansion.

   In the measurements reported here on dunite, only (a) was satisfied.

B. Suggestions for Future Work

   The systematic measurement of the radiative conductivity in silicate minerals still awaits investigation. The results reported here on dunite are exploratory, but
indicate the difficulties involved. Several possibilities suggest themselves for future measurements on natural materials. First, they must be relatively unaltered. If more than a few percent of hydrous mineral is present, drastic changes can be expected above the dissociation temperature of the hydrous mineral. Secondly, the grain boundary separations could be suppressed by conducting the measurements at moderate pressures. And finally, the absorption coefficient could be measured directly as a function of temperature using transmission techniques. The latter has the advantage that a small sample size is used, and it is usually possible to obtain high quality, unaltered natural silicates in small crystals.

A better theoretical understanding of the boundary effects is required in the case where the absorption and scattering coefficients are not wavelength independent. Solution of the radiative transfer equation in geometries other than parallel plane is desirable since the latter is not particularly suited to high temperature measurements. Experimental studies of the boundary effects could be carried out using glasses of varying opacity and position of the lattice absorption edge. Glasses
are suggested because of their homogeneity, chemical stability, and variety. In addition, they have small lattice conductivity, and radiative effects are more readily observed.
CONDUCTIVITY

In order to extract the radiative conductivity from the measurements of the total conductivity, a detailed knowledge of the various conductivity mechanisms is required. The total thermal conductivity may be written as the sum of at least four terms:

\[ K = K_{ph} + K_{el} + K_{ex} + K_{r} \]  \hspace{1cm} (A.1)

where \( K_{ph} \) is the phonon or lattice wave contribution present in all crystalline substances, \( K_{el} \) is the electronic contribution due to "free electrons" as in a metal or semi-conductor, \( K_{ex} \) represents the contribution of various mechanisms operative in a semi-conductor whereby excitation energy is transported down a temperature gradient, and \( K_{r} \) is the radiative or photon contribution arising from the emission and absorption of photons in matter.

The first two terms have received extensive theoretical and experimental attention. The latter two have received some recent theoretical attention but little experimental work has been done. The theories for the
various contributions will be reviewed here for the sake of continuity.

1. **Phonon Conductivity**

Phonon conductivity is the dominant contribution in insulators at low to moderate temperatures. It has been extensively studied by Debye (1914), Compton (1916), Endō (1922), Peierls (1929), Ach. Papapetru (1935), Makinson (1938), Wilson (1953), Berman (1953), and Klemens (1951, 1958). No attempt will be made to review all the theories or modifications to them. Despite them all, the details of the anharmonic coupling between lattice waves which gives rise to thermal resistance still presents one of the most complex problems of solid state physics. Fortunately for the purposes of this investigation, only the gross predictions of the theory are needed, and those only in the temperature range above the Debye temperature $\Theta_D$ where almost all the theories agree.

The concept of a phonon is the elastic wave analogue of a photon in the electromagnetic theory. It is easier to visualize the interaction of particles than waves, and hence the term phonon. Mathematically it may be described as follows. If an elastic wave of wave vector $\mathbf{K}$ and
angular frequency $\omega_k$ is propagated through a crystal, the displacement of an atom at a lattice point $\mathbf{r}$ due to the vibrational mode may be written

$$A_k e^{i(\mathbf{R} \cdot \mathbf{r} - \omega_k t)}$$

(A.2)

where $A_k$ is the amplitude. For each $\mathbf{R}$ there are three independent modes, one longitudinal and two transverse, with corresponding $\omega_k$'s. At the temperature $T$, the average energy associated with this mode is given by Planck's formula

$$\langle E \rangle = \frac{\hbar \omega_k}{[\exp \frac{\hbar \omega_k}{kT} - 1]}$$

(A.3)

This vibrational mode may be represented as $[\exp \frac{\hbar \omega_k}{kT} - 1]^{-1}$ phonons, each of energy $\hbar \omega_k$.

When a temperature gradient is present in a crystal, the phonon distribution is altered from that in the equilibrium state. The resulting phonon diffusion current contributes a term to the total heat flux proportional to the specific heat of the phonons, their velocity and mean free path. If there were no phonon interactions, as in the harmonic vibration approximation, there would be no
thermal resistance, for then the mean free path would be infinite. Therefore, it is the anharmonic terms in the potential field of the crystalline solid that gives rise to phonon scattering and thermal resistance. The transition probabilities for two phonon collisions may be calculated by treating the anharmonic terms as a perturbation in the crystal Hamiltonian; see, for example, Aigrain (1960). The results indicate that only one of the allowed transitions actually permits the decay of momentum in the absence of a thermal gradient, thereby contributing to the thermal resistance. This process has been termed "Umklapp scattering" by Peierls (1929).

In analogy with the conductivity of a gas, the conductivity associated with "Umklapp processes" may be written as (Klemens, 1958)

\[ K_\mu = \frac{1}{3} \sum_i \int S_i \nu_i l_i \, dw \]  

\[(A.4)\]

\[ i = 1, 2, 3 \]

where \( S_i \) is the specific heat of the vibrational modes in the frequency interval \( dw \) of polarization \( i \), \( \nu_i \) is
the velocity of sound, and $l_i$ is the mean free path of the $i$'th polarization.

Phonons may also be scattered at grain boundaries, atomic imperfections, or impurities, but these mechanisms are unimportant in limiting the mean free path except at low temperatures.

The temperature dependence for $K_\mu$ is according to Peierls (1929)

$$K_\mu \propto T^{-1} \text{ for } T >> \Theta_D$$ (A.5)

This, however, is a poor approximation for $T$ moderately greater than $\Theta_D$, and Joffe (1956) gives as a better approximation

$$\frac{1}{K_\mu} \propto T(1 - \frac{1}{3} \frac{\Theta_D}{T} + \frac{1}{24} \frac{\Theta_D^2}{T^2} - \ldots)$$

$$\frac{1}{K_\mu} \propto T(1 - \frac{\Theta_D}{3T}) \text{ for } T > \Theta_D$$

or

$$K_\mu \propto \frac{1}{(T - \frac{\Theta_D}{3})} \text{ for } T > \Theta_D$$ (A.6)

Therefore, the slope of the lattice thermal conductivity vs. temperature curve above $\Theta_D$ should intercept the
abscissa at $T = \frac{0.2}{2}$°K rather than pass through the origin. Joffe's (1956) experiments on potassium chloride and potassium bromide verified this prediction. However, even if a material exhibits a $(T-b)^{-1}$ conductivity dependence in some temperature range, it is not generally correct to subtract the $(T-b)^{-1}$ contribution at higher temperatures and equate the remainder to electronic, photon or excitation contributions because it seems unlikely that the phonon mean free path could decrease much below the atomic spacing of the material (Kingery, 1955). Joffe (1959) reports mean free paths in semiconductors of about one half the lattice constant; in such cases the mean free path showed little dependence on temperature. Therefore, as the temperature is increased, the mean free path for "Umklapp scattering" should make a smooth transition from a $(T-b)^{-1}$ dependence to a $T^0$ dependence when the mean free path approaches atomic dimensions. Kingery (1957) has observed this behavior in certain ceramic oxides. Unfortunately for this investigation, the uncertainty in the temperature dependence of $K_\mu$ at high temperatures makes the task of separating its contribution to the total conductivity much more difficult.
2. **Electronic Conductivity**

The electronic contribution to the thermal conductivity is simply given by the Wiedemann-Franz law:

$$K_{el} = A \left( \frac{k}{e} \right)^2 \sigma T = LT$$  \hspace{1cm} (A.7)

where $L$ is the Lorenz number, $k$ the Boltzmann constant, $e$ the electronic charge, $\sigma$ the electrical conductivity, and $T$ the absolute temperature. $A$ is a parameter which depends upon the degree of degeneracy and the type of scattering. For a degenerate electron gas as in a metallic conductor $A = \frac{k^2}{3}$ whereas for a Boltzmann distribution and thermal scattering $A = (r+2)$ where $r$ is the power in the dependence of the mean free path on the kinetic energy $l = \sigma^r$.

The electronic contribution is generally negligible in insulators and even non-degenerate semiconductors at room temperatures. However, it is not negligible in the mantle of the Earth where temperatures of several thousand degrees centigrade prevail, and the electrical conductivity $\sigma$ is known from the secular variation of the Earth's magnetic field (Verhoogen, 1960).
3. **Excitation Conductivity**

The excitation contribution arises from a large class of heat transporting mechanisms which operate in a semiconductor. Several of these have been reviewed by Joffe (1956, 1959).

One mechanism proposed by Price (1954) has been termed the ambipolar pair diffusion of electrons and holes in a temperature gradient. If a temperature gradient exists in a semiconductor, a carrier concentration gradient will also exist, there being more thermally excited electron-hole pairs at the hot end than at the cold end. The concentration gradient gives rise to a carrier diffusion current. Each electron hole pair transports excitation energy $E_g$ as well as kinetic energy of the order of $kT$. At the cold end, annihilation of the pair releases the transported energy. According to Price, this mechanism contributes a term

$$K_{ex} = 2L \frac{\sigma_+ \sigma_-}{(\sigma_+ + \sigma_-)} \left[ \frac{E_g}{2kT} + 2 + \frac{r}{T} \right]^2 T \quad (A.8)$$

where $\sigma_+$ and $\sigma_-$ are respectively the electron and hole electrical conductivities, $L$, $k$, $T$ and $r$ having been defined in the last section.
This contribution has had rather limited success in explaining departures from \((T-b)^{-1}\) dependence of the thermal conductivity in semiconductors. Joffe (1959) reports one rather convincing case, but for the most part the ambipolar contribution given by the above formula is too small to account for many of the existing anomalies.

Another contribution that has been investigated by Pikus (1957) is the diffusion of excitons in a temperature gradient. An exciton represents an excited state whereby an electron is elevated to an energy level somewhat below the bottom of the conduction band.

The electron-hole pair created in this fashion is bound in the sense that the electron and hole are not free to wander through the crystal independently as when an electron is elevated to the conduction band, but the pair may move through the crystal transporting excitation energy (but not charge) as a result of dipole coupling with neighboring atoms (Heller and Marcus, 1951).

By a similar argument as for the ambipolar contribution, Pikus (1957) gives for the exciton contribution to the thermal conductivity

\[
K_{ex} = kND \left[ (\frac{\Delta E}{kT} + 2)^2 + 2 \right]
\]  

(A.9)
where $N$ is the concentration of excitons, $D$ is the diffusion constant, and $\Delta E$ is the excitation energy for excitons, which is always less than the gap energy $E_g$. Unfortunately, little data is available on $N$, $D$, and $\Delta E$; therefore, direct comparison with existing conductivity anomalies in semiconductors is not possible. What is usually done is to determine $\Delta E$ from the conductivity anomaly. Since $N$ contains the factor $\exp - \frac{\Delta E}{kT}$, a plot of the anomalous conductivity, that is the part that deviates from a $(T-b)^{-1}$ law at high temperature on a log scale vs. $\frac{1}{T}$, should reveal a slope of $-\frac{\Delta E}{k}$ if the extra conductivity is due to $Kex$. This has been done by Jamieson and Lawson (1958) using McQuarrie's (1954) measurements on $\text{AL}_2\text{O}_3$, $\text{MgO}$ and $\text{BeO}$. They found excitation energies of 1.42 ev. for $\text{AL}_2\text{O}_3$ and 1.35 ev. for $\text{MgO}$ on the basis of the departure of the conductivity from a $(T-b)^{-1}$ law between $1000^\circ C$ and $1800^\circ C$. The validity of the calculations seems doubtful in view of the scatter in McQuarrie's (1954) data. Whitmore (1960) performed a similar analysis on the data of Charvat and Kingery (1957) and obtained excitation energies of .25 ev. for $\text{AL}_2\text{O}_3$, .2 ev. for $\text{TiO}$, and .34 ev. for $\text{CaF}_2$. 

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4. **Photon Conductivity**

The photon contribution to the thermal conductivity arises from the interaction of electromagnetic radiation with matter, specifically the emission and absorption of radiation in the presence of a temperature gradient.

The description of the radiation field may be given in terms of the specific intensity of radiation \( I_x(x,y,z,\lambda,m,n,t) \) at the wavelength \( \lambda \), the coefficients of emission \( \eta(\lambda,T) \), absorption \( \alpha \), and scattering \( \sigma \), as well as the state of polarization of the radiation. In the following, the polarization will not be analyzed.

The energy in the wavelength interval \( (\lambda, \lambda + d\lambda) \) traversing an element of area \( dA \) in the direction of the solid angle \( dw \) in a time \( dt \) is given by

\[
dE_x = I_x \cos \theta \ d\lambda \ dA \ dw \ dt \quad (A.10)
\]

where \( \theta \) is the angle between the normal to the surface \( dA \) and the direction of the pencil of radiation.

By integrating \( dE_x \) over all solid angles, we obtain the net energy flow through \( dA \) in time \( dt \) in the wavelength interval \( (\lambda, \lambda + d\lambda) \) as
\[
\frac{dE_\lambda}{\lambda w} = dA \, dt \, d\lambda \int \frac{I_\lambda}{w} \cos \theta \, dw
\]
(A.11)

\[
= dA \, dt \, d\lambda \times \vec{F}_\lambda \cdot \vec{n}
\]

where \( \vec{F}_\lambda \) is a vector whose components are the fluxes parallel to the \( x \), \( y \), and \( z \) axis, and \( \vec{n} \) is a unit vector normal to \( dA \). The vector product \( \vec{F}_\lambda \cdot \vec{n} \) is called the net flux and defines the rate of flow of energy across surface per unit area and per unit wavelength interval. The fundamental equation of transfer may be obtained by counting up losses and gains as the pencil of radiation traverses a small volume of material. This is given for isotropic scattering by

\[
\frac{dI_\lambda}{ds} = -\varepsilon_\lambda \, I_\lambda + \eta(\lambda, T) + \frac{\sigma_\lambda}{4\pi} \int \frac{I_\lambda}{w} \, dw
\]
(A.12)

where \( \varepsilon_\lambda = (\alpha_\lambda + \sigma_\lambda) \) is called the extinction coefficient, and \( ds \) is along the direction of the ray. This equation may be integrated for the path \( s \) as

\[
I_\lambda = \left[ e_{\lambda,\gamma} B(T, \lambda) + (1 - e_{\lambda,\gamma}) I_\lambda^0 \right] e^{-\varepsilon_\lambda (s-s_o)}
\]

\[
+ \int_{s_0}^{s} \left( \eta(\lambda, T) + \sigma_\lambda J_\lambda \right) e^{-\varepsilon_\lambda (s-s')} \, ds'
\]
(A.13)
where $e_{\lambda, \gamma}$ is the emissivity of a surface at $s_o$ in the direction $\gamma$ for wavelength $\lambda$, $B(T, \lambda)$ is Planck's radiation function

$$B(T, \lambda) = \frac{2\pi^2h}{\lambda^5} \frac{1}{(e^{\frac{hc}{\lambda kT}} - 1)} \quad (A.14)$$

$I_{\lambda'}(s_o)$ is the specific intensity at the radiating surface and $J_{\lambda}$ is the mean intensity

$$J_{\lambda} = \frac{1}{4\pi} \int \limits_w I_{\lambda} \, dw \quad (A.15)$$

The equation has a simple interpretation. The first term represents the contribution to the intensity due to a radiating surface at $s_o$. The second term represents the contribution due to radiation emitted and scattered into the pencil from all anterior matter reduced by $e_{\lambda} (s-s')$ to allow for absorption and scattering of the intervening matter. If no radiating surfaces are present, the first term is zero as $s_o = -\infty$.

By integrating the equation for $I_{\lambda}$ over all solid angles, we arrive at an integral equation for $J_{\lambda}$, the mean intensity
\[ 4\pi J_\lambda = \int_A \left[ \varepsilon_{\lambda,\gamma} B(T, \lambda) \right] \frac{\sigma T^4}{\pi r^2} \, \text{d}A + \int_V \left[ \eta(T, \lambda) + \sigma T J_\lambda \right] \frac{\sigma T^4}{\pi r^2} \, \text{d}V \quad (A.16) \]

In the case of local thermodynamic equilibrium, the emission coefficient may be related to Planck's function as

\[ \eta(T, \lambda) = n_2^2 \kappa, B(T, \lambda) \quad (A.17) \]

where \( n_2 \) is the index of refraction. The same interpretation applies to \( J_\lambda \) as to \( I_\lambda \). One term represents the boundary contribution and the other the solid. The law of conservation of energy within an elemental volume of material provides another equation for the mean intensity \( J_\lambda \).

Allowing for heat generation, convection, conduction and radiative transfer, the law of conservation states that

\[ \int_V \left( -A + \varphi c \left[ \mathbf{U} \cdot \text{grad} T + \frac{\partial T}{\partial t} \right] \right) \, \text{d}V \]

\[ = \int_s \left( K \text{grad} T + \mathbf{n} \vec{F} \right) \cdot \text{d}\mathbf{A} \quad (A.18) \]

where \( s \) is the bounding surface of the volume \( V \), \( \varphi \) is
the density, \( c \) the specific heat, \( A \) the heat generated per unit volume, \( K \) the thermal conductivity, and \( \mathbf{\tilde{u}} \) the velocity of deformation of the material. By use of the divergence theorem, the integrands may be equated.

The divergence of the net flux is obtained by integrating the transfer equation over all solid angles and equals

\[
\text{div} (\mathbf{x F}_\lambda) = 4\pi \eta(T, \lambda) - \alpha_\lambda \int I_\lambda \, dw
\]

\[\quad = 4\pi \alpha_\lambda \left[ n_\lambda^2 \, B(T, \lambda) - J_\lambda \right]
\]

which upon integrating over wavelength \( \lambda \) yields

\[
\text{div} (\mathbf{x F}) = 4\pi \int_0^\infty \alpha_\lambda \left[ n_\lambda^2 \, B(T, \lambda) - J_\lambda \right] d\lambda
\]

In the case where \( A = \mathbf{\tilde{u}} = 0 \), the equation of conservation gives

\[
\rho c \frac{\partial T}{\partial t} = K \nabla^2 T + 4\pi \int_0^\infty \alpha_\lambda \left[ n_\lambda^2 \, B(T, \lambda) - J_\lambda \right] d\lambda
\]

This integro-differential equation and the integral equation for the mean intensity \( J_\lambda \) together with the boundary conditions determine the solution to the problem.
Hamaker (1947), Van der Held (1952), Kellet (1952), Gensel (1953) and Clark (1957) have discussed the solution for the radiative contribution. In the case of infinite boundaries, Van der Held (1952) gives to the first order in \( \nabla^2 T \)

\[
\rho c \frac{dT}{dt} = \nabla \cdot \left[ K + \frac{4K}{3} \int_0^\infty \frac{n^2}{\varepsilon_\lambda} \frac{\partial}{\partial T} B(T, \lambda) \, d\lambda \right] \nabla T
\]

\[
= \nabla \cdot \left[ K + K_r \right] \nabla T \quad (A.22)
\]

If the index of refraction and the extinction coefficient are wavelength independent, the radiative conductivity becomes

\[
K_r = \frac{16 \pi^2 \sigma T^3}{3 \varepsilon} \quad (A.23)
\]

where \( \sigma \) is the Stephan Boltzman constant. This latter approximation for \( \varepsilon_\lambda \) is not generally valid. The equation may still be written in the above form with \( \varepsilon \) replaced by \( \bar{\varepsilon} \) which equals

\[
\frac{1}{\bar{\varepsilon}(T)} = \frac{15}{4\pi^4} \int_0^\infty \frac{1}{\varepsilon(\lambda)} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \quad (A.24)
\]
where \( x = \frac{\hbar c}{\lambda kT} \cdot \bar{\varepsilon} \) may be interpreted as the mean of \( \varepsilon(\lambda) \) over the spectrum weighted by the temperature derivative of Planck's function. The integral is temperature dependent even if \( \varepsilon(\lambda) \) is not, for with each new temperature the scale factor for \( \varepsilon(\lambda) \) is changed, and the integral will have a different value unless \( \varepsilon(\lambda) \) is independent of wavelength.

As stated previously, the equation for \( K_r \) given here assumes the boundaries do not contribute to the intensity at a point in the medium. If they do contribute, the problem is greatly complicated and solutions exist for only the simplest geometries.

In non-absorbing or very transparent media, the radiative contribution as given above appears to increase without limit. This, however, is not the case. It is important to realize that only if the boundaries can be neglected is the radiative conductivity an intrinsic property of the material. In all other cases, it depends on the boundary conditions and cannot exceed the infinite space solution. If a material neither absorbs nor scatters radiation, it is meaningless to speak of the radiative conductivity because the radiation does not interact with the material and

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therefore cannot alter the temperature distribution. Instead, it passes through the material unaffected.
In general, the contribution to the conductivity due to radiation will be less than or equal to that given above depending on the size of the sample relative to the mean free path for radiation. Only if the sample has dimensions several times the photon mean free path will the contribution approach the infinite space solution. The derivation here has been given using the wave model for electromagnetic radiation. An alternative derivation based on the particle nature of radiation has been given by Devyatkoa, Moizhes and Smirnov (1959).
APPENDIX B
ERROR ANALYSIS

1. Comparison of Finite and Infinite Cylinder Solution

Since the length to diameter ratio of the salt cylinder is 3.52, it was felt necessary to compare the solutions and see what error is involved in using the infinite cylinder solution, equation (2.1), to compute the thermal conductivity.

In carrying out the solutions, boundary conditions must be specified. At the outer surface, the rate of heat loss is taken as proportional to the temperature difference between the surface and the surrounding medium. This boundary condition, though by no means exact, is more realistic than requiring the outer surface to be at a constant temperature. The latter problem was solved initially and found to give agreement within three decimal places between the finite and infinite cylinder solutions. This agreement, however, was somewhat forced because requiring constancy of temperature at the outer surface insured cylindrical isotherms in the center of the sample.

Infinite Cylinder -- The temperature distribution is given by

\[ T = A + B \ln r \]

with the boundary conditions
\[ 2\pi ak \frac{dT}{dr} \bigg|_{r=a} = -F_o \]

\[ -k \frac{dT}{dr} \bigg|_{r=b} = H(T - T_o) \]

where \( F_o \) = heat flux/unit length \( \left( \frac{\text{cal}}{\text{cm sec}} \right) \)

\( H \) = outer conductivity \( = 10^{-4} \left( \frac{\text{cal}}{\text{cm}^2 \text{ sec} \text{ °C}} \right) \)

\( k \) = conductivity \( = 6.72 \cdot 10^{-3} \left( \frac{\text{cal}}{\text{cm sec} \text{ °C}} \right) \)

\( T_o \) = temperature of surrounding medium.

Evaluation of the coefficients yields:

\[ T - T_o = \frac{F_o}{2\pi k} \left[ \frac{k}{Hb} + \ln \frac{b}{r} \right] \]

\[ T - T_o = \frac{F_o}{2\pi k} \left[ 42.3308 + \ln \frac{b}{r} \right] \text{ for } b = 1.5875 \text{ cm} \]

**Finite Cylinder**
The governing equation is

\[ \nabla^2 T = 0 = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \]

with the boundary conditions

\[ 2\pi a k \frac{\partial T}{\partial r} \bigg|_{r=a} = -\tau_0(z) \]

\[ k \frac{\partial T}{\partial r} \bigg|_{r=b} = -H(T - T_0) \]

\[ k \frac{\partial T}{\partial z} \bigg|_{z=L} = -H(T - T_0) \]

\[ k \frac{\partial T}{\partial z} \bigg|_{z=-L} = H(T - T_0) \]

Letting \( \tau(r,z) = T - T_0 \), and separating variables, gives for the unit solutions

\[ \tau_n = R_n(r) Z_n(z) \]

\[ R_n = A_n I_0(\alpha_n r) + B_n K_0(\alpha_n r) \]

\[ Z_n = C_n \sin \alpha_n z + D_n \cos \alpha_n z \]
where \( \alpha_n \) is the separation constant. The constants are evaluated by satisfying the boundary conditions. The boundary condition at \( r=a \) is satisfied by expanding \( F_0(z) \) in the appropriate complete orthogonal set:

\[
\mathcal{Y}_n = c_n \cos \alpha_n z + d_n \sin \alpha_n z
\]
on the interval \(-L, L\) where

\[
c_n = \frac{H}{k} \sin \alpha_n L + \alpha_n \cos \alpha_n L
\]

\[
d_n = \frac{H}{k} \cos \alpha_n L - \alpha_n \sin \alpha_n L
\]

and the \( \alpha_n \)'s are the positive roots of

\[
\tan 2\alpha L = \frac{2\alpha \frac{H}{k}}{\alpha^2 - \left(\frac{H}{k}\right)^2}
\]

Therefore, \( F_0(z) = \sum_{n=1}^{\infty} A_n \mathcal{Y}_n \) where

\[
A_n = \frac{1}{\left(\alpha_n^2 + \left(\frac{H}{k}\right)^2\right)L + \frac{H}{k}} \int_{-L}^{L} F_0(z) \mathcal{Y}_n dz
\]

In this case, \( F_0(z) = \) constant and is an even function on \(-L, L\).
The solution is then given by

\[
T - T_0 = - \frac{F_0}{\pi k} \sum_{n=1}^{\infty} \frac{I_0(\alpha_n r)[F(K_1, K_0)] + K_0(\alpha_n r)[F(I_1, I_0)]}{I_1(\alpha_n a)[F(K_1, K_0)] + K_1(\alpha_n a)[F(I_1, I_0)]} \\
\cdot \frac{1}{\alpha_n^2} \frac{\sin \alpha_n L[\alpha_n^2 + \left(\frac{H}{k}\right)^2]}{\alpha_n^2 + \left(\frac{H}{k}\right)^2} \cdot \cos \alpha_n z
\]

\[
F(K_1, K_0) = [\alpha_n K_1(\alpha_n b) - \frac{H}{k} K_0(\alpha_n b)]
\]

\[
F(I_1, I_0) = [\alpha_n I_1(\alpha_n b) + \frac{H}{k} I_0(\alpha_n b)]
\]

Convergence is quite rapid and only three terms were computed. The contribution of the fourth term is less than 1/2 percent. The three term approximation is given below for several different radii:

\[
(r = r_1)
T_1 - T_0 = \frac{F_0}{2\pi k} [39.0802 \cos(0.0463)z - 0.0822 \cos(0.4722)z \\
+ 0.0067 \cos(0.9374)z - \ldots]
\]

\[
(r = r_2)
T_2 - T_0 = \frac{F_0}{2\pi k} [38.1905 \cos(0.0463)z - 0.0680 \cos(0.4722)z \\
+ 0.0039 \cos(0.9374)z - \ldots]
\]

\[
(r = a)
T_a - T_0 = \frac{F_0}{2\pi k} [39.8338 \cos(0.0463)z - 0.0982 \cos(0.4722)z \\
+ 0.0109 \cos(0.9374)z - \ldots]
\]
The difference in temperature $T_1 - T_2$ for the finite cylinder is given by

$$T_1 - T_2 = \frac{F_0}{2\pi k} [0.878] \text{ at } z = 0, \text{ the center of the sample.}$$

For the infinite cylinder, the difference is given by

$$T_1 - T_2 = \frac{F_0}{2\pi k} [\ln \frac{r_2}{r_1}] = \frac{F_0}{2\pi k} [0.916]$$

which gives a difference of $\frac{0.916 - 0.878}{0.916} \cdot 100 = 4.1%$.

Since the temperature difference is smaller for the finite cylinder, the values of $k$ computed on the basis of the infinite solution will be higher by about 4 percent. The value often quoted in the literature for this problem is about 1 percent difference. The discrepancy here is due to a length to diameter ratio less than 4:1, and perhaps the use of a more realistic outer boundary condition. If constancy of temperature had been imposed, the agreement would have been of the order of 1 percent. Therefore, the results on sodium chloride are felt to be high by about 4 percent due to using the infinite cylinder solution.

The assumption of constancy of heat generation per unit length can be checked by comparing the temperature
on the inner wall at the center and at the end of the cylinder. This is given by

\[(T_a - T_o) = \frac{F_o}{2\pi k} \quad [39.7465] \quad z=0\]

\[(T_a - T_o) = \frac{F_o}{2\pi k} \quad [38.0308] \quad z=L\]

The difference is 4.3 percent between the center and the end. In apparatus II, \((T_a - T_o)\) never exceeds 100°C; therefore, the winding at the end runs about 4°C cooler than the center. Since the temperature coefficient of resistivity for platinum is .004 per °C, the resistivity and consequently the power per unit length in the center is about 1.7 percent greater than near the ends. In apparatus I, however, \((T_a - T_o)\) may be several hundreds of degrees and the resulting variation of heat generation could be 5 percent or greater.

2. **Estimation of Experimental Errors**

In addition to the determinate systematic error of 4 percent that results from using equation (2.1) for the finite cylinders, there are other systematic and random errors due to inaccurate measurements and meter limitations.
These may be estimated as follows. The total differential of \( k \) is given by

\[
\Delta k = \frac{\partial k}{\partial L} \Delta L + \frac{\partial k}{\partial B} \Delta B + \frac{\partial k}{\partial P} \Delta P + \frac{\partial k}{\partial (T_1 - T_2)} \Delta (T_1 - T_2)
\]

where \( B = \ln \frac{r_2}{r_1} \) and \( P = \) power. The errors \( \Delta L \) and \( \Delta B \) are systematic though indeterminate in sign and therefore are combined as the sum of squares along with the random errors \( \Delta P \), \( \Delta T_1 \), and \( \Delta T_2 \). The limit of error for \( k \) is then

\[
\frac{\Delta k}{k} = \sqrt{\left( \frac{\Delta L}{L} \right)^2 + \left( \frac{\Delta B}{B} \right)^2 + \left( \frac{\Delta P}{P} \right)^2 + \left( \frac{\Delta (T_1 - T_2)}{T_1 - T_2} \right)^2}
\]

The length of the center part of the heater was 2 inches, and it could easily be measured to 1/32 inch giving

\[
\frac{\Delta L}{L} = .015
\]

The radii \( r_1 \) and \( r_2 \) were approximately .2 and .55 inches respectively. They could be measured to within about .3/50 inch using a hand lens and a finely graduated scale. Since the errors are independent, they also add as the sum of squares and \( \Delta B \) is given by
The power was measured with a VTVM having an accuracy of 1 percent full scale. Two voltage measurements were made to determine the power, one on a 10 volt scale and the other on a 30 volt scale. Using apparatus II, typical voltages were $E_1 = 7$ volts and $E_2 = 18$ volts. Again they add as independent errors, and $\frac{\Delta P}{P}$ is given by

$$\frac{\Delta P}{P} = \sqrt{\left(\frac{\Delta E_1}{E_1}\right)^2 + \left(\frac{\Delta E_2}{E_2}\right)^2} = 0.029.$$ 

The temperature difference $(T_1 - T_2)$ could be determined to about $0.25^\circ C$. This was done in two ways during a run, once by taking individual readings and subtracting, and again by putting the thermocouples in series with their emf's bucking one another so as to measure $(T_1 - T_2)$ directly. The two measurements agreed within $0.25^\circ C$. The thermocouples were calibrated against one another between readings on apparatus II; thus no absolute calibration was necessary. Below $150^\circ C$ on apparatus II, the temperature difference $(T_1 - T_2)$ was of the order of $5^\circ C$. At higher temperatures, it was maintained at about $10^\circ C$; therefore, the temperature error is estimated as
\[
\frac{\Delta(T_1-T_2)}{(T_1-T_2)^2} = 0.025
\]

above 150°C on apparatus II.

The maximum error expected for the conductivity \( k \) is then

\[
\frac{4k}{k} = \sqrt{(0.015)^2 + (0.037)^2 + (0.029)^2 + (0.025)^2} = 0.055
\]
or 5.5 percent. More meaningful perhaps are the precision and accuracy of the measurements given by the random and systematic errors respectively.

The expected prevision of the measurements is given by the last two terms and equals

\[
100 \sqrt{(0.029)^2 + (0.025)^2} = 2.2 \text{ percent.}
\]

This is in good agreement with the observations on apparatus II where thermocouple calibration was kept, for example samples 1C and 2C between 150°C and 600°C, though the observed average deviation is somewhat less than that estimated above. The expected accuracy is given by the first two terms and equals

-144-
\[100 \sqrt{(.015)^2 + (.037)^2} = 2.5 \text{ percent.}\]

Samples 1C and 2C, and 1N and 3N provide a measure of the accuracy. The agreement between them is better than 1 percent at all temperatures. Therefore, it appears that the accuracy and precision of the measurements is less than 2 percent. This, however, does not include the 4 percent correction for the use of equation (2.1).

The results on fused quartz agree with the standard curve, Figure 19, within about 2 percent, but there the length to diameter ratio is 4.5:1 and the correction for equation (2.1) is probably negligible.
APPENDIX C

CONDUCTIVITY AND TRANSMISSION DATA

1. Thermal Conductivity Data

The results presented below on pressed sodium chloride powder have been corrected for porosity according to equation (3.1).

SAMPLE 3A -- PRESSED SODIUM CHLORIDE POWDER
Porosity 10 Percent

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>K \cdot 10^{-3} (cal m sec °C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>11.15</td>
</tr>
<tr>
<td>121</td>
<td>9.95</td>
</tr>
<tr>
<td>165</td>
<td>8.73</td>
</tr>
<tr>
<td>214</td>
<td>7.16</td>
</tr>
<tr>
<td>255</td>
<td>6.48</td>
</tr>
<tr>
<td>343</td>
<td>5.22</td>
</tr>
<tr>
<td>407</td>
<td>4.70</td>
</tr>
<tr>
<td>490</td>
<td>4.15</td>
</tr>
<tr>
<td>555</td>
<td>3.90</td>
</tr>
<tr>
<td>605</td>
<td>3.74</td>
</tr>
<tr>
<td>637</td>
<td>3.67</td>
</tr>
</tbody>
</table>
SAMPLE 1B -- PRESSED SODIUM CHLORIDE POWDER
Porosity 11.1 Percent

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K \cdot 10^{-3} \text{ (cal)} \text{ (cm sec)}^{-1} \text{ (°C)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>10.45</td>
</tr>
<tr>
<td>101</td>
<td>9.20</td>
</tr>
<tr>
<td>140</td>
<td>8.12</td>
</tr>
<tr>
<td>192</td>
<td>6.88</td>
</tr>
<tr>
<td>249</td>
<td>5.84</td>
</tr>
<tr>
<td>301</td>
<td>5.03</td>
</tr>
<tr>
<td>348</td>
<td>4.49</td>
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<tr>
<td>389</td>
<td>4.14</td>
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<tr>
<td>437</td>
<td>3.78</td>
</tr>
<tr>
<td>490</td>
<td>3.46</td>
</tr>
<tr>
<td>547</td>
<td>3.23</td>
</tr>
<tr>
<td>579</td>
<td>3.08</td>
</tr>
<tr>
<td>612</td>
<td>3.02</td>
</tr>
<tr>
<td>634</td>
<td>3.01</td>
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</table>

SAMPLE 3B -- PRESSED SODIUM CHLORIDE POWDER
Porosity 9.7 Percent

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K \cdot 10^{-3} \text{ (cal)} \text{ (cm sec)}^{-1} \text{ (°C)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>11.1</td>
</tr>
<tr>
<td>97</td>
<td>10.0</td>
</tr>
<tr>
<td>136</td>
<td>8.55</td>
</tr>
<tr>
<td>182</td>
<td>7.52</td>
</tr>
<tr>
<td>235</td>
<td>6.20</td>
</tr>
<tr>
<td>280</td>
<td>5.40</td>
</tr>
<tr>
<td>340</td>
<td>4.77</td>
</tr>
<tr>
<td>390</td>
<td>4.22</td>
</tr>
<tr>
<td>447</td>
<td>3.81</td>
</tr>
<tr>
<td>508</td>
<td>3.52</td>
</tr>
<tr>
<td>566</td>
<td>3.32</td>
</tr>
<tr>
<td>599</td>
<td>3.15</td>
</tr>
<tr>
<td>646</td>
<td>2.93</td>
</tr>
</tbody>
</table>
### SAMPLE 4B -- PRESSED SODIUM CHLORIDE POWDER
Porosity 10.6 Percent

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K \cdot 10^{-3} (\text{cal/cm sec °C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>9.14</td>
</tr>
<tr>
<td>93</td>
<td>7.65</td>
</tr>
<tr>
<td>120</td>
<td>6.98</td>
</tr>
<tr>
<td>192</td>
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<tr>
<td>239</td>
<td>4.90</td>
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<tr>
<td>279</td>
<td>4.44</td>
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<tr>
<td>339</td>
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<tr>
<td>408</td>
<td>3.48</td>
</tr>
<tr>
<td>457</td>
<td>3.23</td>
</tr>
<tr>
<td>507</td>
<td>3.08</td>
</tr>
<tr>
<td>553</td>
<td>2.95</td>
</tr>
<tr>
<td>598</td>
<td>2.87</td>
</tr>
<tr>
<td>618</td>
<td>2.89</td>
</tr>
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</table>

### SAMPLE 5B -- PRESSED SODIUM CHLORIDE POWDER
Porosity 17 Percent

<table>
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<th>Temperature °C</th>
<th>$K \cdot 10^{-3} (\text{cal/cm sec °C})$</th>
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</thead>
<tbody>
<tr>
<td>44</td>
<td>7.80</td>
</tr>
<tr>
<td>63</td>
<td>7.49</td>
</tr>
<tr>
<td>90</td>
<td>6.90</td>
</tr>
<tr>
<td>126</td>
<td>6.27</td>
</tr>
<tr>
<td>168</td>
<td>5.50</td>
</tr>
<tr>
<td>197</td>
<td>4.96</td>
</tr>
<tr>
<td>274</td>
<td>4.19</td>
</tr>
<tr>
<td>360</td>
<td>3.46</td>
</tr>
<tr>
<td>430</td>
<td>3.03</td>
</tr>
<tr>
<td>505</td>
<td>2.68</td>
</tr>
<tr>
<td>553</td>
<td>2.30</td>
</tr>
<tr>
<td>597</td>
<td>2.23</td>
</tr>
<tr>
<td>651</td>
<td>2.06</td>
</tr>
<tr>
<td>679</td>
<td>2.10</td>
</tr>
<tr>
<td>702</td>
<td>2.02</td>
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<tr>
<td>747</td>
<td>1.92</td>
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</table>
## SAMPLE 2B' — PRESSSED SODIUM CHLORIDE POWDER
### Porosity 12 Percent

<table>
<thead>
<tr>
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<th>K \cdot 10^{-3} \left( \frac{\text{cal}}{\text{cm sec °C}} \right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>12.95</td>
</tr>
<tr>
<td>94</td>
<td>11.50</td>
</tr>
<tr>
<td>136</td>
<td>9.60</td>
</tr>
<tr>
<td>180</td>
<td>8.35</td>
</tr>
<tr>
<td>245</td>
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<tr>
<td>412</td>
<td>4.99</td>
</tr>
<tr>
<td>503</td>
<td>4.30</td>
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<tr>
<td>583</td>
<td>3.63</td>
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<tr>
<td>636</td>
<td>3.61</td>
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<tr>
<td>712</td>
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</table>

## SAMPLE 1C — PRESSSED SODIUM CHLORIDE POWDER
### Porosity 5 Percent

<table>
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<tr>
<th>Temperature °C</th>
<th>K \cdot 10^{-3} \left( \frac{\text{cal}}{\text{cm sec °C}} \right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>8.76</td>
</tr>
<tr>
<td>188</td>
<td>7.58</td>
</tr>
<tr>
<td>266</td>
<td>6.31</td>
</tr>
<tr>
<td>318</td>
<td>5.62</td>
</tr>
<tr>
<td>354</td>
<td>5.23</td>
</tr>
<tr>
<td>403</td>
<td>4.80</td>
</tr>
<tr>
<td>495</td>
<td>4.12</td>
</tr>
<tr>
<td>567</td>
<td>3.73</td>
</tr>
<tr>
<td>622</td>
<td>3.55</td>
</tr>
<tr>
<td>666</td>
<td>3.51</td>
</tr>
<tr>
<td>713</td>
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<tr>
<td>752</td>
<td>3.56</td>
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<tr>
<td>752</td>
<td>3.47</td>
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</table>
SAMPLE 2C — PRESSED SODIUM CHLORIDE POWDER
Porosity 5 Percent

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>K \cdot 10^{-3} (\text{cal/cm sec °C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(original run)</td>
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</tr>
<tr>
<td>145</td>
<td>8.72</td>
</tr>
<tr>
<td>214</td>
<td>7.10</td>
</tr>
<tr>
<td>303</td>
<td>5.76</td>
</tr>
<tr>
<td>313</td>
<td>5.64</td>
</tr>
<tr>
<td>361</td>
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<td>444</td>
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<tr>
<td>540</td>
<td>3.89</td>
</tr>
<tr>
<td>576</td>
<td>3.68</td>
</tr>
<tr>
<td>618</td>
<td>3.71</td>
</tr>
<tr>
<td>(rerun heating)</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>5.87</td>
</tr>
<tr>
<td>359</td>
<td>4.95</td>
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<td>431</td>
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<td>701</td>
<td>3.26</td>
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<tr>
<td>703</td>
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<tr>
<td>706</td>
<td>3.18</td>
</tr>
<tr>
<td>709</td>
<td>3.22</td>
</tr>
<tr>
<td>712</td>
<td>3.26</td>
</tr>
<tr>
<td>(rerun cooling)</td>
<td></td>
</tr>
<tr>
<td>647</td>
<td>3.36</td>
</tr>
<tr>
<td>585</td>
<td>3.63</td>
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</tbody>
</table>

SAMPLE 1N — NATURAL ROCKSALT

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>K \cdot 10^{-3} (\text{cal/cm sec °C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>17.0</td>
</tr>
<tr>
<td>85</td>
<td>14.85</td>
</tr>
<tr>
<td>114</td>
<td>13.40</td>
</tr>
<tr>
<td>150</td>
<td>11.92</td>
</tr>
<tr>
<td>203</td>
<td>9.99</td>
</tr>
<tr>
<td>248</td>
<td>8.88</td>
</tr>
<tr>
<td>283</td>
<td>8.16</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>Sample 3N -- Natural Rocksalt</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>145</td>
<td></td>
</tr>
<tr>
<td>214</td>
<td></td>
</tr>
<tr>
<td>289</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Sample 18 -- Synthetic Single Crystal Sodium Chloride</th>
<th>K \cdot 10^{-3}(\frac{\text{cal}}{\text{cm sec °C}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td></td>
<td>12.60</td>
</tr>
<tr>
<td>188</td>
<td></td>
<td>10.50</td>
</tr>
<tr>
<td>260</td>
<td></td>
<td>8.70</td>
</tr>
<tr>
<td>343</td>
<td></td>
<td>7.30</td>
</tr>
<tr>
<td>434</td>
<td></td>
<td>6.20</td>
</tr>
<tr>
<td>451</td>
<td></td>
<td>6.02</td>
</tr>
<tr>
<td>533</td>
<td></td>
<td>5.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Fused Quartz</th>
<th>K \cdot 10^{-3}(\frac{\text{cal}}{\text{cm sec °C}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td></td>
<td>3.59</td>
</tr>
<tr>
<td>106</td>
<td></td>
<td>3.56</td>
</tr>
<tr>
<td>122</td>
<td></td>
<td>3.68</td>
</tr>
<tr>
<td>219</td>
<td></td>
<td>3.96</td>
</tr>
<tr>
<td>379</td>
<td></td>
<td>4.54</td>
</tr>
<tr>
<td>518</td>
<td></td>
<td>5.55</td>
</tr>
<tr>
<td>654</td>
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<td>7.08</td>
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<tr>
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<tr>
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</table>

(rerun) 65 3.53
## DUNITE

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K \cdot 10^{-3}(\text{cal cm sec}^{-1} \text{°C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(original run)</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>12.3</td>
</tr>
<tr>
<td>164</td>
<td>11.0</td>
</tr>
<tr>
<td>184</td>
<td>10.5</td>
</tr>
<tr>
<td>272</td>
<td>9.45</td>
</tr>
<tr>
<td>384</td>
<td>8.20</td>
</tr>
<tr>
<td>509</td>
<td>6.54</td>
</tr>
<tr>
<td>(rerun)</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>3.95</td>
</tr>
<tr>
<td>158</td>
<td>3.90</td>
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<tr>
<td>220</td>
<td>3.88</td>
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<td>2.88</td>
</tr>
<tr>
<td>1105</td>
<td>2.76</td>
</tr>
</tbody>
</table>

### 2. Transmission Data

The data presented here have been obtained by dividing the recorded transmission spectra $I_t$ by the background spectra $I_0$ and drawing a smooth curve through the points.
PRESSSED SODIUM CHLORIDE POWDER  
Porosity 10 Percent

Microstructure similar to that of B series.

<table>
<thead>
<tr>
<th>Wavelength (microns)</th>
<th>Percent Transmission</th>
<th>( \frac{I_t}{I_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d = .324 \text{ mm} )</td>
<td>( d = .497 \text{ mm} )</td>
</tr>
<tr>
<td>1</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>2</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>3</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>4</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>5</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>6</td>
<td>12.25</td>
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<tr>
<td>7</td>
<td>12.25</td>
<td>4.75</td>
</tr>
<tr>
<td>8</td>
<td>12.25</td>
<td>4.75</td>
</tr>
</tbody>
</table>

FUSED QUARTZ

<table>
<thead>
<tr>
<th>Wavelength (microns)</th>
<th>Percent Transmission</th>
<th>( \frac{I_t}{I_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d = 2.62 \text{ mm} )</td>
<td>( d = 8.9 \text{ mm} )</td>
</tr>
<tr>
<td>1</td>
<td>92.5</td>
<td>90.0</td>
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<tr>
<td>2</td>
<td>92.5</td>
<td>90.0</td>
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<td>2.5</td>
<td>92.5</td>
<td>90.0</td>
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<td>62.5</td>
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<td>12.5</td>
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<tr>
<td>4.25</td>
<td>17.5</td>
<td>1.5</td>
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<tr>
<td>4.5</td>
<td>13.0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>4.75</td>
<td>2.0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>5.0</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Wavelength (microns)</td>
<td>Percent Transmission ($\frac{I}{I_0}$)</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d = .465 \text{ mm}$</td>
<td>$d = .673 \text{ mm}$</td>
</tr>
<tr>
<td>1</td>
<td>14.0</td>
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</tr>
<tr>
<td>1.5</td>
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<td>16.5</td>
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<td>43.0</td>
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<td>2.5</td>
<td>47.0</td>
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<tr>
<td>2.75</td>
<td>42.5</td>
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<td>1.5</td>
</tr>
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BIBLIOGRAPHY


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BIOGRAPHICAL NOTE

The author was born in St. Paul, Minnesota on January 24, 1933 and moved to Milwaukee, Wisconsin shortly thereafter. At Milwaukee Washington High School, he was nominated to the National Honor Society, and graduated in 1951. The same year, he entered the University of Wisconsin. While there, the author was a member of the University rowing team and was elected captain in his senior year. He received a B. S. degree in Geology in June, 1955, and entered the U. S. Army with an R. O. T. C. commission in the fall of that year. Sixteen months of the two year tour were spent with an infantry unit in Korea. Upon being discharged in September, 1957, he entered the Massachusetts Institute of Technology Graduate School, where he has since been awarded a National Science Foundation Fellowship in the summer of 1959 and the Gulf Research and Development Fellowship for the school year 1960-61.