

Thermal Conductivity of Dielectric Solids at High Pressure*

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(Received 28 February 1967)

The thermal conductivity K of KCl, KBr, fired talc, dunite, and eclogite was measured to pressures as high as 19 kbar and to temperatures as high as 450°C. Fluid pressure was supplied by dry nitrogen. A Manganin resistance gauge and Pt versus Pt-13% Rh thermocouples measured the pressure and temperature, respectively. Data were fitted with the surface $K = C_1/(T+T_0) - C_2/(P+P_0)$ in the sense of least squares by means of a CDC 1604 computer. Conductivities were found to increase nonlinearly with pressure, the slope of the surface decreasing at higher pressures.

INTRODUCTION

THE only other published measurement¹ of thermal conductivity of dielectrics at high pressure used an axial symmetry with cylindrical layers of pressure fluid between the specimen and the thermometers. This geometry introduced correction factors as large as 30%. Modern technology has made available larger pressure cells, sensitive and stable amplifiers which invite the use of differential thermocouples, and precision recorders which enable the observer to take data rapidly and insure thermal equilibrium.

These advances, together with renewed interest in geophysics and in the anharmonic properties of solids, invite further research in which the lattice constant can be altered by the application of pressure. The results described here will show that the rapid rise of thermal conductivity with pressure at low pressures, which Bridgman observed and attributed to the fluid medium, are actually a property of the solid specimen.

APPARATUS

Cylindrical specimens 2½-in. long and having a ¾-in. diam were split on a plane through the cylindrical axis. One-half was slotted to accommodate a 10-mil platinum axial heater wire with potential leads, and two pairs of 3-mil thermocouple wires of Pt versus Pt-13% rhodium at nominal distances of 50 and 138 mils from opposite sides of the axis. The alkali-halide specimen halves were bonded together with collodion, whereas No. 1 Sauereisen cement was used for the other minerals.

The pressure cell was designed after that of Birch.² A truncated steel cone having a ¾-in. axial bore was rammed into a mating steel ring which exerted an inward force tending to balance the bursting force of the pressure fluid inside. Sealing the bottom of the bore was a gasketed vega steel plug fitted with seven Amagat conical electrical pins. A piston sealing the bore from the top used a Bridgman seal having an unsupported area of 0.08 in.², or 17½%. The steel plug and piston

were actuated independently by two 500 ton hydraulic rams. The press assembly was only 41-in. high by 18 in. in diam, and afforded an experimental chamber 4 in. high by ¾ in. in diam in which to put specimens, transducers, and in which to create further environmental changes. See Fig. 1.

In this experiment, temperature capability to 1000°C was added by means of a 10-mil platinum furnace wire wound on a ⅞-in.-diam soapstone form. Windings were accelerated in such a way that the absolute temperature varied by less than 2% over a 1 in. segment of each of the specimens measured. See Fig. 2. Pressure was sensed by a 3-mil nylon-covered-40 Ω manganin gauge, and monitored by a 10 ma current from a bridge circuit. The gauge was calibrated by a precision bourdon gauge at 0.00100 and at 2.00 kbar, and a linear extrapolation formula was assumed. This scheme was reproducible and successfully predicted an 18.0-kbar transition in KBr.

DATA AND RESULTS

Data for each specimen were fitted to the surface

$$\text{conductivity} = C_1/(T+T_0) - C_2/(P+P_0) \quad (1)$$

by means of the University of Texas CDC 1604 computer. T_0 was set at 273.16°C. C_1 and C_2 were optimized

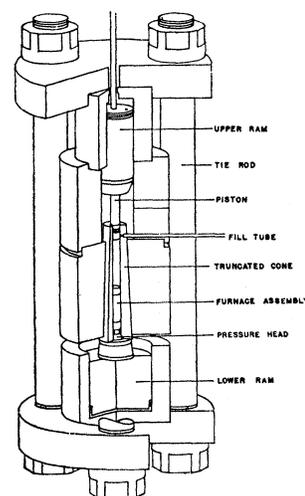


Fig. 1. Cutaway drawing showing construction of pressure system.

* Work supported by the Petroleum Research Fund of the American Chemical Society.

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¹ P. W. Bridgman, *Am. J. Science*, Ser. V VII, 81 (1924).

² F. Birch and E. C. Robertson, U. S. Office of Naval Research, Final Report Contract No. Nr-032400, Harvard University, 1957 (unpublished).

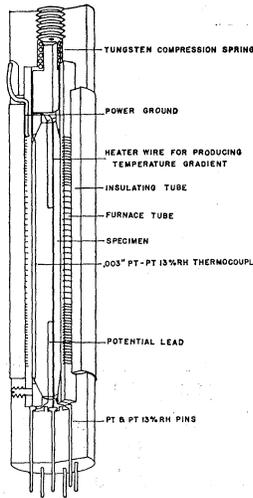


FIG. 2. Cutaway drawing of furnace and sample holder. All nonmetallic material is fired talc.

in the sense of least squares using rounded off values of P_0 . An interpolation formula which varied inversely with the absolute temperature invariably led to a higher residual.

Since iron-free italian soapstone was extensively used in the furnace assembly, it was measured as a preliminary study. The specimen was heated to 1000°C for 3 h to drive off waters of hydration, then the halves were cemented together with Sauereisen No. 1 cement. It was surprising to note that there was an unusually large increase of thermal conductivity with pressure at pressures below 2 kbar. See Fig. 3.

The potassium-chloride specimens were machined from optical grade crystals from the Harshaw company and were advertised to have an impurity content not greater than 50 parts per million. Four runs were made on two specimens. Run 20 on specimen KCl(01) and run 21 on specimen KCl(02) used only two spring loaded tapered collars to hold the halves together. Runs 22 and 23 on KCl(02) had a thin layer of collodion binding the interface. The curve for run 21 was consistently lower than the curves for runs 22 and 23, perhaps because heat was transported across the boundary to the unslotted half of the specimen. It is important to note, however, that the slope for both mountings was greater at low pressures, thus the increased conduction of the

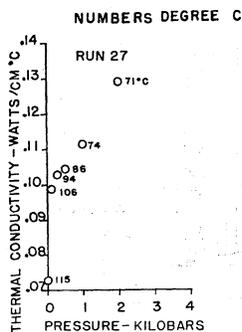


FIG. 3. Thermal conductivity of fired talc as a function of pressure.

nitrogen medium cannot account for the nonlinearity. The collodion filler was still intact after each run in which it was used. See Fig. 4.

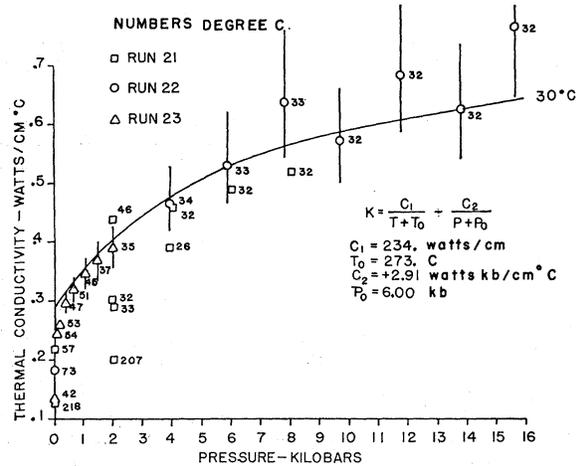


FIG. 4. Thermal conductivity of potassium chloride showing the interpolated 30°C curve.

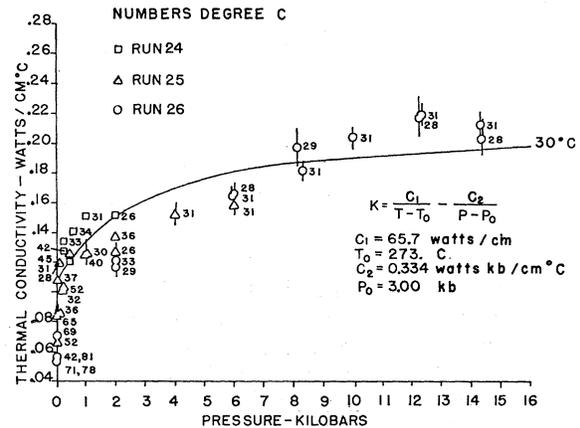


FIG. 5. Thermal conductivity of potassium bromide showing the interpolated 30°C curve.

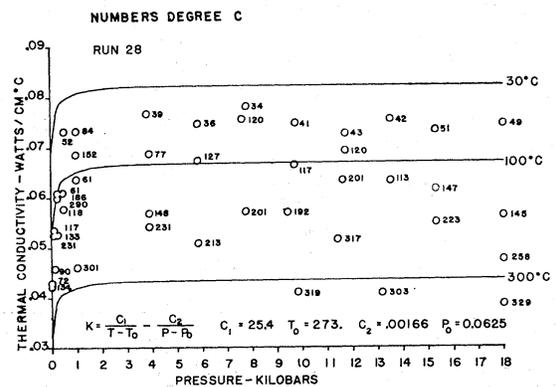


FIG. 6. Thermal conductivity of dunite showing interpolated isotherms.

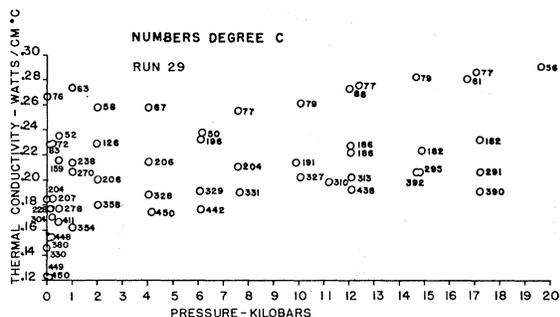


FIG. 7. Thermal conductivity of eclogite. The precision of data did not justify computing interpolated values.

Error bars on the graphs indicate the maximum and minimum values made possible by errors in reading the temperature difference, which was by far the largest contributing factor to the over-all error. The 30°C interpolation curve is drawn and the number to the right of each point is the temperature in °C. The temperature difference between the inner and outer thermocouples was nominally 1% of the absolute temperature.

Potassium bromide resembles the chloride except for the increased ratio of the constituent atomic masses, which should cause a lower conductivity due to the increased anharmonicity. Again, the bulk material was supplied by Harshaw and was bonded with collodion filler. Three runs were made on specimen KBr(04); run 24 to 2 kbar, run 25 reproducing run 24 and extending pressures to 6 kbar, and run 26 from 2 to 14 kbar. The results show that the bromide has lower conductivity as was expected, and a reproducible curvature not unlike that of the chloride. See Fig. 5.

A sample of Jackson Co., North Carolina dunite containing³ over 90% forsterite (magnesian olivine) with some serpentine and minor chromite, was ground to size and cemented with Sauereisen No. 1 cement. The material was granular but did not alter its texture or color after cyclings to pressures of 18 kbar and temperatures of 300°C. At 400°C the sample became reddish indicating oxidation and/or loss of waters of hydration. A sharp increase of conductivity was again noted at low pressures, substantiating the soapstone data, and levelled off at higher pressures as was observed with the more compressible materials. See Fig. 6.

An eclogite specimen was fabricated in the same manner as the dunite above. The data were not fitted to an interpolation formula but the temperatures are written into the side of each datum point. See Fig. 7.

CONCLUSIONS

If one plots the dispersion curve for a dielectric solid in ω - k space, one will find a sinusoidal curve as shown

³ D. W. Barker, Geology Department, University of Texas (private communication).

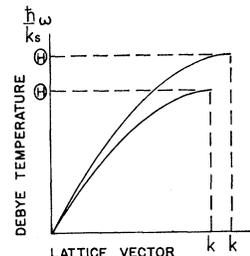


FIG. 8. Dispersion curve for a dielectric solid in ω - k space.

below. See Fig. 8. The application of pressure will have two effects: (a) to decrease the lattice spacing, hence increasing the size of the Brillouin zone, and (b) to increase the group velocity $d\omega/dk$, or the slope of the curve. At 16 kbar the lattice spacing of the alkali halides is diminished by only about 3%, whereas the group velocity is increased⁴ by about 15%. These lead, according to the diagram, to an increased Debye temperature Θ , which, when substituted into the Peierls formula

$$\text{conductivity} = T^a \exp(\Theta/bT), \quad (2)$$

predicts an increased thermal conductivity. If one plots the log of the conductivity versus $d\omega/dk$, one should, on the basis of the Peierls' formula, obtain a straight line. However, the values of the log of the conductivity obtained from the curves cannot be expected to lead to a linear plot since the temperature part of the interpolation formula was of the form (1) and not (2). The interpolation formula (1) does not represent a deduction from physical considerations, but is intended only as a visual clarification of the data. At higher temperatures and pressures, radiative transfer and convection become important heat transport mechanisms; therefore, (1) should not be extrapolated.

Until now, the most feasible approach in calculating the lattice component of the thermal conductivity in the earth's mantle was to apply Bridgman's linear interpolation formula to known conductivities of similar materials at atmospheric pressure. The data found here, however, indicate that the lattice conductivity of polycrystalline dielectric minerals can be expected to increase by 50–100% over the first 2–3 kbars, then to increase less rapidly at higher pressures.

ACKNOWLEDGMENTS

The authors are indebted to Robert Brandt, who for twenty years has served this laboratory with his skill as a master instrument maker, and to Dr. William Chambers for many valuable discussions. The authors would like to express their gratitude to the Petroleum Research Fund of the American Chemical Society for financial support of this work.

⁴ D. S. Hughes, J. Appl. Phys. Letters 3, 119 (1963).