AIP Journal of Applied Physics

Pressure dependence of the thermal conductivity of pyrophyllite to 40 kbar

Wei Chen and D. L. Decker

Citation: Journal of Applied Physics **71**, 2624 (1992); doi: 10.1063/1.351056
View online: http://dx.doi.org/10.1063/1.351056
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/71/6?ver=pdfcov
Published by the AIP Publishing

Pressure dependence of the thermal conductivity of pyrophyllite to 40 kbar

Wei Chen and D. L. Decker
Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602

(Received 26 April 1991; accepted for publication 4 December 1991)

A mathematical model for calculating the temperature distribution as a function of power delivered to a line source and the thermal conductivity of the surrounding medium in the pressure cell of a cubic-anvil press was derived. The model will handle anisotropic thermal conductivities. A simple sample assembly consisting of a line source and two or three thermocouple junctions is described. A comparison of measured to calculated temperatures yields the thermal conductivity. Thermal conductivity measurements were made on natural pyrophyllite and baked pyrophyllite to 40 kbar. For the natural pyrophyllite the thermal conductivity parallel to the bedding plane at room temperature increased with pressure from 13 to 15 (mcal/s cm K) over the pressure range but for the baked material it decreased with pressure.

INTRODUCTION

Thermal conductivity measurements on insulating solids at high pressure have important industrial and geophysical applications. The pressure dependence of the thermal conductivity of solids is also essential in order to know the temperature distribution in an internally heated pressure cell.

The value of the thermal conductivity as a function of pressure for pipestone, a material with mechanical properties similar to those of pyrophyllite, measured by Bridgman[1] predicted a temperature distribution considerably different from what we find both theoretically and experimentally in an internally heated pyrophyllite pressure cell within a cubic-anvil press. We concluded that there must be a difference in the thermal conductivity for pipestone and pyrophyllite and determined to measure the latter as a function of pressure.

In 1955 Carte[2] reported the thermal conductivity of African pyrophyllite at atmospheric pressure and 40 °C to be 12 ± 1.5 mcal/cm s K and decreasing with increasing temperature. He also noted a reduction in the thermal conductivity of this material after heat treatment for 3 h to temperatures greater than 600 °C. It was also pointed out that pyrophyllite is anisotropic with the thermal conductivity being nearly twice as large in the bedding plane as perpendicular to it. Carte made no measurements under pressure.

Measurements at General Electric Research Laboratory[3] indicated that pipestone and pyrophyllite differ little in thermal conductivity and their measured value for pipestone is about twice as large as reported by Bridgman. Their measured value for pyrophyllite agrees well with Carte. They made measurements at high pressure and elevated temperatures between 1500 and 1600 °C and found a value for the thermal conductivity similar to the value at atmosphere pressure and room temperature. At these temperatures however the pyrophyllite has transformed into kyanite and coesite.

There are also unpublished data by Darbha[4] in a M.Sc. thesis at the University of Western Ontario giving the thermal conductivity, κ, of American pyrophyllite. Parallel to the bedding plane he measured κ to vary from 12.6 to 13.7 mcal/cm s K at 83 °C as the pressure increases from 20 to 42 kbar and from 9.9 to 10.6 mcal/cm s K at 244 °C over the same pressure range.

We repeated the measurement of the pressure dependence of the thermal conductivity of pyrophyllite parallel to the bedding plane and also measured this same quantity for pyrophyllite after it was baked overnight at 850 °C to remove water of hydration. We required this latter data because we have been thermally treating the diagonal end caps of the experimental cubic shaped pressure cells used in this laboratory over the past several years.[5]

Usual methods for high-pressure measurements of thermal conductivity use the radial heat flow geometry with a thin electrically heated wire acting as a continuous or transient line source (see Bäckström,[6] Andersson, and Bächström;[7] and Andersson *et al.*[8]). The majority of high-pressure determinations of thermal conductivity rely on steady-state methods (Bridgman,[1] and Hughes and Sawin[9]). We use the simple radial heat flow situation in the steady-state and create a mathematical model to simulate this measurement including anisotropy of the thermal conductivity and correctly reflecting the geometry of the cell boundaries rather than assuming a cylindrical heat sink with an infinitely long source (see MacPherson and Schloessin[10]). One could also do the problem by numerical solution and thus include heat loss along the thermocouple and the central heated wire.

MATHEMATICAL MODEL

The experiment was performed in a cubic-anvil press. The configuration of this measurement is shown in Fig. 1. Because of the anisotropic nature of pyrophyllite, the thermal conductivity will be a tensor. If the line heat source defines the z axis and the bedding plane of the pyrophyllite is in the x–y plane, then the tensor will be diagonal with $\kappa_{\parallel}$ and $\kappa_{\perp}$ defining the thermal conductivities of the pyrophyllite parallel and perpendicular to the bedding plane, respectively. The temperature distribution which satisfies a Poisson equation, modified for this anisotropy, with the cube's surfaces as a zero temperature reference is given by

$$T(\mathbf{r})=\frac{2P}{\kappa_\perp l}\sum_{m,n=1}^{\infty}\frac{\sinh\{k/2[1-(2z/l)]\}\sinh\{k/2[1+(2z/l]\}}{k^2\cosh k}\frac{\sin(k_m h/l)}{k_m h/l}\frac{\sin(k_n h/l)}{k_n h/l}\cos\frac{2k_m x}{l}\cos\frac{2k_n y}{l} \quad (1)$$

where $\mathbf{r}$ is measured from the center of the cube. P is the total power dissipated in the source line, l and h are the edge length of the cube and the thickness of the source line, respectively, and $k_m=(2m-1)\pi/2$, $k_n=(2n-1)\pi/2$, $k^2=(\kappa_\parallel/\kappa_\perp)(k_m^2+k_n^2)$. If the temperature is measured in the $z=0$ plane, and h approaches zero, the solution can be simplified to

$$T(\mathbf{r}')=\frac{P}{\kappa_\parallel l}f\left(\mathbf{r}',\frac{\kappa_\parallel}{\kappa_\perp}\right) \quad (2)$$

with $\mathbf{r}'=(x,y,0)$ and $f[\mathbf{r}',(\kappa_\parallel/\kappa_\perp)]=f_1(\mathbf{r}')-f_2[\mathbf{r}',(\kappa_\parallel/\kappa_\perp)]$.

$$f_1(\mathbf{r}')=\frac{1}{\pi}\sum_{m=1}^{\infty}\frac{\cos(2m-1)\pi x/l\,\sinh[(2m-1)\pi/2(1-2|y|/l)]}{(2m-1)\cosh\frac{(2m-1)\pi}{2}}, \quad (3)$$

$$f_2\left(\mathbf{r}',\frac{\kappa_\parallel}{\kappa_\perp}\right)=\frac{4}{\pi^2}\sum_{m,n=1}^{\infty}\frac{\cos(2m-1)\pi x/l\cos(2n-1)\pi y/l}{[(2m-1)^2+(2n-1)^2]\cosh[\pi/2\sqrt{(\kappa_\parallel/\kappa_\perp)}\sqrt{(2m-1)^2+(2n-1)^2}]}. \quad (4)$$

The double series in f_2 converges as $e^{-(m+n)}/(m^2+n^2)$ and the summation in f_1 converges as $e^{-\alpha m}/m$ with $\alpha>0$ when $|\mathbf{r}'|\neq 0$. The summation f_2 converges to 1 part in 10^6 for m and $n<6$ and f_1 converges but the required number of terms increases as one approaches the central heat source. It can be seen that f_1 corresponds to the solution of an infinitely long square column with a source line along the center of the column and zero temperature on the surrounding surfaces. Therefore, we can consider f_2 as a correction for the finite length of the column and for anisotropy of the thermal conductivity.

Equation (2) can be evaluated at two points $\mathbf{r}_1'$ and $\mathbf{r}_2'$, and after dividing the two resulting equations one finds the following equation in the ratio $\kappa_\parallel/\kappa_\perp$:

$$\frac{P}{T_m(\mathbf{r}_1')}f\left(\mathbf{r}_1',\frac{\kappa_\parallel}{\kappa_\perp}\right)-\frac{P}{T_m(\mathbf{r}_2')}f\left(\mathbf{r}_2',\frac{\kappa_\parallel}{\kappa_\perp}\right)=0, \quad (5)$$

where $T_m(\mathbf{r}_1')$ and $T_m(\mathbf{r}_2')$ are the measured temperatures. One solves Eq. (5), numerically for $\kappa_\parallel/\kappa_\perp$ and then uses Eq. (2) to obtain $\kappa_\parallel$.

EXPERIMENT

The pyrophyllite cube measures $l=23$ mm on an edge after being compressed at each face by six tungsten carbide anvils driven, under mutual constraint, by six hydraulic rams. In order to best simulate the theoretical calculation, we chose a 0.25-mm diameter chromel wire as a line heat source passing through the cube as shown in Fig. 1. The pyrophyllite cube was oriented such that the bedding plane was perpendicular to the line heat source. We used the wax and point heat source technique described by Carte[2] to determine the bedding plane. A current between 0 and 5.5 A is passed through the chromel wire. The power generated by the source line is so small that the temperature within the cube remains near room temperature as inferred by Figs. 2 and 3. The types of experiments were performed, one with a differential thermocouple with junctions at $\mathbf{r}_1'$ and $\mathbf{r}_2'$ and a second thermocouple measuring the temperature between $\mathbf{r}_3'$ and a point on the cube surface (see Fig. 1) and the second type with two thermocouples each measuring temperature differences between $\mathbf{r}_1'$ and the surface and $\mathbf{r}_3'$ and the surface. All junctions are on the midplane of the cube. The temperature gradient at a position close to the heat source line is much greater than one at a position near the cube edge but errors in measurement of position of the thermocouple junctions are more damaging near the heat source, therefore a compromise is made in choosing the position for the junctions. In the first experiment $\mathbf{r}_1'$ and

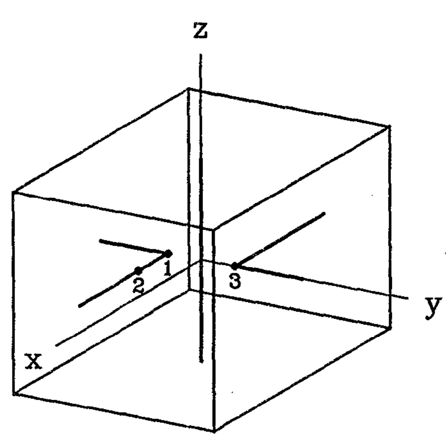

FIG. 1. The configuration of the pyrophyllite cube, line source, and placement of the thermocouple junctions.

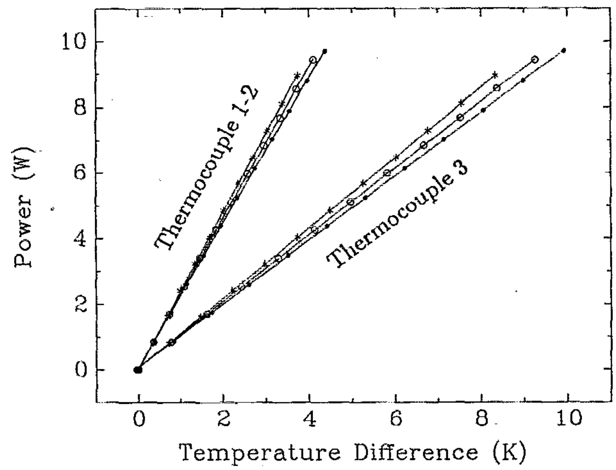

FIG. 2. The power vs temperature difference corresponding to several different pressures in kbar (dot—5, circle—10, asterisk—38) for natural pyrophyllite.

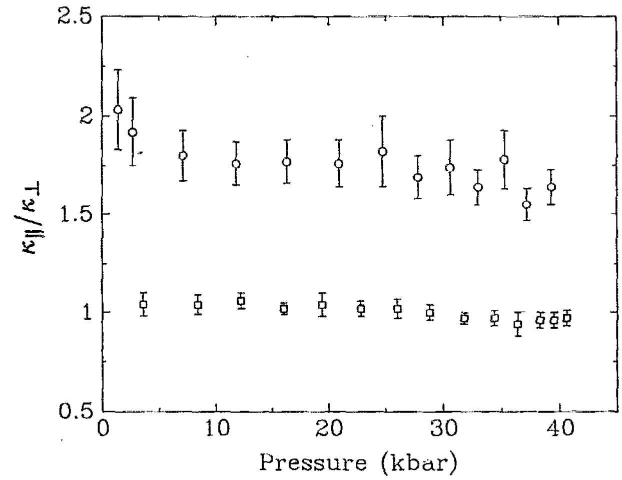

FIG. 4. $\kappa_{\parallel}/\kappa_{\perp}$ vs pressure for natural (circles) and baked (squares) pyrophyllite.

$\mathbf{r}_3'$ were 4.6 mm from the heat source toward the cube faces and $\mathbf{r}_2'$ at (5.2,4.7) mm. In the second experiment $\mathbf{r}_1' = 7.3$ mm and $\mathbf{r}_3' = 5.2$ mm. Considering that it is difficult to derive an analytical solution which includes the effect of the thermal conductivity of the thermocouple probes themselves, we used very thin (0.076 mm) thermocouple wire to minimize this effect. Similar experiments were performed with pyrophyllite which was baked over night at 850 °C.

The internal pressure in the cube is calibrated according to the observation of abrupt changes in the electric resistance on the phase changes of Bi I–II (26 kbar) and melting of mercury (13 kbar) in conjunction with previous calibration curves for this press. The pressure determined by this method is accurate to only ± 1 kbar. Only a very small pressure gradient, less than ± 0.2 kbar, exists throughout the pyrophyllite cube that forms the sample holder.[11] In the gasket region there is a large decrease in pressure but the thermocouples are well into the sample holder and far from the gaskets. Measurements are reported on increasing pressure only, because the hysteresis in this type of system does not allow one to know the pressure on reducing the load. Measurements on reduced load gave similar values to those shown but we cannot assign a pressure to them.

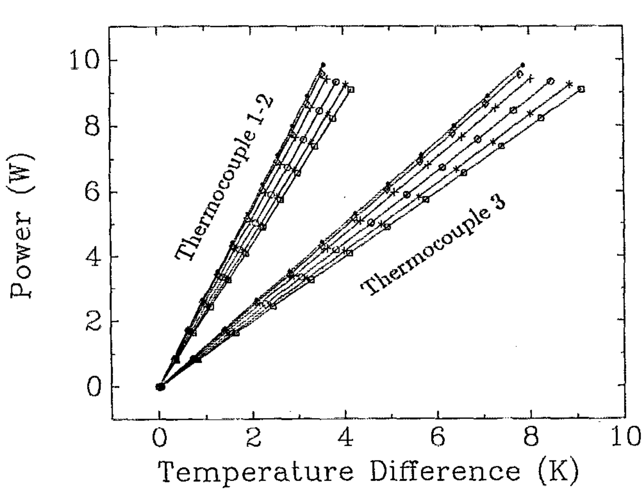

FIG. 3. The power vs temperature difference corresponding to several different pressures in kbar (dot—8, diamond—16, plus—23, circle—29, asterisk—34, and square—40) for baked pyrophyllite.

RESULTS AND CONCLUSIONS

In this measurement, we vary the power in the line source and observe the variation of temperatures at the thermocouple junctions in the cubic cell. The power versus temperature at several different pressures is shown in Figs. 2 and 3. As predicted in Eq. (2) there is a linear relation between power and the temperature difference between any two points in the cell. The function f_1 depends only on the positions of the thermocouple junctions which were measured to an accuracy of ± 0.1 mm after removing the cell from the pressure chamber. The function f_2 depends upon both position and the ratio $\kappa_{\parallel}/\kappa_{\perp}$. The ratio $P/T(\mathbf{r}')$ is then determined from the slope of the curves in these figures.

These results were used in Eq. (5) to calculate $\kappa_{\parallel}/\kappa_{\perp}$ and graphed in Fig. 4. Only data above 10 kbar is used in the analysis for the thermocouple junction positions may vary until the gaskets are formed. There is a considerable error in this measurement but the results for unbaked pyrophyllite indicate no measurable effect of pressure on $\kappa_{\parallel}/\kappa_{\perp}$ and are consistent with the reported value of 1.8 at atmospheric pressure.[2] The result for the baked material is consistent with an isotropic interpretation with $\kappa_{\parallel}/\kappa_{\perp} = 1$. Due to the limited precision with which the thermocouple junctions were known $\kappa_{\parallel}/\kappa_{\perp}$ for natural pyrophyllite is between 1.4 and 2.2 and that for the baked pyrophyllite between 0.8 and 1.6. Because the thermocouple must remain at a fixed position as the pressure is increased, after the gaskets are formed, the variation of $\kappa_{\parallel}/\kappa_{\perp}$ versus pressure is quite accurately represented by the data. The error bars in

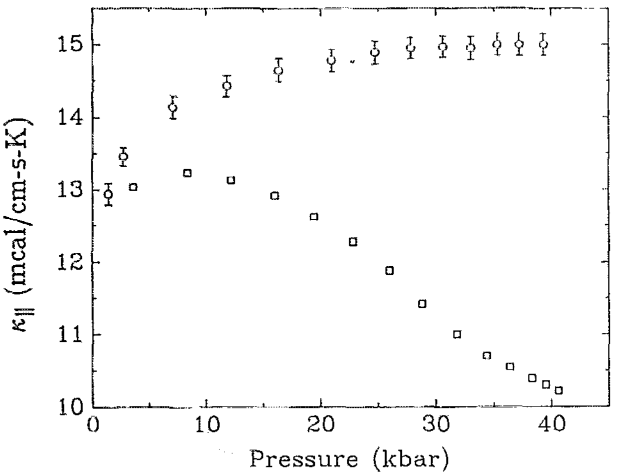

FIG. 5. Thermal conductivity parallel to the bedding plane vs pressure for natural (circles) and baked (squares) pyrophyllite.

the figure come from the uncertainty in determining the slopes of power versus temperature and is representative of the accuracy of the measurement of the pressure effect on $\kappa_{\|}/\kappa_{\perp}$. The ratio for natural pyrophyllite averages 1.7 ± 0.1 which is in agreement with Carte's zero pressure value. The baked material appear to be isotropic. We could not observe any anisotropy by the wax test on baked material.

To determine $\kappa_{\|}$ we used Eq. (2) with $\kappa_{\|}/\kappa_{\perp}=1.7\pm0.1$ for natural pyrophyllite and 1.0 ± 0.1 for the baked material. The measurement with three thermocouple junctions has an estimated error of $\pm6\%$ in $\kappa_{\|}$ due to the uncertainty of the position measurements and that with two thermocouples had an uncertainty of $\pm12\%$ for the same reason. The two measurements agreed with each other within these uncertainties. We thus averaged the results of the two runs which results are shown in Fig. 5. The overall uncertainty in the final value for natural pyrophyllite is $\pm7\%$. The accuracy of the measurements with the baked pyrophyllite is 10% due to precision with which the positions of the junctions could be measured. Once the gaskets have been formed, above about 10 kbar, the relative positions of the thermocouples are unchanged and the error bars in Fig. 5 show only the uncertainty in the measurements neglecting this position uncertainty. This shows the relative accuracy of the measured variation with pressure. The pressure effect on the emf of the thermocouples is negligible at the temperature of this study but was considered.[12] For the natural pyrophyllite the thermal conductivity at room temperature increased with pressure from 13 to 15 (mcal/s cm K) up to 40 kbar but for the baked material it decreases with pressure. The results are not reliable at pressures below the point where the pyrophyllite crushes and flows to fill up all voids in the cell, that is before it makes intimate contact with the very small thermocouple wires. This is especially true for the baked material which is hardened and has a greater yield strength. Therefore the results below 10 kbar are suspect.

The analysis of the temperature distribution in the cell of the given geometry is greatly superior to the usual use of the simple equation for an infinite line source used in analyzing many measurements of thermal conductivity.[10] This formula, $\kappa=(P/2\pi l\Delta T)\ln(r_1/r_2)$, gives results for κ which are 14% higher than the more exact analysis used in this paper for the positions of the differential thermocouples in this experiment. It would also be very difficult to adapt that method of analysis to materials with anisotropic thermal conductivity.

The measured value of $\kappa_{\|}$ is consistent with results of Carte[2] and Darbha.[4] We conclude that our analysis gives an estimate of the ratio of $\kappa_{\|}/\kappa_{\perp}$ but more importantly shows that the ratio does not change with pressure. Our measurements are consistent with the interpretation that $\kappa_{\|}/\kappa_{\perp}$ has the value ~1.8 as reported in the literature for natural pyrophyllite and that the material formed after baking out the water of hydration from pyrophyllite is isotropic with respect to thermal conductivity. We do not understand why the thermal conductivity of this material would decrease with pressure.

[1] P. W. Bridgman, Am. J. Sci. **7**, 80 (1924).
[2] A. E. Carte, Brit. J. Appl. Phys. **6**, 326 (1955).
[3] H. M. Strong, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths & Co., Washington, 1962), Chap. 5.
[4] D. Darbha, M. Sc. thesis (Univ. of Western Ontario), 1976, unpublished.
[5] D. L. Decker, J. D. Jorgensen, and R. W. Young, High Temperatures—High Pressures **7**, 331 (1975).
[6] G. Bäckström, Proceedings, *Seventh Symposium on Thermophysical Properties*, edited by A. Cezairliyan (ASME, New York, 1977), p. 169.
[7] P. Andersson and G. Bäckström, Rev. Sci. Instrum. **47**, 205 (1976).
[8] P. Anderson, R. G. Ross, and G. Bäckström, J. Phys. C **13**, L73 (1980).
[9] D. S. Hughes and F. Sawin, Phys. Rev. **161**, 861 (1967).
[10] W. R. MacPherson and H. H. Schloessin, High Temperatures—High Pressures **15**, 495 (1983).
[11] B. C. Deaton and R. R. Graf, Rev. Sci. Instrum. **34**, 45 (1963).
[12] P. J. Freud and P. N. La Mori, in *Accurate Characterization of The High-Pressure Environment*, edited by E. C. Lloyd, NBS Special Publication 326 (NBS, 1971), p. 67.