

Specific heat of solids at high pressures from simultaneous measurements of thermal conductivity and diffusivity

P Andersson, G Bäckström

Department of Physics, University of Umeå, S-901 87 Umeå, Sweden

Received 14 December 1971; in revised form 20 March 1972

Abstract. A method of determining the specific heat of solids at high pressures, from simultaneous measurements of thermal conductivity and diffusivity in a cylindrical geometry, is described. Results are reported for polytetrafluoroethylene (Teflon) in the range 0-30 kbar at 300 K. With increasing pressure both the thermal conductivity and diffusivity increase strongly and approximately linearly, while the specific heat decreases, most strongly at low pressures.

1 Introduction

There are only a few reports in the literature on experimental studies of the specific heat of solids under pressure. The pressure-transmitting medium has of necessity high thermal conductivity, and therefore heavy heat losses are encountered in conventional calorimetric measurements. By the use of helium as the medium Trapeznikowa and Miljutin (1939) were, however, able to extend this direct method to 2 kbar in the case of solid CH_4 . Ho *et al.* (1966) circumvented the problem of heat loss by putting the entire high-pressure apparatus in the calorimeter. The heat capacity of the sample consequently became only a small fraction (2.5-5%) of the total, but additional measurements on the empty tool permitted a correction to be made, and their final data for uranium at 10 kbar could be given with a precision of 5-10%.

More recently Jura and Stark (1969) attempted to reduce the heat loss in a calorimetric experiment by shortening the measuring time to 100 μs . Conductors offer this possibility, since they may be heated homogeneously by an electric current, and since information about the temperature may be drawn from the resistance change during the heating cycle. For the specific heat of Fe, measured to 100 kbar, these authors claimed an accuracy of 5%. This method has been further developed by Loriers-Susse *et al.* (1971), who also showed that heat-loss corrections of several percent have to be applied, even if the measurements are carried out within 100 μs .

The present work describes a procedure for the determination of specific heat up to high pressures from measurements on a steady and an oscillating-temperature field. Although the method is in principle applicable to any material, it is more convenient for insulators than for conductors, and consequently could be regarded as a complement to the method of Jura and Stark.

2 Theory

From the definition of the diffusivity a at constant pressure we obtain

$$c_p = \frac{\lambda}{a\rho},$$

where c_p is specific heat per unit mass at constant pressure, λ thermal conductivity, and ρ mass density. The variation of density with pressure is known accurately for many substances and, if both λ and a are measured, c_p may be obtained. It suffices to measure λ and a relative to their values at atmospheric pressure, the latter values being well known from calorimetric work.

FEB 16 1973

Only a few measurements of thermal conductivity have been reported since the pioneer work of Bridgman (1924). Two of these are from this laboratory (Rosander and Bäckström, 1969, 1970) and were performed by axial heating of a cylindrical sample in a 'belt' type high-pressure apparatus according to Daniels and Jones (1961). In the well-known Ångström method the diffusivity is determined from observations of a one-dimensional temperature wave in a bar. We have modified this method for the cylindrical geometry already used in our conductivity experiments, which enables us to measure a and λ simultaneously. In this manner, a and λ are determined under the same conditions as regards pressure, chemical composition, grain size, and shape distortion under pressure. The precision of the resulting c_p is thus considerably higher than if two separate samples had been used.

The sample is heated along its axis by an electric current, the power varying according to $P = P_0(1 + \exp i\omega t)$. The temperature is measured at two points having radial coordinates r_1 and r_2 , the results being denoted $T(r_1, t)$ and $T(r_2, t)$, and a measurement of the amplitude ratio or a measurement of the relative phase of the two oscillating functions suffices for calculating a . Measurements of the time averages $\langle T(r_1, t) - T(r_2, t) \rangle$ and $\langle P \rangle$, on the other hand, permit λ to be calculated.

In measurements of λ the properties of the material at $r > r_2$ are of no consequence, as long as the properties depend only on r and not on the other cylindrical coordinates, θ and z . In the determination of a , however, the medium surrounding the cylindrical sample could influence the result unless precautions are taken. This situation is best illustrated using a one-dimensional model, where an analytical solution of the equation of heat diffusion may be obtained. The sample is considered as an insulated, homogeneous rod, extending from $x = 0$ to $x = b$. The heater is situated at $x < 0$, and its properties are irrelevant to the problem. The medium is taken to be semi-infinite, extending from $x = b$ to $x = \infty$, an approximation which will be justified by the following analysis.

A solution of the equation

$$a \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t}$$

is to be found for the case of a heating power

$$P = P_0(1 + \exp i\omega t)$$

entering at $x = 0$. After the transients have vanished the solution within the sample becomes

$$T_s(x, t) = C - \frac{P_0}{\lambda_s} x + A[\exp i(\omega t - k_s x) - B \exp i(\omega t + k_s x)], \quad (1)$$

where C is a constant, and

$$A = \frac{P_0 \exp(-k_s x)}{\lambda_s k_s (1 + i) \{1 + R \exp[-2k_s b(1 + i)]\}},$$

$$B = R \exp(-i2k_s b) \exp[-2k_s(b - x)],$$

where in turn we have used the abbreviations

$$k_s = \left(\frac{\omega}{2a_s}\right)^{1/2}, \quad k_m = \left(\frac{\omega}{2a_m}\right)^{1/2}, \quad R = \frac{\lambda_m k_m - \lambda_s k_s}{\lambda_m k_m + \lambda_s k_s},$$

the subscripts s and m referring to sample and medium respectively.

The first term between the brackets of solution (1) represents a wave travelling in the direction of the x axis, whereas the second term represents a reflected wave. The attenuation α from x_1 to x_2 may be written

$$\alpha = \exp[-k_s(x_2 - x_1) - ik_s(x_2 - x_1)](1 - B_2 \exp 2ik_s x_2 + B_1 \exp 2ik_s x_1), \quad (2)$$

where $B_i \equiv B(x_i)$ and terms in higher powers of B_i are neglected. Since $|R| < 1$, we have

$$|B_1| < |B_2| < \exp[-2k_s(b - x_2)]$$

and for a given a_s it is thus always possible to make $|B_2|$, and hence $|B_1|$, as small as one wishes by choosing sufficiently large values of ω and $(b - x_2)$. This means that the second bracket of the right-hand side of equation (2) may be made as close to unity as one wishes, and hence that the error due to the reflected wave may be made negligible.

The thermal diffusion equation

$$a \nabla^2 T = \frac{\partial T}{\partial t}$$

for an infinitely long cylindrical sample has the solution (Carslaw and Jaeger, 1959)

$$T_s(r, t) = C - \frac{P_0 \ln r}{2\pi l \lambda_s} + F[K_0(\xi \sqrt{i}) \exp i\omega t - G I_0(\xi \sqrt{i}) \exp i\omega t], \quad (3)$$

where, as before, the transient part has been left out. In equation (3) l is the length of the heater, K_0 and I_0 are the modified Bessel functions, and $\xi = r(\omega/a_s)^{1/2}$ corresponds to $k_s x \sqrt{2}$ in equation (1). If we form the time average $\langle T_s(r_1, t) - T_s(r_2, t) \rangle \equiv \Delta T$, equation (3) yields

$$\lambda_s = \frac{P_0 \ln(r_2/r_1)}{2\pi l \Delta T}, \quad (4)$$

which is used for determining the thermal conductivity.

For $\xi \gg 1$ the functions K_0 and I_0 have the following asymptotic behaviour

$$|K_0(\xi \sqrt{i})| \propto \frac{\exp(-\xi \sqrt{2})}{\sqrt{\xi}}, \text{ and } |I_0(\xi \sqrt{i})| \propto \frac{\exp(\xi \sqrt{2})}{\sqrt{\xi}},$$

and hence the coefficient of I_0 must be zero in the solution for the surrounding medium. The function I_0 in the solution (3) for the sample corresponds to the reflected wave in equation (1). Just as in the one-dimensional case, the relative error in a_s due to the reflected wave is expressed by the coefficient G , obtained by numerical fitting of the solutions for the sample and the medium at the cylindrical interface. Also, in the cylindrical case, G may be reduced to any desired level by proper choice of the frequency ω and of the outer observation point r_2 .

If r_1 and r_2 are the radii at which the temperature is measured, the definition $\xi = r(\omega/a_s)^{1/2}$ yields $\xi_1 = (r_1/r_2)\xi_2$ for any given pressure, and the ratio r_1/r_2 may be regarded as constant during the compression of a homogeneous sample. The attenuation α of the wave now becomes

$$\alpha = \frac{K_0(\xi_2 \sqrt{i})}{K_0(\xi_1 \sqrt{i})} = \frac{K_0(\xi_2 \sqrt{i})}{K_0(r_1 \xi_2 \sqrt{i}/r_2)} = \psi(\xi_2) \exp i\phi(\xi_2).$$

The amplitude ratio ψ and the phase shift ϕ may now be calculated by a computer for various values of the parameter r_1/r_2 . On putting the theoretical $\psi(\xi_2)$ and $\phi(\xi_2)$ equal to the corresponding experimental values of amplitude ratio and phase shift, one obtains two values of ξ_2 , which theoretically should coincide. The diffusivity is determined from the definition of ξ_2

$$a_s = \frac{\omega r_2^2}{\xi_2^2}. \quad (5)$$

Two experimental values obtained for ξ_2 and thus for a_s are, however, not trivially identical. Equation (2) indicates that the presence of a reflected wave may influence the magnitude and phase of α differently, and it could therefore be expected that insufficient care in eliminating the reflexion would result in different values of a_s for the two methods. This has also been observed experimentally in the cylindrical case. A comparison between the results from amplitude and phase measurements thus serves as a test of the internal consistency of this experiment.

3 Experimental procedure

Figure 1 shows the sample and the high-pressure cell. Bismuth and manganin wires were used for pressure calibration, and each wire was put in a single turn around the sample. With the exception of the leads for the heater current, all wires were brought out from the cell between double pyrophyllite gaskets at the bottom piston. The electronic instrumentation is shown schematically in figure 2. A current $I = I_0 |\cos \frac{1}{2} \omega t|$ is driven through the heater spiral. The power developed will then vary sinusoidally at the frequency ω , and a stationary heat wave is eventually established. The two sine signals derived from the thermocouples at r_1 and r_2 are

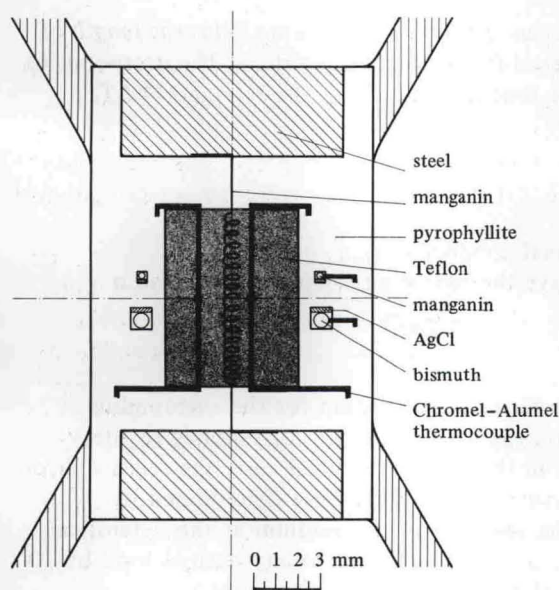


Figure 1. The sample and the high-pressure cell.

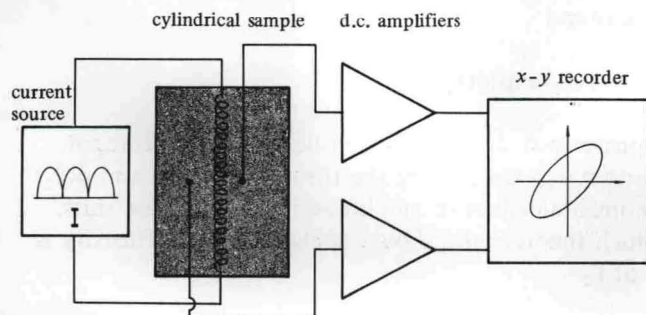


Figure 2. Schematic diagram of the electronic instrumentation.

amplified and visualized on an x - y recorder. In a Teflon sample of the size given by figure 1 the time required for the signals to become stationary, within the tracing accuracy of the recorder, is about 1 min. A one-dimensional estimate of this time interval yields $5r_2^2/a = 80$ s, and this estimate may thus be used with some confidence in predicting the behaviour under other conditions.

Figure 3 shows a photograph of a recording obtained at a wave period of 10 s. A close analysis of the shape of this ellipse proves that the contribution of harmonics to the signals is less than 2%. The attenuation and phase shift needed for calculating the thermal diffusivity were obtained by measuring the parameters of the ellipses.

The coordinates of the centre of an ellipse are sufficient to determine $\langle T(r_1, t) - T(r_2, t) \rangle$ and hence also the thermal conductivity λ . In practice, however, it is generally more convenient to perform this measurement by switching over to a constant current, after which ΔT may be measured by a single microvoltmeter. A typical value of the current was $I = 0.23$ A through a heater resistance of 5Ω , resulting in a temperature drop $\Delta T = 5$ K.

The pressure corresponding to each thermal measurement was obtained by assuming the pressure to be proportional to the resistance change of the manganin wire, calibration being furnished by the bismuth transitions. The pressure is thus measured in a peripheral region, whereas it is the value in the central region which is relevant. The pressure difference between the centre and the Bi loop outside the sample was measured in separate experiments at ~ 25 kbar by observing the synchronism of the transitions, and it was found that the error resulting from inhomogeneity of pressure was less than 1 kbar for increasing pressure, and negligibly small for decreasing pressure. In view of this result and the small amount of hysteresis encountered in the thermal measurements, it was concluded that the pressure determined is representative of the whole sample.

The conductivity λ is calculated from equation (4) using measured data for P_0 and ΔT . The ratio r_2/r_1 is assumed to be independent of the pressure, since the volume of the manganin heater wire was only a small fraction (5%) of the volume of the sample inside the radius r_1 . The length l of the spiral, and hence of the sample, has to be known, however, as a function of pressure. In a hydrostatic medium it would be justified to take $l \propto V^{1/3}$, but in the solid medium used the possible deformation as well as the compression of the sample has to be considered. The deformation was explored as a function of pressure in a separate experiment. A coil of copper wire was wound on the cylindrical surface of the sample, and pressure was applied under conditions similar to those used in the thermal measurements. The resistance of the coil was measured for various pressures, and from these data the variation of the coil

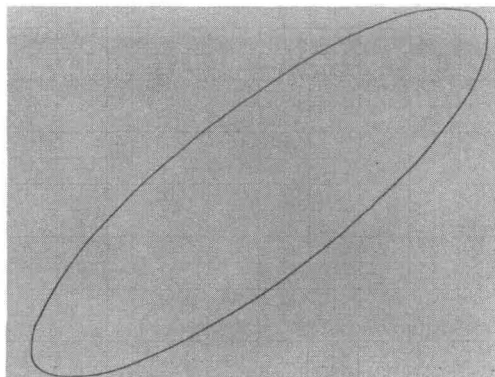


Figure 3. Photograph of a recording.

diameter was calculated using Bridgman's results (1938) on the resistivity of Cu. The average result of several measurements is that the sample diameter increased at a rate of $0.1\% \text{ kbar}^{-1}$. The length could now be obtained from compressibility data on Teflon (Bridgman, 1948). According to equation (5) the results on the radial expansion can be used directly when calculating the diffusivity a_s .

For specific heat we have

$$c_p = \frac{\lambda}{\rho a} = \frac{P_0 \ln(r_2/r_1) \xi_2^2}{2\pi\omega\Delta T \rho l r_2^2} = \frac{P_0 \ln(r_2/r_1) \xi_2^2}{2\omega\Delta T m},$$

m being the mass of the sample inside radius r_2 . In this case, therefore, no knowledge of the geometrical factors is required, with the exception of the ratio r_2/r_1 just discussed.

Since equation (4) for λ applies to an infinitely long cylinder, the question arises of the influence of finite size. The resulting error was estimated by considering the solution for a finite cylinder (of radius R), heated along the axis, while the cylindrical boundary and the flat ends are kept at a constant temperature (Carslaw and Jaeger, 1959), the ratio l/R being used as a parameter. These calculations indicate that the end effect contributes 4% to the measured value of λ at zero pressure, and that this error would change with pressure insofar as l/R is influenced. The end effect was found to be 9% at the maximum pressure. This rather uncertain correction was not introduced in the final results but must be considered as an additional uncertainty. It was found from the theoretical estimates that the end correction decreases to a negligible level for a modest increase in l/R , and this precaution is to be taken in future applications of the technique.

The error caused by finite sample length in the determination of a may be treated in terms of waves reflected off the end surfaces. The one-dimensional theory provides the estimate that the influence due to finite length is smaller than that due to the finite radius of the sample, which has already been discussed. In the case of the end effect there is some phase cancellation which diminishes the amplitude of the perturbation. Even the error in a could thus be reduced to negligible proportions by an increase in sample length of only a few millimeters.

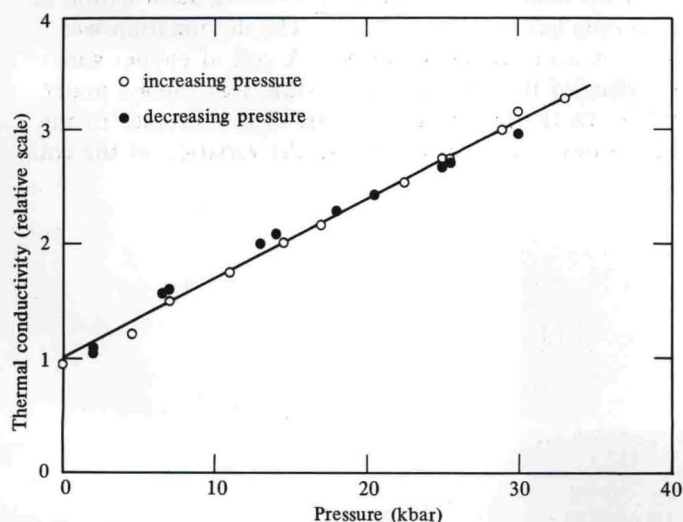


Figure 4. Thermal conductivity of Teflon as a function of pressure (from two pressure cycles on one sample).

4 Results

Teflon samples were used in the first tests of the method. Figure 4 shows corrected values of the thermal conductivity λ to about 30 kbar, obtained from one of the samples. The straight line is the least-squares fit to the points. The final result for the slope of λ , obtained by averaging data from four different samples, is $(7.6 \pm 0.8)\% \text{ kbar}^{-1}$, referred to the value at atmospheric pressure.

Figure 5 shows the corresponding values for the thermal diffusivity a , which is also seen to increase approximately linearly with pressure. The agreement between the amplitude method and the phase method is seen to be reasonable, which indicates that the reflected wave [equation (3)] had been attenuated to a sufficiently high degree. According to our theoretical estimates the contribution due to the reflexion is less than 1% below 10 kbar and less than 5% at 30 kbar, assuming $R = 1$, which evidently is too high. The average pressure coefficient is $(9.3 \pm 1.6)\% \text{ kbar}^{-1}$ for the diffusivity.

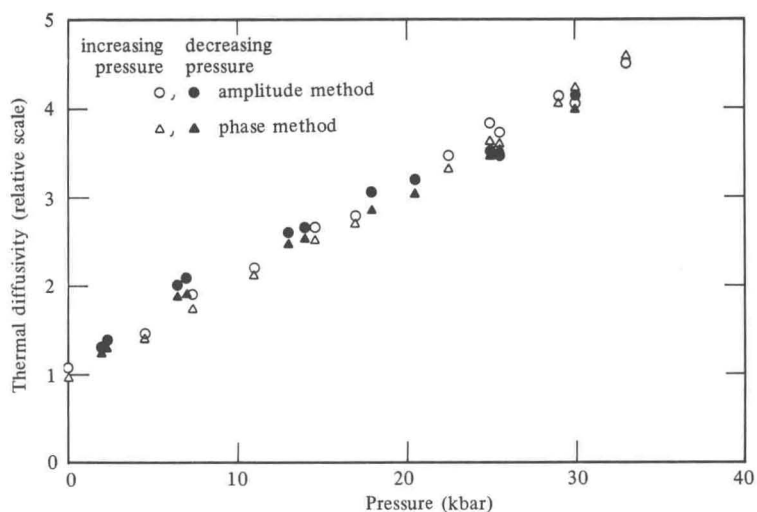


Figure 5. Thermal diffusivity of Teflon as a function of pressure (from two pressure cycles on one sample).

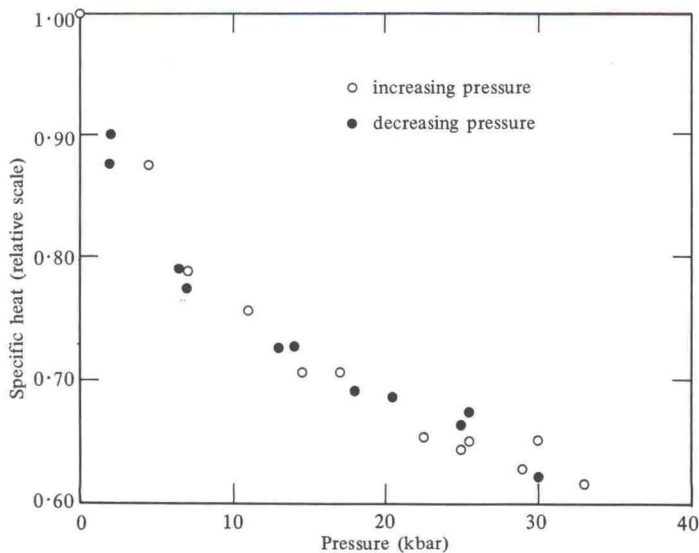


Figure 6. Specific heat of Teflon as a function of pressure (from two pressure cycles on one sample).

Figure 6 presents the specific heat as obtained from one sample, and figure 7 summarizes the results of all the measurements. The general shapes of the four individual curves are quite similar, and the main difference actually arises from the uncertainty in the measurements at atmospheric pressure. Data obtained from virginal samples cannot be given much weight, since the pressure cells originally contain cavities due to the mechanical tolerances of the parts which enter. It is not always possible, however, to reach zero pressure after the first and second pressure cycles, since it is precisely on unloading that the leads tend to break. Consequently, the statistical uncertainty is greater for zero pressure than for higher values.

According to a phase diagram for Teflon proposed by Weir (1953) there are phase transitions at room temperature, first at a fraction of a kbar, and again at 6 kbar. The latter transition induces a volume change of 2%, already reported by Bridgman (1948) and shown for comparison in figure 7. Weir (1954) used thermal expansion and compressibility data to calculate the change in c_p over the 6 kbar transition and obtained a decrease of 17%, referred to the value at atmospheric pressure. As may be judged from figures 4 and 5, which present the results from one sample only, the ratio of λ and a does not behave abnormally at 6 kbar, and a discontinuity of 17% is quite incompatible with the results for all of our four samples. It is true that we find a decrease in c_p of 20% over the first 10 kbar, but even if the transition is slow, it would not have any effect below 6 kbar, and, even if non-hydrostatic conditions are allowed for, it is not likely that the width of the pressure distribution would exceed 1 kbar at the transition. A possible explanation of this discrepancy is that the data used by Weir (1954) are not accurate enough to warrant a calculation of a 17% change.

The fact that no discontinuity appears at 6 kbar in any of the quantities measured may alternatively be accounted for by the lack of crystalline order in the Teflon used. The samples taken for this work were from commercial grade Teflon, having a mass density of 2.15 g cm^{-3} , from which it can be estimated that the substance is crystalline to 55%. In previous work where a 6 kbar transition was observed and a value of the crystallinity or the density was given, the crystallinity had been higher than 68%. It should also be mentioned that attempts to detect the volume change at

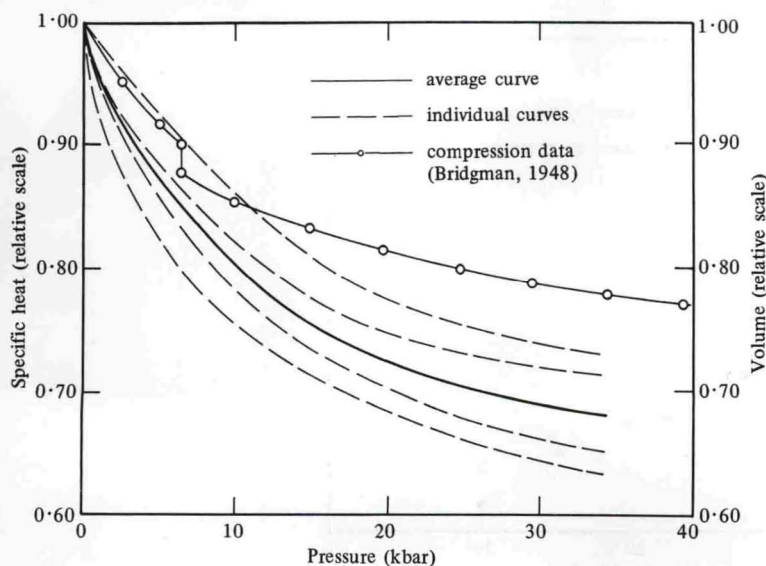


Figure 7. Summary of results on the specific heat of Teflon as a function of pressure.

6 kbar with our variety of Teflon (Cedergren and Bäckström, 1972) have so far yielded negative results, although the experimental sensitivity by far exceeded 2%.

Phase transitions have also been reported at room temperature and atmospheric pressure. Since our data are referred to their values under approximately these conditions, it is important to be aware of any possible variation of the thermal properties across these transitions. For this purpose λ was investigated as a function of temperature at atmospheric pressure, using the same geometry as in the other experiments. The variation, if any, over the transition region was found to be less than 3% with the Teflon at our disposal, whereas other workers have reported 5–8% variation for presumably different modifications of the substance.

There are no previous data in the literature on α and c_p as functions of pressure. As far as the pressure coefficient of λ is concerned, Barker and Chen (1970) reported $8.6\% \text{ kbar}^{-1}$ to 4 kbar, which is in reasonably good agreement with the present results.

Acknowledgement. This work was supported financially by the Swedish Natural Science Research Council.

References

- Barker, Jr., R. E., Chen, R. Y. S., 1970, *J. Chem. Phys.*, **53**, 2616–2620.
Bridgman, P. W., 1924, *Am. J. Sci.*, **7**, 81–102.
Bridgman, P. W., 1938, *Proc. Am. Acad. Arts Sci.*, **72**, 157–205.
Bridgman, P. W., 1948, *Proc. Am. Acad. Arts Sci.*, **76**, 71–87.
Carslaw, H. S., Jaeger, J. C., 1959, *Conduction of Heat in Solids* (Oxford University Press, Oxford).
Cedergren, M., Bäckström, G., 1972, *Rev. Sci. Instr.*, **43**, 686–688, and private communication.
Daniels, W. B., Jones, M. T., 1961, *Rev. Sci. Instr.*, **32**, 885–888.
Ho, J. C., Phillips, N. E., Smith, T. F., 1966, *Phys. Rev. Letters*, **17**, 694–696.
Jura, G., Stark, Jr., W. A., 1969, *Rev. Sci. Instr.*, **40**, 656–660.
Loriers-Susse, C., Bastide, J.-P., Bäckström, G., 1971, Paper presented at the 9th Annual Meeting of the European High Pressure Research Group, Umeå; to be fully published later.
Rosander, T., Bäckström, G., 1969, *Phys. Rev. Letters*, **29A**, 517–518.
Rosander, T., Bäckström, G., 1970, *Physica Scripta*, **1**, 269–271.
Trapeznikowa, O. N., Miljutin, G. A., 1939, *Nature*, **144**, 632.
Weir, C. E., 1953, *J. Res. Nat. Bur. Std.*, **50**, 95–97.
Weir, C. E., 1954, *J. Res. Nat. Bur. Std.*, **53**, 245–252.