Improved hotwire procedure for thermophysical measurements under pressure

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A new and simplified version of the circuitry for the transient hot-wire method is presented. The circuitry provides a wide range of currents allowing probe wires of various diameters to be used in order to match the thermal properties of the specimen to be investigated. The analysis of the temperature increase during the heat pulse is based on the exact solution for a heated wire immersed in a medium. Data are corrected for varying power. The method was tested by computer simulations and by measurements of the thermal conductivity (λ) and the heat capacity per unit volume (ρc_p) of glycerol at room temperature and atmospheric pressure, and for CsCl and NaCl at room temperature and at pressures up to 2 GPa. The results on glycerol and CsCl are in excellent agreement with previous works. The inaccuracy in λ and ρc_p is estimated as 1%–2% and 3%–5%, respectively, but the standard deviation of the measurements is as low as 0.2% for λ and 1% for ρc_p. The improved procedure makes it possible to detect systematic errors caused by reflection of the heat pulse from the walls of the high-pressure cell. This error, which reveals itself by a curvature of the residual, defined as the difference between fitted function and data, was demonstrated in the case of NaCl. A theoretical estimate of the influence of perturbations due to reflection was also carried out and it was found that the error mainly affects the value of ρc_p.

INTRODUCTION

The transient hot-wire method[1] has frequently been used for determining thermal conductivities of gases and liquids under elevated pressure. In our laboratory it has been used[2-4] for measurements on solids as well as liquids up to 2.5 GPa. In the previous version of the procedure,[3,5] a Ni wire with potential taps was heated electrically at constant power for about 1 s. The temperature increase was recorded versus time on the basis of the wire resistance, which was measured by means of a specially designed electronic bridge.[2] For fitting we used an approximation valid at small times and another approximation valid at large times,[3] both checked against the exact expression for the temperature rise. Temperature data pertaining to intermediate times, where neither approximation is accurate, were rejected. In practice only one temperature point, at 400–1000 μs, could be accepted in the region of small times. This first temperature point was important, since it permitted us to determine the heat capacity per unit volume (ρc_p) of the specimen surrounding the wire probe, in addition to the thermal conductivity (λ) usually obtained. The first temperature point was, however, also the most difficult one to measure because of the presence of the switching transient at zero time. Another practical problem with the previous system was the dynamical behavior of the feedback circuit, which involved an analog multiplier in order to provide constant power during the pulse. It was not easy to obtain stable operation as well as short rise time over a wide range of load currents. The A/D converter previously used had an effective sampling time of only a few μs, which made it quite sensitive to interfering spikes. In summary, we found it desirable to simplify the circuitry as much as possible, making use of the best instruments commercially available at the present time. An additional goal was to provide a considerably increased range of current, so that the probe wire diameter may be changed to match the thermal properties of the specimen being investigated. Finally, we wished to abandon the approximate fitting functions and to base the analysis on the exact solution for a heated wire in a medium, which would permit us to use all measured temperature points.

I. FITTING PROCEDURE

The exact solution for the temperature rise ΔT of an infinitely long, straight, infinitely conducting wire in an infinitely large specimen is[6]

$$\Delta T = \frac{2q_0\alpha^2}{\pi^3\lambda} \int_0^\infty \frac{1 - \exp(-\tau u^2)}{u^3\Delta(u,\alpha)}\,du, \qquad (1)$$

where $q_0 =$ constant heating power per unit length, $\alpha = 2\rho c_p/\rho_w c_w$, $\tau = \lambda t/\rho c_p r^2$, $t =$ time, $\rho =$ density of specimen, $c_p =$ specific heat capacity of specimen, $r =$ radius of wire, $\Delta(u,\alpha) =$ combination of Bessel functions, $\rho_w =$ density of wire, $c_w =$ specific heat capacity of wire. The time taken by our PDP-11/84 to compute one temperature value using Simpson's formula is about 2 s, which means that direct calculation of the integral expression in a fitting procedure would be prohibitively time consuming. However, the integral is a function of only two variables, and it may be tabulated and interpolated in two dimensions. High-speed polynomial interpolation[7] may be achieved if the increment

in each variable is constant. In view of the fact that ΔT rises most steeply at small τ we actually use a table with constant increments in the logarithms of α and τ. A total of 9706 real values proved to be sufficient if a third-order interpolation polynomial was used. Interpolated values were extensively tested against integrated values according to Eq. (1) and, as expected, the largest deviation occurred at small α and τ. An interpolation error of one part in 10^4 was considered acceptable. The interpolation subroutine finally adopted yields the integral value as well as the first and second derivatives of the integral with respect to the interpolation variable.

As will be explained in detail in the next section, the new strategy is to measure average wire temperatures over 20-ms intervals, rather than instantaneous values. The implication is that the fitting function must be equal to the average, from $t - 10$ ms to $t + 10$ ms, of $\Delta T(t)$ in Eq. (1). For the first 20-ms interval, starting at about 1 ms, a Simpson sum of Eq. (1) must be used. For the following measuring intervals it suffices to correct the value $\Delta T(t)$ for the curvature of the function. We obtain the curvature from the second derivative calculated in the subroutine just described.

Values of the parameters λ and ρc_p are obtained by least-squares analysis, using successive linearization of the fitting function[7]. We have only modified this classical method by maximizing the step lengths in parameter space to avoid sudden divergence. For the implementation of the method one needs to calculate the partial derivatives of the fitting function with respect to λ and ρc_p. These we obtain by a simple transformation of the first derivatives with respect to α and τ given by the interpolation subroutine.

II. CIRCUITRY AND MEASUREMENTS

The circuit for generating the heater current is shown in Fig. 1. The hot-wire resistance R is in series with a manganin resistance R_m. The latter is implemented by a twisted, bifilar manganin wire, 1.6 mm in diameter. It is essential that the resistance of the manganin wire be kept constant during the heating pulse. Calculations showed that the temperature rise of the manganin wire, assuming no heat loss, would be about 10 K if the current is 15 A. The resistance of manganin is constant within one part in 10^5 from 25 to 40 °C.[8] Thus the condition of constant R_m is fulfilled, since in most cases the current is below 10 A. Constant voltage over the load $R + R_m$ is achieved during the pulse by two HEXFET power transistors in parallel using a fast operational amplifier (OPA 102) and a transistor (BC 140) in the feed-back loop. The constant current to the summing point of the OPA 102 is derived from a 6.3-V reference Zener diode and a set of metal film resistors R_i. The current regulator operates whenever the logical input P is low. In the high state, on the other hand, P supplies sufficient current to the adding point to block the current through the load. The circuit is capable of delivering up to 20 A with a rise time of 20 μs and an output voltage stability of two parts in 10^5 over a typical heat pulse.

All critical parts of the measurement system are controlled by a PDP-11/84 computer via an IEEE-488 (HPIB) bus. The resistor R_i controlling the main current is selected by relays, driven by a digital output card in a Hewlett–Packard 6942A Multiprogrammer. Another of the output bits is used to trigger a specially designed clock, based on a quartz oscillator. The clock delivers the pulse P of selectable length and also a series of equally spaced trigger pulses. These latter pulses are connected to the external trigger inputs of two $6\frac{1}{2}$-digit HP 3456A voltmeters. By means of a HP 3495A Multiplexer the voltmeters may be connected, under program control, over the resistances R and R_m. The voltmeters are set to integrate over an interval of 20 ms, which assures high immunity to mains interference. For maximum speed, the voltmeters are set to transfer readings to their internal memories, which are interrogated by the computer after the completion of the heat pulse. For maximum precision the voltmeters are set in autozero mode, and the smallest trigger interval used is 50 ms.

An inherent software delay between a trigger pulse and the start of signal integration is a feature of the voltmeters used. The trigger delay time has been measured[9] using a specially designed, accurately linear ramp voltage generator, which starts in synchronism with pulse P (Fig. 1). On the 1-V range the delay was 1.13 ms with a scatter of about 0.02 ms. Time values for readings are defined in the following as pertaining to the middle of the integration interval.

Since the nickel wire is used as a thermometer, as well as a heater, data are required concerning the electrical resistivity as a function of temperature (T) and pressure (P). In fact one only needs to know the variation of the resistance of a sample of wire versus T and P. We have carried out calibration experiments from 78 to 450 K at atmospheric pressure using a platinum thermometer. Resistances were measured by an a.c. bridge (F26 from Automatic Systems Laboratories Ltd, U.K.), and the results were reduced to the form

$$R = R_s f(T), \tag{2}$$

where R_s is the resistance at a standard temperature, T_s. We assumed that the variation under hydrostatic pressure could be represented by a factor $1 + \epsilon P$, ϵ being a constant:

$$R = R_s (1 + \epsilon P) f(T). \tag{3}$$

The pressure coefficient ϵ, was determined at room temperature to be -1.66×10^{-2} GPa^{-1}.

The hot-wire experiments proceed as follows. Since the density of nickel is known, the volume of a piece of the nickel wire can be determined by weighing. From a measurement of its length we calculate the average radius r_{00}. After attaching the two potential leads by spot welding we measure the distance L_{00} between the two junctions by means of a workshop microscope.

After mounting the wire probe in the pressure vessel we begin by taking data at atmospheric pressure and room temperature T_{00}. The thermocouple voltage is normally measured twice, at an interval of 20 s, in order to ascertain the temperature drift as well. Neglecting heating during a pulsed resistance measurement the initial wire resistance R_0 may be obtained from the voltage drops (U_R, U_m in Fig. 1) and the previously measured value (R_m) of the manganin resistance. The first measurement during a pulse then yields the value R_{00} corresponding to the temperature T_{00} and atmospheric pressure. As the pressure is increased and the tem-
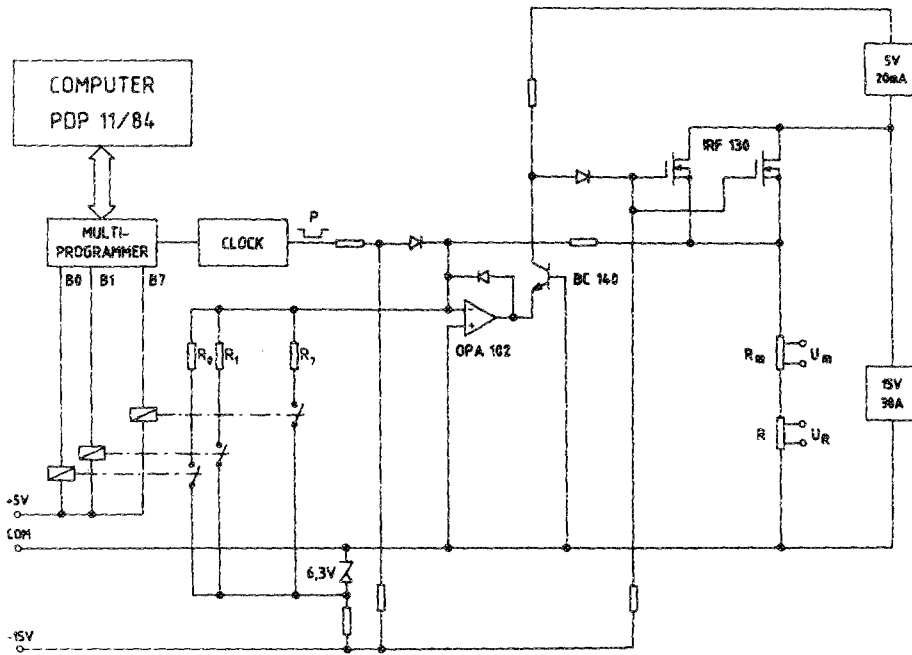
FIG. 1. Circuit for generating the heater current.

perature varied, L and r change, partly due to plastic deformation of the specimen.

In order to analyze the dynamic temperature data we need to know the static quantities L_0 and r_0^2 pertaining to each heating event. These geometrical parameters enter into the expressions for the power per unit length (q) and τ in Eq. (1).

We find the quantities L_0 and r_0^2 at T_0, P_0 in the following manner. Equation (3) may be written, using ρ_e for the electrical resistivity,

$$R_0 = R_s(1 + \varepsilon P_0)f(T_0) = \rho_{es}L_s(1 + \varepsilon P_0)f(T_0)/\pi r_s^2 . \tag{4}$$

We also have the relations

$$R = \rho_e L/\pi r^2 , \tag{5}$$

$$L = L_s[1 + \alpha_L(T - T_s)](1 - \kappa P)^{1/3}, \tag{6}$$

$$r^2 = R_s^2[1 + 2\alpha_L(T - T_s)](1 - \kappa P)^{2/3}, \tag{7}$$

where α_L is the linear expansivity and κ the isothermal volume compressibility of the wire material. Equating the two expressions (4) and (5) for R, then substituting L and r^2 from Eqs. (6) and (7), we obtain for the resistivity under hydrostatic conditions

$$\rho_e = \rho_{es}(1 + \varepsilon P)f(t)[1 + \alpha_L(T - T_s)](1 - \kappa P)^{1/3}. \tag{8}$$

If this expression for ρ_e is used in Eq. (5), the latter yields the resistance of the wire probe at T, P under hydrostatic conditions. In particular we have

$$R_{00} = \rho_{e00}L_{00}/\pi r_{00}^2$$

$$= \rho_{es}f(T_{00})[1 + \alpha_L(T_{00} - T_s)]L_{00}/\pi r_{00}^2. \tag{9}$$

We now assume that the resistivity and the volume ($L\pi r^2$) remains constant under any plastic deformation that might occur under non-hydrostatic pressure. We then obtain, for the wire resistance under pressure P_0 and temperature T_0

$$R_0 = \rho_{es}(1 + \varepsilon P_0)f(T_0)[1 + \alpha_L(T_0 - T_s)](1 - \kappa P_0)^{1/3}L_{00}[1 + \alpha_L(T_0 - T_{00})](1 - \kappa P_0)^{1/3}(1 + \delta)/$$

$$\pi r_{00}^2[1 + 2\alpha_L(T_0 - T_{00})](1 - \kappa P_0)^{2/3}(1 - \delta)^{-1}, \tag{10}$$

where δ is the longitudinal strain of the wire probe. Forming the ratio of the resistances we have

$$R_0/R_{00} = [1 + \alpha_L(T_0 - T_s)][1 + \alpha_L(T_0 - T_{00})](1 + \varepsilon P_0)(1 + \delta)^2 f(T_0)/$$

$$[1 + 2\alpha_L(T_0 - T_{00})][1 + \alpha_L(T_{00} - T_s)]f(T_{00}), \tag{11}$$

from which we compute the length between potential taps

$$L_0 = L_{00}\left(\frac{f(T_{00})[1 + \alpha_L(T_{00} - T_s)](1 - \kappa P_0)^{2/3}[1 + 3\alpha_L(T_0 - T_{00})]R_0}{f(T_0)(1 + \varepsilon P_0)[1 + \alpha_L(T_0 - T_s)]R_{00}}\right)^{1/2} \tag{12}$$

and the radius squared

$$r_0^2 = r_{00}^2\left(\frac{f(T_0)(1 + \varepsilon P_0)[1 + \alpha_L(T_0 - T_s)](1 - \kappa P_0)^{4/3}[1 + 3\alpha_L(T_0 - T_{00})]R_{00}}{f(T_{00})[1 + \alpha_L(T_{00} - T_s)]R_0}\right)^{1/2} . \tag{13}$$

This shows that ideal measurements of R, in which the temperature of the wire remains equal to that of the thermocouple, provide knowledge of r_0 and L_0 at various pressures and temperatures. In real measurements R will change by 1%–3% because of heating, but we shall see that it is possible to calculate the initial resistance, which is equivalent to the ideal value.

In an actual measurement the voltage drops U_R and U_m are sampled repeatedly at times

$$t_i = 11.13 \times 10^{-3} + (i-1)\Delta t, \tag{14}$$

where $i = 1, 2, ..., n$ and t_i is the time in seconds at the center of the integration interval. Typical values of the parameters are $n = 29$ and $\Delta t = 50$ ms. The power developed between potential leads, averaged over ± 10 ms, is obtained as $P_i = U_{Ri} U_{mi} / R_m$. This value is not accurately constant but may change by as much as 1%, depending on the ratio R/R_m. As a result $q_i = P_i / L_0$ varies with time. We thus correct the measured temperature increments to values corresponding to the initial value of q.

The measured resistance values $R_i = U_{Ri} R_m / U_{mi}$ are to be converted to wire temperatures. Eq. (3) gives

$$R_i / R_0 = f(T_i) / f(T_0) \tag{15}$$

and inverting the function $f(T)$ we obtain

$$T_i = f^{-1}[R_i f(T_0)/R_0]. \tag{16}$$

If R_0 were accurately known, this equation would now permit us to compute wire temperature increments, and the function $\Delta T(t)$ obtained from Eq. (1) could immediately be fitted to these data. Fortunately, $T_i - T_0$ depends only weakly on R_0, which can easily be calculated by iteration. In the nonlinear fitting procedure, estimated values are assigned to the parameters λ and ρc_p in the first loop of the iteration. With these initial values Eq. (1) may be used to calculate an expected value of ΔT at t_1, yielding $T_1 = T_0 + \Delta T(t_1)$. With R_1 known from measurements, Eq. (11) then gives an approximate value of R_0, and Eq. (16) generates values of T_i. The values of λ and ρc_p obtained by the fitting routine then give a better value of R_0. Subsequently, T_i values are calculated again, and the procedure is repeated until the change is less than 0.1% in λ and 0.5% in ρc_p. Usually this condition is fulfilled after two or three loops. We know by experience that the changes in λ and ρc_p on further iteration would be smaller by a factor of about 10.

After the above data reduction, values of the temperature rise are available. However, these values correspond to the actual rate of heating $q(t)$, which is not constant as required by Eq. (1). We may write $q(t) = q_0 + k(t)$, where the increment $k(t)$ vanishes at $t = 0$. Let us also simplify the notation in Eq. (1) by writing $\Delta T_{q_0} = q_0 F(t)$, the function F also depending on $\lambda, \rho c_p, \rho_w c_w$ and r_0. The contributions to the temperature rise caused by q_0 and $k(t)$ may now be superimposed. A short pulse of power $k(t')$ and length $\Delta t'$ at time t' induces a temperature rise of

$$\Delta T_{kp}(t) = k(t')F(t-t') - k(t')F[t-(t'+\Delta t')]. \tag{17}$$

If $k(t)$ now is represented by a staircase function, the temperature response will be a sum of terms according to Eq. (17). In the limit of vanishing $\Delta t'$ we have

$$\Delta T_k = -\int_0^t k(t') \left(\frac{\partial F(t-t')}{\partial t'} \right) dt'. \tag{18}$$

Partial integration of Eq. (18) yields

$$\Delta T_k = \int_0^t \left(\frac{dk(t')}{dt'} \right) F(t-t') dt'$$

$$= \int_0^t \left(\frac{dq(t')}{q_0 dt'} \right) \Delta T_{q_0}(t-t') dt'. \tag{19}$$

The final result is

$$\Delta T_{q_0} = \Delta T_q - \Delta T_k$$

$$= \Delta T_q - \int_0^t \left(\frac{dq(t')}{q_0 dt'} \right) \Delta T_q(t-t') dt'. \tag{20}$$

The last equality is only approximate, since ΔT_{q_0} was replaced by ΔT_q. The integral value is, however, relatively small and the resulting accuracy sufficient. The measured temperature values may thus be reduced to constant q_0 by numerical computation of Eq. (20).

III. TEST OF THE METHOD

A. Computer simulation

The fitting procedure, including the routine for correction to constant power, was tested by computer simulations. We thus calculated simulated values for the quantities measured in a real experiment, U_{Ri} and U_{mi}. After addition of Gaussian noise, these values were used as input to the fitting routine.

The calculations of U_{Ri} and U_{mi} were made in two steps. For a given set of $\lambda, \rho c_p, T_0, r_0^2$, and $q(t)$, the temperature rise of the hot wire at times t_i was calculated according to Eq. (1). Then typical experimental values of R_o, R_m, and L_0 were introduced and the voltages U_{Ri} and U_{mi} calculated using resistivity data. Simulations were made for different combinations of $\lambda, \rho c_p$, and r_0^2, and in all cases the starting values were retrieved. The correction procedure for varying power proved to work satisfactorily for both increasing and decreasing $q(t)$ up to 5 % change.

B. Experimental

We chose to test the method by measurements on glycerol, CsCl, and NaCl, since the thermophysical properties are well known for these substances. For glycerol and NaCl, experiments were carried out using Ni wires of two different diameters, 0.1 and 0.3 mm, but in the experiment on CsCl only a 0.3-mm wire was used.

The measurements on glycerol were performed at room temperature and atmospheric pressure. We used a Teflon cell with an inner diameter of 39 mm and a height of 18 mm, shown in Fig. 2. The Ni wire was mounted horizontally as a semi-circular loop. Usually the wire is mounted vertically in hot-wire experiments on liquids, in order to minimize the influence of convection. In highly viscous liquids such as glycerol, however, convection creates no problem and a horizontally mounted wire can be used. The purity of the glycerol was of grade *pro analysi*.

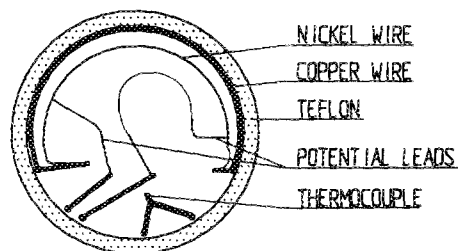The NaCl and CsCl used were powders of > 99.5% pu-

NICKEL WIRE
COPPER WIRE
TEFLON
POTENTIAL LEADS
THERMOCOUPLE

FIG. 2. Top view of the high-pressure cell.

rity, obtained from Riedel–de Haën AG and Merck, respectively. They were dried for 24 h at 120 °C in an oven and then compacted in a steel die under a pressure of 0.1 GPa to form polycrystalline plates, 39 mm in diameter and 8 mm thick. The Ni hot-wire was mounted as a semi-circular loop between two plates of the specimen in a Teflon-lined pressure cell. The whole assembly was loaded into a piston-cylinder apparatus of 45-mm internal diameter, and pressure was generated by a hydraulic press. Details of the general experimental arrangements have been given elsewhere.[10,11]

C. Results on glycerol

Results on λ and ρc_p for glycerol at room temperature and atmospheric pressure are shown in Table I. Each value is an average of 100 measurements. Using 0.1-mm wire, the standard deviation of the measurements was 0.18% for λ and 0.9% for ρc_p. For comparison we have included results of some other workers, and the agreement is 1% for both λ and ρc_p. It was also possible to obtain accurate results using the 0.3-mm wire, if 0.1-mm potential leads were used. However, with 0.3-mm potential leads λ increased and ρc_p decreased by about 3%.

One of the classical sources of error associated with hot-wire experiments is the finite length of the wire. This end effect has been studied by several workers[15-22] and is defined as the difference between the temperature rise of an infinitely long wire given by Eq. (1) and the average temperature rise of a wire of finite length, which will be cooled down by axial heat losses at its ends. Knibbe[17] gives a worst-case analysis for a wire soldered to supports having infinite heat capacity. The temperature rise at the ends of the wire is then zero. His

expression shows that the end effect increases with the ratio r/L, where L is the wire length and r the radius. The end effect also increases with the ratio λ_w/λ, λ_w being the thermal conductivity of the wire material. In most hot-wire experiments the value of r/L is within the range of 5×10^{-5}– 2×10^{-4},[17,18] yielding errors of the order of a fraction of 1%. In our case r/L is 1.25×10^{-3} for the 0.1-mm wire and 3.7×10^{-3} for the 0.3-mm wire. According to the worst-case analysis, the relative end effect in measurements on glycerol would then be 5% and 10%, respectively. The end effect can be reduced by a certain percentage depending on the finite heat capacity of the supports.

Our way of reducing the end effect is to attach potential leads sufficiently far away from the ends of the wire, so that the temperature reduction of the part of the wire between the potential leads can be neglected. However, the heat capacity of the potential leads themselves might cause a temperature reduction. This explains the difference between the results obtained with the 0.3-mm wire, using 0.1 and 0.3-mm potential leads. Thus we conclude that our high values of r/L are acceptable under these conditions, but it is important to minimize cooling by the potential leads by making them as thin as possible.

D. Results on CsCl

Results on $\lambda(P)$ for CsCl at room temperature are shown in Fig. 3. The line is a least-squares fit to the points. The zero-pressure intercept λ_0, the slope $(\partial \lambda/\partial P)_T$, and the pressure coefficient of λ, $\lambda^{-1}(\partial \lambda/\partial P)_T$ for CsCl from this and previous works are given in Table II. Gerlich and Andersson[23] used the previous version of the hot-wire method in measurements on CsCl, and their results on λ agree with the present ones within 1%. Values of $c_p(P)$ were calculated using density and compressibility data.[24] The zero pressure value of c_p for CsCl from the present work is 308 J kg^{-1} K^{-1}, and the agreement with the calorimetric literature value[25] is within 1%.

TABLE I. Thermal conductivity and heat capacity per unit volume of glycerol at 297 K and atmospheric pressure. Results and comparison with previous work.

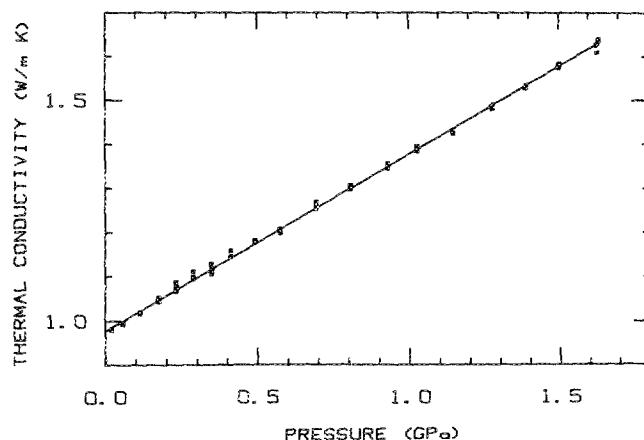| Reference	λ (W m^{-1} K^{-1})	ρc_p (MJ m^{-1} K^{-1})
This work		
0.1-mm wire	0.2843	3.02
0.3-mm wire and		
0.1-mm potential leads	0.2851	3.09
0.3-mm wire and		
0.3-mm potential leads	0.2929	3.00
Touloukian et al.[12]	0.2877	
Touloukian and Makita[13]		2.992
Vargaftik[14]		2.997

FIG. 3. Thermal conductivity as a function of pressure for CsCl at 296 K. The straight line is a least-squares fit to the data points.

TABLE II. Isothermal pressure dependence of the thermal conductivity λ, of CsCl and NaCl fitted to equations of the form $\lambda = A + BP$, the unit of P being GPa.

Material	A (W m⁻¹ K⁻¹)	B (W m⁻¹ K⁻¹ GPa⁻¹)	B/A (GPa⁻¹)	T (K)
CsCl[a]	0.978	0.40	0.408	296
CsCl[b]	0.970	0.40	0.412	296
NaCl,[a] 0.1-mm wire	5.80	1.74	0.300	298
NaCl,[a] 0.3-mm wire	5.89	1.81	0.307	298
NaCl[c]	6.02	1.84	0.306	298
NaCl[d]	6.15	2.01	0.327	298
NaCl[e]	5.79	...	...	298

[a] This work.
[b] Ref. 23.
[c] Ref. 26.
[d] Ref. 27.
[e] Ref. 28.

E. Results on NaCl

In the experiments presented in this article, a theoretical expression for the temperature rise is fitted to data. Normally, the values of the residual, defined as the difference between fitted function and data, are randomly scattered with an average of zero. However, in the experiments on NaCl a systematic deviation was detected. By computer simulation it was found that deviations of the kind observed in the experiments can be caused if a temperature perturbation exists that increases with time. A possible source of error is the finite dimensions of the specimen. One of the boundary conditions for Eq. (1) is that the specimen be infinitely large. In our apparatus the shortest distance between wire and cell walls is 5 mm. If the thermal diffusivity of the medium is high enough, the reflected pulse from the cell walls might cause a measurable perturbation in the measurements.

An estimate of the reflection was made in the following way: The shape of the specimen was approximated by a circular cylinder, with the wire at the axis and the Teflon wall at the surface. Since the thermal conductivity of Teflon is very low compared with that of NaCl, we assumed the heat flux across the cell boundary to be zero. The temperature rise in an infinite medium due to heating of the wire was calculated using an expression given by Carslaw and Jaeger[6] (p. 261). The heat flux at a radius corresponding to the distance between wire and cell wall was obtained by numerical derivation. In order to establish zero flux across the cell boundary, a flux the same magnitude but directed toward the axis was superimposed. The temperature perturbation in the center of the cylinder due to this flux was then calculated using an expression in Carslaw and Jaeger[6] (p. 203). A calculation was made for a cylinder 5 mm in diameter and using values for λ and ρc_p valid for NaCl. For a wire diameter of 0.3 mm the fitting procedure yielded a value of λ 3% too low and a value of ρc_p 16% too high. The corresponding values for a 0.1-mm wire were 3.3 and 60%.

The reason the error in ρc_p increases when the 0.1-mm wire is used can be found considering the properties of Eq.

(1). It was found that at the time at which the first point is measured, the temperature of the 0.3-mm wire reaches 20% of its final value. The corresponding value for the 0.1-mm wire is 41%. This shows that the values obtained using 0.3-mm wire give a better description of the behavior of the function at the beginning of the heating pulse than those obtained using 0.1-mm wire. Since the initial resistance of the Ni wire is determined by fitting, this information is very important. The thinner wire should thus be more sensitive to temperature perturbations.

The zero-pressure intercept λ_0, the slope $(\partial \lambda / \partial P)_T$, and the pressure coefficient of λ, $\lambda^{-1}(\partial \lambda / \partial P)_T$ for NaCl from this and selected previous works are given in Table II. The difference between the results from this article and those of Håkansson and Andersson,[26] obtained using the previous hot-wire method, is 4% for the 0.1-mm wire and 2% for the 0.3-mm wire. The table includes results on NaCl obtained by Pierrus and Sigalas,[27] who used a plane source technique. The difference in λ between our result using the 0.3-mm wire and theirs is 4% at zero pressure. Brydsten et al.[28] used a dynamic hot-strip method, and their result for λ at atmospheric pressure is 1.7% lower than our result for the 0.3-mm wire. A more complete comparison between previous results for $\lambda(P)$ of NaCl is shown in Fig. 3 of Ref. 26. The low-pressure value of c_p using the 0.3-mm wire is 978 J kg⁻¹ K⁻¹, which is 14% higher than the literature value,[29] 859 J kg⁻¹ K⁻¹. The value of c_p obtained using the 0.1-mm wire is as much as 40% larger than the literature value. These deviations from the literature values confirm the theoretical estimate of the reflection. We thus conclude that the systematic errors in the measurements on NaCl were caused by the finite size of the specimen. It would no doubt be possible to obtain accurate values on λ and ρc_p also for NaCl, if the dimensions of the specimen were large enough.

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