THERMAL CONDUCTIVITY
OF SOME METALS UNDER
PRESSURE

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SUMMARY

Although measurements of a wide variety of physical properties have been carried out under pressure during the last decades, data for thermal conductivity under pressure are sparse. This is especially so in the case of metals, where the experimental difficulties are very large. In this work a new method to make such measurements is presented, together with experimental results for copper, silver, gold, and aluminium at room temperature and pressures up to 2.5 GPa.

The first part of the work describes in some detail the method used. This method is a variation of the well known Ångström method. The measured property is thus not the thermal conductivity, but instead the thermal diffusivity. Both the Ångström method, and the variation of this used in this work, are described in detail. Several further simplifications of the method are also investigated. The experimental equipment is described in detail, as is also the construction of samples and pressure cells.

After a description of the experimental procedure, experimental results are presented for the thermal diffusivity of the metals studied, at pressures up to 2.5 GPa. These data are converted to thermal conductivity data by the use of available data on density and specific heat capacity for these metals under pressure. In a few cases, theoretically calculated values for the latter quantity are used. After a brief look at the theory for the thermal conductivity of metals, the experimental results are compared to simple theoretical predictions. The agreement is found to be good. Contrary to theoretical predictions, however, the electronic Lorentz function is found to increase with increasing pressure for the noble metals.

PUBLICATIONS


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<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 METHOD</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>2.2 Angström's method</td>
<td>7</td>
</tr>
<tr>
<td>2.3 The cylindrical heat wave method</td>
<td>11</td>
</tr>
<tr>
<td>2.4 Some preliminary experiments</td>
<td>12</td>
</tr>
<tr>
<td>2.5 A modified Angström method</td>
<td>15</td>
</tr>
<tr>
<td>2.5.1 The radial heat loss modification</td>
<td>15</td>
</tr>
<tr>
<td>2.5.2 Some simplified methods</td>
<td>19</td>
</tr>
<tr>
<td>2.5.3 Errors in the simplified methods</td>
<td>23</td>
</tr>
<tr>
<td>2.6 Tests of new method</td>
<td>28</td>
</tr>
<tr>
<td>2.7 Some further modifications of the method</td>
<td>34</td>
</tr>
<tr>
<td>2.7.1 Reflected waves</td>
<td>34</td>
</tr>
<tr>
<td>2.7.2 Measuring the thermal properties of the pressure transmitting medium</td>
<td>37</td>
</tr>
<tr>
<td>2.8 Some comments on Yukutake's method</td>
<td>38</td>
</tr>
<tr>
<td>2.9 &quot;Hot wire&quot; method</td>
<td>41</td>
</tr>
<tr>
<td>3 MEASUREMENT SYSTEM</td>
<td>43</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>43</td>
</tr>
<tr>
<td>3.2 Signal generation</td>
<td>45</td>
</tr>
<tr>
<td>3.3 Signal analysis</td>
<td>49</td>
</tr>
<tr>
<td>3.3.1 Signal analyzer</td>
<td>49</td>
</tr>
<tr>
<td>3.3.2 Noise filtering</td>
<td>50</td>
</tr>
<tr>
<td>3.4 Determination of amplitude and phase angle</td>
<td>54</td>
</tr>
<tr>
<td>3.5 Tests of the measurement system</td>
<td>57</td>
</tr>
<tr>
<td>4 HIGH PRESSURE EQUIPMENT</td>
<td>59</td>
</tr>
<tr>
<td>4.1 Belt apparatus</td>
<td>59</td>
</tr>
<tr>
<td>4.2 Piston and cylinder apparatus</td>
<td>60</td>
</tr>
<tr>
<td>5 EXPERIMENTAL DETAILS</td>
<td>63</td>
</tr>
<tr>
<td>5.1 Sample construction for measurements at atmospheric pressure</td>
<td>63</td>
</tr>
<tr>
<td>5.1.1 Measurements at room temperature</td>
<td>63</td>
</tr>
<tr>
<td>5.1.2 Measurements below room temperature</td>
<td>64</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.2 High pressure measurements</td>
<td>66</td>
</tr>
<tr>
<td>5.2.1 Belt cells</td>
<td>66</td>
</tr>
<tr>
<td>5.2.2 Piston and cylinder cells</td>
<td>69</td>
</tr>
<tr>
<td>5.3 Pressure calibration</td>
<td>72</td>
</tr>
<tr>
<td>5.4 Correction to measured values</td>
<td>74</td>
</tr>
<tr>
<td>5.5 Experimental procedure</td>
<td>76</td>
</tr>
<tr>
<td>5.6 Error analysis</td>
<td>78</td>
</tr>
<tr>
<td>5.6.1 Absolute value of thermal diffusivity</td>
<td>78</td>
</tr>
<tr>
<td>5.6.2 Pressure dependence of thermal diffusivity</td>
<td>81</td>
</tr>
<tr>
<td>6 THERMAL PROPERTIES OF AN EPOXY RESIN</td>
<td>83</td>
</tr>
<tr>
<td>6.1 Experimental details</td>
<td>83</td>
</tr>
<tr>
<td>6.2 Results</td>
<td>83</td>
</tr>
<tr>
<td>6.3 Calculation of heat loss coefficients for a metal sample</td>
<td>88</td>
</tr>
<tr>
<td>7 THERMAL CONDUCTIVITY OF METALS: EXPERIMENTAL RESULTS</td>
<td>91</td>
</tr>
<tr>
<td>7.1 Copper</td>
<td>91</td>
</tr>
<tr>
<td>7.1.1 Commercial copper wire</td>
<td>91</td>
</tr>
<tr>
<td>7.1.2 High purity copper</td>
<td>95</td>
</tr>
<tr>
<td>7.2 Silver</td>
<td>98</td>
</tr>
<tr>
<td>7.3 Gold</td>
<td>100</td>
</tr>
<tr>
<td>7.4 Aluminium</td>
<td>102</td>
</tr>
<tr>
<td>7.4.1 Thermal conductivity at high pressure</td>
<td>102</td>
</tr>
<tr>
<td>7.4.2 Thermal conductivity at low temperature</td>
<td>104</td>
</tr>
<tr>
<td>8 THEORY OF THERMAL CONDUCTION IN METALS</td>
<td>108</td>
</tr>
<tr>
<td>8.1 Introduction</td>
<td>108</td>
</tr>
<tr>
<td>8.2 Lattice thermal conductivity</td>
<td>108</td>
</tr>
<tr>
<td>8.2.1 Thermal conductivity at atmospheric pressure</td>
<td>108</td>
</tr>
<tr>
<td>8.2.2 Pressure dependence of the lattice thermal conductivity</td>
<td>112</td>
</tr>
<tr>
<td>8.3 Electronic thermal conductivity</td>
<td>114</td>
</tr>
<tr>
<td>8.3.1 Thermal conductivity at atmospheric pressure</td>
<td>114</td>
</tr>
<tr>
<td>8.3.2 Pressure dependence of the electronic thermal conductivity</td>
<td>126</td>
</tr>
<tr>
<td>9 DISCUSSION</td>
<td>131</td>
</tr>
<tr>
<td>9.1 Lattice thermal conductivity</td>
<td>131</td>
</tr>
</tbody>
</table>
9.2 Electronic thermal conductivity

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APPENDIX A: PRESSURE DEPENDENCE OF THE THERMAL CONDUCTIVITY, THERMAL DIFFUSIVITY, AND SPECIFIC HEAT OF SOME POLYMERS
   A.1 Introduction
   A.2 Experimental details
   A.3 Results

APPENDIX B: A LOW NOISE PREAMPLIFIER
   B.1 Introduction and definitions
   B.2 Theory
   B.3 Amplifier design and construction
   B.4 Measured results

APPENDIX C: FORMULAS FOR CALCULATION OF q AND $\phi$

REFERENCES
INTRODUCTION

During the last decades the interest in the thermal transport properties of materials has been increasing, for many reasons. The impending energy crisis has already resulted in large efforts being concentrated on methods of minimizing heat losses from buildings, mainly by increasing the thermal insulation. The space programs have spurred the development of high temperature materials for thermal insulation, which are vital for the safe return to earth of space vehicles. In general engineering, of course, thermal conductivity data have always been important. In many applications, heat must be conserved, as in ovens; in other cases heat must be transported away as efficiently as possible, as in electronic power circuits or automobile brakes.

Thermal conductivity is also interesting from a theoretical point of view. Since heat is always transported through a solid medium by some kind of carrier, thermal conductivity measurements can be used to obtain information on these carriers, be they electrons (in a metal) or atomic vibrations (in a non-metal). It would thus be expected that such an important quantity should have been very accurately measured and extensively tabulated for a large number of substances over a large range of temperatures.

The fact is, however, that the thermal conductivity proves to be an extremely elusive parameter. Measurements of this quantity are very difficult to perform, and the accuracy is not always very high. If we compare with the electrical resistance, we know that this can, in most cases, be quite simply measured to an accuracy of one part in a thousand. In the case of the thermal conductivity, an absolute accuracy of ten percent is not easily obtained; very few, well equipped laboratories can state with certainty that they can obtain an accuracy better than one percent. A brief survey of the extensive data compilations by Touloukian et al. (1970a, 1970b) shows that measured values of the thermal conductivity of a material can indeed differ by tens of percent between different works, making an evaluation of thermal conductivity data very difficult. The problem in the measurements is, mainly, that heat losses to the surroundings from the sample are very difficult to control, since heat can propagate in so many ways - by conduction, convection, and radiation. A good electrical insulator is easily found, but "perfect" thermal insulators are virtually non-existent.
When trying to measure thermal conductivity under pressure the situation is further complicated by the fact that pressure must be transmitted to the sample by some medium, which might be a gas, a liquid or a solid. It is a sad fact that all practical media are good or fairly good thermal conductors; or, at least, they very rapidly increase their thermal conductivities under pressure. If a liquid or gaseous pressure medium is used there are also problems with convective heat flow. These facts show that, if measurements of thermal conductivity normally are difficult, measurements under pressure are still much more difficult. In fact, very few workers have tried such measurements. Bäckström (1978) has reviewed most of the experimental work done in this area, and we shall here sum up only what has been done on the thermal conductivity of metals.

The earliest measurements we know of are those of Lussana (1918) and those of Bridgman (1922). Both these workers measured the thermal conductivities for several metals. As a case history we can study their results for copper, the metal that has been most thoroughly studied. Lussana found the pressure coefficient to be positive, having the value $1 \times 10^{-2}$ GPa$^{-1}$ while Bridgman found a negative coefficient $-7.5 \times 10^{-2}$ GPa$^{-1}$. Both workers used a static longitudinal heat flow method (see section 2.1). This method was later criticized by Starr (1938). Working in Bridgman's laboratory, he improved the method, eliminating convective heat flow, and obtained more accurate values for the pressure coefficients of the thermal conductivity for the noble metals. For copper he found the pressure coefficient to be $2.9 \times 10^{-2}$ GPa$^{-1}$. Averkin et al. (1972) also made measurements on copper, using a method similar to that of Bridgman, and obtained a similar pressure coefficient: $-6.4 \times 10^{-2}$ GPa$^{-1}$. There is thus a large span in results for this metal, as for most others investigated.

The short list of works above is nearly complete, when it comes to collecting the available results for metals under pressure. The only further results known to us are those of Itskevich and Kraidnov (1975a, 1975b) for lead at 2 - 12 K and pressures to 0.8 GPa, and those of Szafrański and Baranowski (1975) for palladium and manganin. The latter work only describes the pressure dependencies relative to platinum, and since the pressure dependence of the thermal conductivity of platinum is not accurately known, the results are so far of little value.
The present work describes an attempt to resolve the many questions regarding the thermal conductivity of metals under pressure by developing a new, accurate method of measurement. The attempt has been successful. Such a new method has been developed, and has been applied to a measurement of the thermal conductivities of gold, silver, copper and aluminium under pressure. The results have then been compared to the predictions of simple theoretical models, and the agreement will be shown to be good.

Some readers may ask what is the practical value of this work. Such a question is very difficult to answer. The direct practical use of the results obtained is very small. The results might be of some value for engineers calculating the heat flow through metal constructions carrying heavy loads, or in pressurized reactors in industries or power stations; however, in these cases the only practical value comes from the fact found that the thermal conductivity varies very little with pressure. The main interest in this work lies probably more in basic science. A change of pressure and thus of volume of a metallic crystal also changes all the allowed energy levels for the electrons in the crystal. A temperature change, on the other hand, in most cases changes only the number of electrons in the different energy levels. Measuring a certain property, like the thermal conductivity, as a function of both temperature and volume will therefore allow us to gain more insight into the basic properties of the material, enabling us eventually to understand better the world around us.
2 METHOD

2.1 Introduction

The thermal conductivity, \( \lambda \), is usually defined from Fourier's law

\[
\mathbf{U} = -\lambda \nabla T, \tag{2.1}
\]

where \( \mathbf{U} \) is the vector heat current density and \( T \) is the temperature. In the general case \( \lambda \) is a tensor, and it is therefore necessary to measure the components of \( \lambda \) in different directions. For isotropic materials, however, such as amorphous and polycrystalline materials, and for cubic crystals, \( \lambda \) is a constant. In this case both the experimental methods and the theoretical analysis can be very much simplified. All of the metals studied in this work have cubic lattices, and we shall therefore in the following assume \( \lambda \) to be a constant.

There are many methods available to measure \( \lambda \) for solids and only a few will be mentioned here. We shall concentrate on methods suitable for determining \( \lambda \) for metals. For further studies of these and other methods the interested reader is referred to the excellent reviews given in the two-volume work edited by Tye (1969).

The methods commonly used can be divided into two groups: Static and dynamic methods. In the static methods a sample is heated at some point by a constant power \( P \), while some other part of the sample is connected to a heat sink at constant \( T \). When a steady state situation has been established the heat current density is calculated from the known \( P \) and the dimensions of the sample, and the temperature gradient is measured. It is then possible to calculate \( \lambda \) directly from equation (2.1). At atmospheric pressure these methods are generally considered to give the most accurate results. However, at all but the very lowest temperatures great care must be taken to minimize heat losses, and the methods are generally quite time-consuming and difficult to use.

The most common method of this type is that of longitudinal heat flow in a rod. In this method one end of a sample rod is clamped to a heat sink and the other end is heated with a constant \( P \). The steady state
temperature gradient is then measured between two or several points along the rod. This method has been used by most previous workers in measuring $\lambda$ for metals under pressure. As shown by Starr (1938), however, this method is very difficult to use correctly at high pressure. Heat losses from the sample and the heater are very large and depend strongly on pressure. Since much of the heat losses occur by convection they are also very difficult to calculate exactly for correction purposes. A further complication is that the measurement of the temperature gradient involves the measurement of the temperatures at two points on the sample, and thus it is necessary to know the variation with pressure of the emf of the thermocouples used.

Another similar method of the static type is to use a long, cylindrical sample and to apply the heating power $P$ on the cylinder axis while the outer cylindrical surface is kept at constant $T$. The resulting radial temperature gradient is then measured to obtain $\lambda$. This method was used by Bridgman (1922) for measurements of $\lambda$ on lead and tin. The method has also been used successfully for measuring $\lambda$ under pressure for many insulating solids (Andersson and Bäckström 1972, 1973a, b; Andersson 1973; Alm and Bäckström 1974; Alm 1976). For metals this method has several disadvantages, however. The worst of these is the difficulty in satisfying the boundary condition that the cylindrical surface must be isothermal, since the sample under pressure is in most cases surrounded by a medium of lower thermal conductivity. Also, for many metals it is difficult to obtain or machine samples of satisfactory homogeneity.

Szafránski and Baranowski (1975) used a static, comparative method to measure $\lambda$ under pressure for palladium and manganin. This method has the drawback that it only measures $\lambda$ relative to a standard material, which in their case was platinum. In view of the uncertainties of previous measurements it must be considered very difficult to find a suitable reference material with known pressure dependence of $\lambda$, and thus this method is at present rather uncertain.

In the dynamical methods the temperature distribution in the sample varies with time and the measurement time is generally less than in the steady state methods. Heat losses are either negligible because of the short times used or can be eliminated from the equations by
other measurements. In most cases measurements of the input power to the sample are not required, nor are measurements of absolute temperature differences, as the calculations required often involve only relative temperature changes. For these reasons dynamic methods would seem ideally suited for measurements under pressure. One drawback is that $\lambda$ can rarely be measured directly with these methods, but instead the quantity $a = \lambda / \rho c_p$, called the thermal diffusivity, is obtained from the experiments. The thermal conductivity can, however, easily be calculated from $a$ if the density $\rho$ and the specific heat capacity $c_p$ of the sample are known. Another drawback is that these methods sometimes give a somewhat lower accuracy, due to the more complicated measurements and calculations necessary.

Dynamical methods can be divided into two groups, those that use periodic heating and those using pulse heating. In the latter group two general classes exist: Either a very short pulse or flash of energy is released in the sample and the resulting temperature variation after the pulse is recorded, or a very long pulse is applied and the temperature rise during the pulse is studied. Below we shall deal very briefly with only one method of the latter type, the so called "hot wire" or thermal conductivity probe method (section 2.9).

The main method used in this investigation belongs to the first group of dynamical methods mentioned, those using periodic heating. Here a periodically varying power is applied to the sample and the resulting periodical temperature variations are recorded and used to calculate $a$. This method will be described in detail in the following sections.
2.2 Angström's method

The method chosen for the high pressure experiments is based on the so-called Angström method, first described by Angström (1861). Recent reviews of the theory and use of this method are given by Parrott and Stuckes (1975) and by Danielson and Sidles (1969). The Angström method will be dealt with in detail in this section, and our modifications will be introduced later when the shortcomings of the original method have been demonstrated.

The principle of this method is to use a sample in the form of a long rod or bar, one end of which is heated by a periodically varying power. The periodic variations of temperature in this end will cause heat waves to travel down the sample. By an analysis of the wave velocity and attenuation it is possible to calculate \( a \). A very good analysis of the theory of the Angström method is given by Carslaw and Jaeger (1959, p. 133). This analysis will be closely followed below.

Suppose that we have a rod of constant cross-sectional area \( A \) and perimeter \( p \). The rod is oriented along the \( x \)-axis and we consider an element of volume bounded by the sections at \( x \) and \( x + \Delta x \) (see figure 2.1). The rod is surrounded by a system in which the temperature \( T = T_0 \). Heat is supposed to flow through the rod in the direction of the positive \( x \)-axis. The quantity of heat flowing into the volume element at \( x \) during the time interval \( \Delta t \) is, from equation (2.1),

\[
Q_x = \lambda \cdot A \cdot \left( -\frac{\partial T}{\partial x} \right)_x \cdot \Delta t
\]

The heat flowing out of the element at \( x + \Delta x \) during the same time is

\[
Q_{x+\Delta x} = \lambda \cdot A \cdot \left( -\frac{\partial T}{\partial x} \right)_{x+\Delta x} \cdot \Delta t.
\]

Some heat is used to change the temperature of the volume element by \( \Delta T \); this can be written as

\[
Q_h = A \cdot \Delta x \cdot \rho \cdot c_p \cdot \Delta T.
\]

Finally, some heat is lost to the surrounding system by radiation from the surface. Supposing that the temperature difference between the
system and the rod is small this heat loss is directly proportional to the temperature difference. We assume that the temperature in the volume element is \( T \) and that \( T_0 = 0 \), for simplicity, and also that the coefficient of proportionality is \( H \). Then we obtain the heat loss during the time \( \Delta t \) as

\[
Q_1 = p \cdot \Delta x \cdot H \cdot T \cdot \Delta t.
\]

The total energy is conserved. We can therefore sum all contributions to the heat flow to find

\[
\lambda \cdot A \left[ \left( \frac{\partial T}{\partial x} \right)_{x+\Delta x} - \left( \frac{\partial T}{\partial x} \right)_x \right] \cdot \Delta t/\Delta x = A \cdot \rho \cdot c_p \cdot \Delta T + p \cdot H \cdot T \cdot \Delta t
\]

In the limit when \( \Delta x \to 0 \) and \( \Delta t \to 0 \) we obtain

\[
\lambda \cdot A \frac{\partial^2 T}{\partial x^2} = A \cdot \rho \cdot c_p \frac{\partial T}{\partial t} + p \cdot H \cdot T
\]

By a rearrangement of constants and by introducing \( \alpha = \lambda/\rho \cdot c_p \) this can be written as

\[
\alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} + \frac{p \cdot H}{A \cdot \rho \cdot c_p} \cdot T
\]
We simplify this equation by introducing a constant \( \mu \), defined as \( \mu = (p \cdot H)/(A \cdot p \cdot c_p) \), and we finally obtain the differential equation governing the flow of heat in the rod as

\[
\alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} + \mu T
\]  

(2.2)

We suppose that the rod is heated at \( x = 0 \) by a periodically varying power. The temperature at \( x = 0 \) can then be described by a Fourier series in \( n\omega \), where \( \omega \) is the angular frequency of the heater power variations. It is sufficient, then, to find a solution for the case when the temperature at \( x = 0 \) varies with time \( t \) as \( \exp(i\omega t) \); the solution for an arbitrary periodic temperature variation can then be obtained as a sum of such solutions. We can assume that \( T(x, t) = F(x) + G(x)\exp(i\omega t) \). The function \( F(x) \) gives only the steady state temperature distribution and is thus of no further interest in this section. We substitute \( T(x, t) = G(x)\exp(i\omega t) \) into equation (2.2), whence

\[
\alpha \frac{\partial^2 G(x)}{\partial x^2} = (i\omega + \mu)G(x)
\]

The solution to this equation must tend to zero as \( x \to \infty \) and we find

\[
B \exp(\alpha x + i(\beta x + \omega t))
\]

(2.3)

or, taking the real part only,

\[
T(x, t) = B \exp(\alpha x) \cos(\beta x + \omega t).
\]

(2.3a)

\( \alpha, \beta \) In these expressions \( \alpha \) and \( \beta \) are given by

\[
\alpha = -\left[\frac{1}{2\alpha}(\mu + (\mu^2 + \omega^2)^{1/2})\right]^{1/2}
\]

(2.4a)

\[
\beta = -\left[\frac{1}{2\alpha}(-\mu + (\mu^2 + \omega^2)^{1/2})\right]^{1/2}
\]

(2.4b)

Using the expressions above it is possible to find \( \alpha \) from experiments in several ways. Suppose that the temperatures at two points on the rod are recorded as functions of time. The distance between the points is \( L \). If the amplitude of the temperature wave at the first point is \( B \), then the amplitude at the second point is \( B \exp(\alpha L) \) and the relative change in amplitude between the two points is \( q = \exp(\alpha L) \). In a
similar way we find the change in phase of the wave between the points as \( \phi = \beta \zeta \). The velocity of the wave is given by \( v = \omega / \beta \).

It is now possible to eliminate \( \mu \) from the equations above either by measurements of \( q \) and \( \phi \) (or, equivalently, \( v \)) at a single \( \omega \) or by measurements of \( q, \phi, \) or \( v \) at two different frequencies. The first possibility was used by Angström (1861). He found a very simple final expression for \( a \) in terms of \( q \) and \( \phi \):

\[
a = \frac{\omega \zeta^2}{2 \cdot \phi \ln q}
\]

(2.5)

The second possibility has been used by King (1915), who measured \( v \) at two different frequencies, and by Starr (1937) who calculated \( a \) using \( q \) at two different values of \( \omega \). Different variations of these basic methods and details of the theoretical analysis and experimental difficulties are treated to some depth by Danielson and Sidles (1969). Some recent developments and variations of the method are given by Gonska and Kierspe (1969), Horch (1975), Papp et al. (1977) and Yukutake (1974). The latter attempted to use this method for measurements of \( a \) at high pressures. However, for reasons to be explained below, his results can not be expected to be very accurate.

As can be seen from equation (2.5) this method has several advantages if it could be used at high pressures. Firstly, no knowledge of the heating power is required to calculate \( a \). Also, heat losses from the sample are taken into account through \( \mu \). Secondly, only relative temperature changes are measured and thus no knowledge is required of the thermopower of the thermoelements used. In fact, any temperature transducers can be used, provided only that they are linear for a range of several K.
2.3 The cylindrical heat wave method

Another periodic heat flow method has been used previously in this laboratory for measurements of $a$ for polymers under pressure (Andersson and Bäckström, 1972, 1973b; Andersson, 1973). In this method a cylindrical specimen is used and heat is supplied by a long heater on the cylinder axis. The heating power is a periodic function of time and the resulting radial heat wave is studied with the help of thermocouples inserted in the specimen on different radii.

The differential equation (2.2) obtained above is only a special case of the general equation of heat conduction (Carslaw and Jaeger, 1959; p. 9)

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

For an infinitely long cylinder, in which the temperature at a radius $r = 0$ varies as $T = \exp(i\omega t)$, this equation has the steady state solution (Carslaw and Jaeger, 1959; p. 193)

$$T(r, t) = C \cdot K_0 [r(i\omega/a)^{1/2}]$$  

where we have used the boundary condition that $T(r, t)$ tends to zero as $r \to \infty$. The radial heat flux $u$ per unit area at a radius $r$ can be found from equation (2.1) as $u(r) = -\lambda \frac{\partial T}{\partial r}$. Eliminating the constant $C$ we find

$$u(r) = -\lambda \frac{\partial T}{\partial r} = \lambda \cdot T \cdot (i\omega/a)^{1/2} \frac{K_1[r(i\omega/a)^{1/2}]}{K_0[r(i\omega/a)^{1/2}]}$$  

In the expressions above $K_0$ and $K_1$ are modified Bessel functions of complex arguments. All terms corresponding to initial transients and to steady flow with $\omega = 0$ have been left out.

From measured values of $T(t)$ at two different radii it is possible to calculate $a$ using equation (2.6). This can be done using either the phase difference or the attenuation of the wave between the two measuring points. A detailed description of the procedure used has been given by Andersson and Bäckström (1972).

This method has several advantages. Since $a$ can be calculated from the measured data in two ways, errors due to reflection of the heat wave
at the sample boundary or elsewhere can be detected. Also, by simply switching over to a constant heater power the thermal conductivity \( \lambda \) can be determined directly on the same specimen, using the static method described briefly in section 2.1. This makes possible a direct determination of \( c_p = \lambda / a \cdot p \). Unfortunately it is generally not possible to use this method for metals, due to their very high values of \( \lambda \) and \( a \). The damping of the heat wave is not strong enough for reflected waves to be extinguished. As for the corresponding static method it is also very difficult to obtain an isothermal outer surface on the cylinder under pressure.

This method was, however, used to measure \( a \) and \( \lambda \), and thus \( \rho c_p \), for several polymers under pressure (Andersson and Sundqvist, 1975). Since this measurement is not in the main line of this work, but rather served as a test of the equipment used, the results are only briefly summarized in appendix A.

2.4 Some preliminary experiments

In view of the many advantages of the Angström method it was decided to investigate the possibility of using it for measurements of \( a \) for metals under pressure. Some preliminary experiments were therefore made on samples surrounded by different liquid and solid media.

In these experiments ordinary commercial copper wires, 0.5 to 1.0 mm in diameter, were used as samples. The samples were constructed as described in section 5.1.1, and the equipment used was that described in section 3.

The thermal diffusivity of the copper samples was measured under the following circumstances:

1) The sample was placed in a vacuum-tight container which was evacuated to about \( 10^{-2} \) torr. In this case only radiation losses were important.
2) The sample was kept in air at normal pressure. Small conduction and convection losses were introduced.
3) The sample was placed in a cup which was filled with glycerol. Due
to the high viscosity of this liquid, a large part of the heat loss was probably due to conduction from the sample, even if there was some convection, mostly at the hot end of the sample.

4) The cup was filled with water. In this case both conduction and convection losses were quite heavy.

5) The sample was encapsulated in Araldite, an epoxy resin. In this case all heat losses were by conduction.

In all cases experiments were carried out for several values of the period of heating, $T = 2\pi/\omega$, in the range 1 to 20 seconds. After some early difficulties it was possible to obtain consistent results in cases 1) and 2) for different specimens, results that also were practically independent of $\omega$. In cases 3), 4), and 5), there was a very strong variation of $\alpha$ with $\omega$ and, in the liquids, a large statistical scatter in the results. Also, the results for the latter three cases were lower than those obtained in the first two cases by a factor which varied from 1 to 10. Some representative results are shown in figure 2.11. The absolute values of $\alpha$ obtained for the samples in air or in a vacuum were between 5 and 20% too low compared to the TPRC recommended values (Touloukian et al., 1973). This was considered to be less important, since the purity of the samples was unknown.

The experiments outlined above showed clearly that the original Ångström method would not give satisfactory results in a high pressure experiment using a solid or liquid pressure transmitting medium. This was rather unexpected, since Yukutake (1974) used a variation of this method to measure $\alpha$ for quartz at high pressure and temperature. In all his experiments the sample was surrounded by a solid pressure transmitting medium. Still, his results for $\alpha$ at atmospheric pressure were in reasonable agreement with those of other workers.
Fig. 2.II Some typical results for the thermal diffusivity of copper at 300 K, obtained by Angström's method.
A: Sample 3, in a vacuum of $10^{-2}$ torr
B: Sample 3, in air
C: Sample 4, in glycerol
D: Sample 5, in Araldite, an epoxy resin
2.5 A modified Angström method

2.5.1 The radial heat loss modification

As was shown by the experimental results presented in section 2.4 the original Angström method is not capable of giving correct results for \( \alpha \) in the cases where heat loss occurs by other mechanisms than radiation from the sample surface. In deriving equation (2.5) heat losses were assumed to be proportional to the temperature difference between the specimen and the surrounding medium. However, when heat is lost by conduction from the sample the heat capacity of the immediate surroundings must be taken into account. The effect of this heat capacity is to introduce a phase difference between the heat losses and the temperature wave. This was pointed out by Starr (1937), although later authors (Parrott and Stuckes, 1975; Danielson and Sidles, 1969; Yukutake, 1974) still state that the coefficient \( \omega \) is capable of taking into account any type of heat loss.

The problem of using a sample encased in a thermally insulating medium has previously been studied by Eichhorn (1964). He made the assumption that the sample radius was large enough so that the problem could be regarded as a simple one-dimensional heat loss problem. From his analysis he found the following expression for \( \alpha \):

\[
\alpha = \frac{\omega \cdot \ell^2}{2 \cdot \phi \cdot \ln q} \left[ 1 + \Omega / \omega^{1/2} \right]
\]  

(2.8)

where

\[
\Omega = (p \cdot \rho_m \cdot c_m / A \cdot \rho_p \cdot c_p)(a_m / 2)^{1/2}
\]

Equation (2.8) is seen to be equal to Angström's original expression (2.5) except for the correction term \( \Omega / \omega^{1/2} \). However, it is difficult to use this expression in an actual experiment since the correction term contains both the density \( \rho_m \), the specific heat capacity \( c_m \), and the thermal diffusivity \( a_m \) of the pressure transmitting medium. All these quantities must be accurately known as functions of pressure, especially since the correction term for most pressure media is numerically about 1 to 5 at atmospheric pressure, and increases with pressure.
In most cases, however, such data are not available. We would therefore like to find a method in which no knowledge of the thermal properties of the medium is necessary.

To obtain a more general solution to the heat conduction problem we make the assumption that the propagation velocity of the temperature wave in the metallic sample is much higher than that of the radial temperature wave in the surrounding medium. Furthermore, the damping of the wave in the sample is much less than in the medium. These assumptions are roughly equivalent to the assumption that $\alpha >> \alpha_m$. Under these assumptions the situation is quite similar to that studied in section 2.3: We have, essentially, a cylindrical metal rod, the temperature of which varies periodically with time. This is surrounded by an infinite cylindrical medium in which radial temperature waves propagate out towards infinity. Heat losses from the sample to the surrounding medium can be described by equation (2.7), which can be written as

$$u(R, T) = \lambda_m T \cdot (i\omega/\alpha_m)^{1/2} \cdot \frac{K_1[R(i\omega/\alpha_m)^{1/2}]}{K_0[R(i\omega/\alpha_m)^{1/2}]} \quad (2.7a)$$

where subscript $m$ on $\lambda$ denotes the medium and where $R$ is the radius of the sample, which in the following will be assumed to be cylindrical. The heat loss term $Q_1$ defined in section 2.2 must now be replaced by

$$Q_1 = p \cdot \Delta x \cdot u(R, T) \cdot \Delta t.$$ 

By carrying out the same calculations as above in section 2.2, and by introducing a new complex constant $\mu = \mu_1 + i\mu_2$, such that

$$\mu = \mu_1 + i\mu_2 = \frac{2\lambda_m}{R\beta c_p} \cdot \frac{(i\omega)^{1/2}}{\alpha_m} \cdot \frac{K_1[R(i\omega/\alpha_m)^{1/2}]}{K_0[R(i\omega/\alpha_m)^{1/2}]} \quad (2.9)$$

a new differential equation, similar to (2.2), is found:

$$\alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} + (\mu_1 + i\mu_2)T \quad (2.10)$$

The solution to this equation must still be of the same form as before, that is $T(x, t) = G(x)\exp(i\omega t)$. Introducing this expression into (2.10) gives
\[ a \frac{\partial^2 G}{\partial x^2} = \left[ \mu_1 + i(\omega + \mu_2) \right] G \]

By putting \( G(x) = \exp x(\gamma_1 + i\gamma_2) \) this reduces to the equations

\[ a (\gamma_1^2 - \gamma_2^2) = \mu_1 \quad (2.11a) \]
\[ 2a \gamma_1 \gamma_2 = \omega + \mu_2 \quad (2.11b) \]

These equations have the solutions

\[ \gamma_1^2 = \frac{1}{2a} \left\{ \mu_1 + \left[ \mu_1^2 + (\omega + \mu_2)^2 \right]^{1/2} \right\} \quad (2.12a) \]
\[ \gamma_2^2 = \frac{1}{2a} \left\{ - \mu_1 + \left[ \mu_1^2 + (\omega + \mu_2)^2 \right]^{1/2} \right\} \quad (2.12b) \]

The results are very similar to those obtained for the original Angström method. In fact, if \( \mu_2 = 0 \) we have \( \gamma_1 \equiv \alpha \) and \( \gamma_2 \equiv \beta \). As in section 2.2 it is, of course, necessary for \( \gamma_1 \) and \( \gamma_2 \) to be negative to give a physically acceptable solution for \( T(x, t) \). However, we now have two heat loss constant, \( \mu_1 \) and \( \mu_2 \), to eliminate instead of one, and this is a more difficult problem than that of the elimination of \( \mu \) in the Angström method.

To obtain a solution which is independent of heat losses we must consider measurements of both \( \phi \) and \( q \) at two different frequencies. At frequency \( \omega_i \), we have the constants \( \gamma_{1i}, \gamma_{2i}, \mu_{1i} \), and \( \mu_{2i} \), and we measure \( \phi_i \) and \( q_i \). Using equation (2.11a) it is possible to write

\[ \frac{\mu_{1i}}{\mu_{2i}} = \frac{\gamma_{1i}^2 - \gamma_{2i}^2}{\gamma_{1i}^2 - \gamma_{2i}^2} \]

We now define a function \( Q_1 = \mu_{1i}/\mu_{2i} \) such that

\[ \frac{\mu_{1i}}{\mu_{2i}} = \frac{\text{Re} \mu(\omega_1)}{\text{Re} \mu(\omega_2)} = Q_1 \left[ \omega_1/\omega_2, R \left( \frac{i\omega_1}{\alpha_m} \right)^{1/2} \right] \]

In the same way we define a function \( Q_2 = \mu_{21}/\mu_{22} \). Using (2.11b)

\[ \frac{\mu_{21}}{\mu_{22}} = \frac{2a \gamma_{11} \gamma_{21} - \omega_1}{2a \gamma_{12} \gamma_{22} - \omega_2} = \frac{\text{Im} \mu(\omega_1)}{\text{Im} \mu(\omega_2)} = Q_2 \left[ \omega_1/\omega_2, R \left( \frac{i\omega_1}{\alpha_m} \right)^{1/2} \right] \quad (2.14) \]

If \( \omega_1/\omega_2 \) is considered as a given constant it is possible to calculate
Fig. 2.111 The function $Q_2 = Q_2(Q_1)$ for $\omega_2/\omega_1 = 2$, 4, and 5.

$Q_1$ and $Q_2$ as functions of $R(i\omega_1/\alpha_m)^{1/2}$, and thus to find $Q_2 = Q_2(Q_1)$. As an example figure 2:111 shows $Q_2 = Q_2(Q_1)$ for $\omega_1/\omega_2 = 2, 4, \text{and } 5$.

The different $\gamma_{ji}$ can all be measured in terms of $\phi_i$ and $q_i$, and thus $Q_1$ can be found experimentally from equation (2.13). From this value of $Q_1$ we can find $Q_2$. Equation (2.14) can now be rewritten to yield

$$a = \frac{\omega_2 Q_2 - \omega_1}{2(\gamma_{12} \gamma_{22})^{1/2} - \gamma_{11} \gamma_{21}}$$

Thus it is possible to find $a$ in this way without any exact knowledge of the thermal properties of the medium, provided only $a_m << a$. The final expression for $a$ can be expressed in terms of the measured parameters $\ell$, $\phi_i$ and $q_i$ only as
A measurement of \( a \) by this method makes some rather complicated mathematical calculations necessary. This is of no great importance, since these calculations can be handled by an electronic computer. A more serious drawback with equation (2.15) is that both the numerator and the denominator are obtained by the subtraction of two terms, both of which are numerically of the same order of magnitude. It is therefore necessary to measure both \( q \) and \( \phi \) with very high accuracy if a high accuracy is desired for \( a \). In view of these difficulties it might therefore prove worth while to study further the equations obtained, to see if there exist any simpler, approximate methods of sufficient accuracy.

\[
a = \frac{(Q_2 w_2 - w_1) \ell^2}{2(Q_2 \phi_2 \ln q_2 - \phi_1 \ln q_1)}
\]  
(2.15)

2.5.2 Some simplified methods

First, it should be noted that \( a \) can be determined directly from any one of the two equations (2.11a) and (2.11b), if only \( \mu_1 \) or \( \mu_2 \) is known. If all the thermal properties of the medium are known these coefficients can easily be calculated from equation (2.7a). This way of finding \( a \) from a measurement of \( q \) and \( \phi \) at one \( \omega \) only is of course very similar to Eichhorn's method (equation (2.8)) and could be considered as a generalization of this, valid whenever \( \alpha \approx \alpha_m \). An attempt to use this method has indeed been made, using equation (2.11b), which is more suitable for this purpose than equation (2.11a). This will be further described in section 6.

One of the simplest ways to find a method in which no knowledge is required of the thermal properties of the pressure medium is to develop Eichhorn's method, equation (2.8), further. The correction factor \( \Omega \) is a function of pressure, \( P \), and \( T \) but not of \( \omega \). It is thus possible to eliminate \( \Omega \) from the equation (2.8) by measurements of \( \phi_i \) and \( q_i \) at two different frequencies, \( \omega_1 \) and \( \omega_2 \). Carrying out the necessary calculations we obtain a somewhat complicated expression for \( a \) of the form
\[ a = \left[ (D_1^2 - 4D_2D_3)^{1/2} - D_1 \right]^{\xi^2/2} D_2 \]  

\[ \text{where} \]

\[ D_1 = 4\omega_1 \omega_2 (\phi_2 \ln q_2 - \phi_1 \ln q_1), \]

\[ D_2 = 4\left[ \omega_2 (\phi_1 \ln q_1)^2 - \omega_1 (\phi_2 \ln q_2)^2 \right], \]

\[ D_3 = \omega_1 \omega_2 (\omega_1 - \omega_2). \]

Here is thus a second way to determine \( a \) without a knowledge of the thermal properties of the pressure medium. This method is capable of giving quite accurate results for a specimen encased in a solid medium. Since the method is based on Eichhorn's one-dimensional heat loss approximation, however, it is still necessary that the dimensions of the sample, and also \( \omega \), are large enough.

Turning now to the more exact expression (2.7a) for the heat loss from the sample, we want to find out under what circumstances this can be simplified. From Abramowitz and Stegun (1970) we find that

\[ K_1(x_i^{1/2})/K(x_i^{1/2}) \rightarrow 1 \text{ as } x \rightarrow \infty. \]

In our case this corresponds to large \( \omega \) and \( R \) and a small \( \sigma_m \), since \( x = R(\omega/\sigma_m)^{1/2} \). For large values of \( R(\omega/\sigma_m)^{1/2} \) we can therefore write

\[ \mu = \mu_0 (1 + i) \]

where we have, from (2.9) and (2.8), with \( p/A = 2/R \),

\[ \mu_0 = \omega_1^{1/2}(2p_m c_m/R \cdot p \cdot c_p) (\sigma_m/2)^{1/2} = \Omega \omega_1^{1/2} \]  

(2.17)

The equations (2.11a) and (2.11b) can now be written

\[ a(y_1^2 - y_2^2) = \mu_0 \]  

(2.18a)

\[ 2a \cdot y_1 y_2 = \omega + \mu_0 \]  

(2.18b)

Putting in the exact expression (2.17) for \( \mu_0 \) in (2.18b) gives us
\[ a = \frac{\omega}{2\gamma_1} \left[ 1 + \frac{2}{R} \cdot \frac{\rho_m c_m}{\rho c_p} \cdot \left( \frac{a_m}{2\omega} \right)^{1/2} \right] = \frac{\omega}{2\phi \ln q} \left[ 1 + \Omega/\omega^{1/2} \right] \]

which is identical to the expression (2.8) derived by Eichhorn (1964) in another way, but with basically the same assumptions.

By eliminating \( \mu \) between (2.18a) and (2.18b) we can find another simple solution. This is

\[ a = \frac{\omega}{2\gamma_1} \frac{\gamma^2}{\gamma_2} - \gamma_1 \]

or, in terms of measured variables,

\[ a = \frac{\omega}{2\phi \ln q + \phi^2 - (\ln q)^2} \tag{2.19} \]

This is very similar to Angström's original expression (2.5) and differs from this only by a correction term in the numerator. This correction term is closely connected to the original Angström heat loss coefficient \( \mu \), which can be found as \( \mu = - a[\phi^2 - (\ln q)^2]/\ell^2 \) from equations (2.4a) and (2.4b). It is easily seen that, as heat losses increase, the value of \( a \) given by (2.19) can differ appreciably from that given by the original Angström expression (2.5). Equation (2.19) is very simple to use. Measurements are only necessary at a single frequency, and no knowledge of the thermal properties of the surrounding medium is necessary. Unfortunately the range of validity of this equation is rather restricted, as will be seen below.

Finally, for \( \mu = \mu_0 (1 + i) \) a very simple solution can be found directly from equation (2.12b). Writing \( \mu_0 = \Omega \omega^{1/2} \) from (2.17) we have

\[ \gamma_2^2 = \frac{1}{2a} \left\{ - \Omega \omega^{1/2} + \left[ \Omega^2 \omega + (\omega + \Omega \omega^{1/2})^2 \right]^{1/2} \right\} \]

This can be rewritten as

\[ a = \frac{1}{2\gamma_2^2} \left[ - \Omega \omega^{1/2} + \omega \left[ 1 + 2 \Omega/\omega^{1/2} + 2\Omega^2/\omega \right]^{1/2} \right] \]

If \( \omega \) is large enough \( \omega >> \Omega^2 \). The expression above can then be approximated by
where the approximation \((1 + x)^{1/2} \approx 1 + x/2\) for \(x \ll 1\) is used.

The final expression for \(a\) can be written in terms of measured variables as

\[
a = \frac{\omega \ell^2}{2\beta^2}
\]

(2.20)

This is a remarkably simple expression which only involves the relative phase angle of the heat wave at the two measuring points. The expression is remarkable in still another way. It was derived assuming conductive heat loss only, a complex loss coefficient \(\mu = \omega 1/2(1 + i)\) and a high value of \(\omega\). The simple final expression arises from a fortunate cancellation of terms. However, exactly the same expression can be derived from the original Ångström method if we assume that heat losses are negligible, that is, \(\mu = 0\), as can easily be seen from equation (2.4b). Since we can obtain the result (2.20) for two so widely differing situations we can guess that this simple "phase method" might be a very useful method to measure \(a\). We shall see below that this method is, in fact, valid over a large range of heat loss conditions.

In the case \(\mu = 0\) there is also a solution for \(a\) corresponding to equation (2.4a), in which only \(q\) need be measured:

\[
a = \frac{\omega \ell^2}{2(\ln q)^2}
\]

(2.21)

We can obtain a similar expression from (2.12a) assuming, as before, \(\mu = \mu_0(1 + i)\) with \(\mu_0 = \omega 1/2\):

\[
a = (\mu_0 + [\mu_0^2 + (\omega + \mu_0)^2]^{1/2})/2 \gamma_1^2 = (\omega + 2\omega \cdot \omega 1/2)/2 \gamma_1^2
\]

This can be written in terms of \(\phi\) and \(\ell\) as

\[
a = \frac{\omega \ell^2}{2(\ln q)^2} (1 + 2\omega/\omega 1/2).
\]

(2.22)

The last equation is very similar to Eichhorn's expression (2.8), except that it does not contain \(\phi\) and that the correction factor is twice as large. Although \(q\) is much easier to measure than \(\phi\), equation (2.22) is not of much practical use since it has several drawbacks:
The correction factor is large and makes a knowledge of the thermal properties of the pressure transmitting medium indispensable, and the equation itself is only valid for large values of $\omega$.

In this section several possible methods to measure $\alpha$ under pressure have been presented. It has been shown that it is possible to determine $\alpha$ from any of the equations (2.8), (2.11a), (2.11b), (2.15), (2.16), (2.19), (2.20), and (2.22), provided that certain conditions are fulfilled. In the following section we shall take a closer look at these conditions and study the accuracy of the above methods under different circumstances.

2.5.3 Errors in the simplified methods

Of the methods presented above, the most accurate one should be that using equation (2.15). This method was derived assuming $a \gg a_m$. What this means in actual numbers has not been specified, and, in fact, no exact analysis of this condition has been made. In most experiments presented in this work $a \approx 1 \text{ cm}^2/\text{s}$ while $a_m$ is of the order of $1 \cdot 10^{-3} \text{ cm}^2/\text{s}$, and therefore no doubt has been felt about the validity of the method in these cases. This is also verified experimentally (see section 2.6). If it was desired to use this method in a case where $a$ was, say, only ten times $a_m$, some preliminary experiments would certainly be needed to establish the validity of the method. This could be done by measuring $a$ using values of $\omega$ over a large range, as has been done in this case. If the measured values of $a$ for different $\omega$ differ from each other and from accepted values, the method should be used with caution.

In this section it will be assumed that the method described above is exact and gives correct results for $\alpha$. We shall have a closer look at the simpler methods presented in section 2.5.2, and establish under what conditions it is possible to use any one of them.

First, it can be seen that a calculation of $a$ from (2.11a) or (2.11b) is possible whenever the "exact" method is valid, since these two equations take account of radial heat loss in the same way. The similar
Eichhorn expression (2.8), however, is not always valid, and need be analysed further. This is of course also true for the modified Eichhorn method (2.16), which has the great advantage that no knowledge of the thermal properties of the pressure transmitting medium is required. This advantage is also shared by the methods based on equations (2.19) and (2.20), which therefore are both potentially very useful. The last possibility investigated, that using equation (2.22), however, will not be analysed here, since this method has been judged less useful than the very similar Eichhorn method (2.8).

To find in what range of heat loss conditions the simpler methods give the same result as the "exact" method some numerical calculations have been made. To do this equations (2.11a) and (2.11b) have been used to express \( a \) in terms of \( y \) and \( y^* \) as

\[
a_e = \omega/[2y_1 y_2 - (\mu_2/\mu_1)(y_1^2 - y_2^2)] \tag{2.23}
\]

This result is assumed to be exact, and the results of the simplified methods can be numerically compared to this formula.

As an example we can use the simple expression (2.19) for \( a \); this can be written in terms of \( y \) as

\[
a_1 = \omega/[2y_1 y_2 + y_2^2 - y_1^2]
\]

and thus we find

\[
a_e/a_1 = (2y_1 y_2 + y_2^2 - y_1^2)/[2y_1 y_2 - (\mu_2/\mu_1)(y_1^2 - y_2^2)].
\]

With the help of equations (2.11a) and (2.11b) this can easily be rewritten as

\[
a_e/a_1 = 1 + (\mu_2 - \mu_1)/\omega. \tag{2.24}
\]

This expression can now be numerically evaluated for all values of \( \mu_1 \) and \( \mu_2 \) of interest, and the relative error of \( a_1 \) relative to the "exact" value \( a_e \) can thus be found.

To make possible a quick assessment of the validity of any of the simple methods such calculations have indeed been carried out. The
conditions for heat loss from the sample are here described by the two parameters $\eta$ and $Z$, defined as

$$\eta = R(\omega/a_m)^{1/2}$$

and

$$Z = \rho_m c_m/\rho c_p.$$  

With these parameters it is possible to write $\mu$ as

$$\mu = (2Z\omega^{1/2}/\eta) K_1(\eta^{1/2})/K_0(\eta^{1/2}).$$

When the error of a method, relative to the "exact" method, has been calculated for a number of values of $Z$ and $\eta$ it is possible to construct an "error map" for this method in the $\eta$-$Z$ plane. Such an error map can be used to estimate the minimum $\omega$ or $R$ needed in an experiment to obtain a certain accuracy, since $a_m$ and $Z$ in most cases can be estimated with sufficient accuracy. It might also be possible to use such a map to obtain a correction factor for an experimental result, should that be desired. The error map for the expression (2.19) relative to (2.15), as calculated from (2.24), is shown in figure 2.IV. From this map it can be seen that the error increases with increasing $Z$ and decreasing $\eta$. For errors larger than 50% the increase is very fast, and for a certain line in the $\eta$-$Z$ plane the result diverges. For large values of $Z$ and/or small $\eta$ the calculated values of $a$ are negative. This method should therefore be used with some caution and only when the necessary conditions for validity are known to be fulfilled.

Similar error maps can be produced for the other methods. The most interesting of these maps is that for the "phase" method (2.20). This is shown in figure 2.V. For $Z << 1$ or $Z >> 1$ the error is approximately the same for this method as for that in figure 2.IV. For $Z = 1$, however, there is a very interesting error "valley", where the error might be very small although the geometrical parameter $\eta$ is unfavourable. In many cases this very simple method should therefore be preferred.
Fig. 2.IV "Error map" for the expression (2.19) relative to (2.15). Below the line for infinite error negative results for $a$ are obtained.
Fig. 2.V Error map for the "phase method", equation (2.20). On the dashed line the error is zero. Note the large area of validity for this method when $\theta \leq 1.$
over the method of equation (2.19).

Figure 2.VI shows a map giving the boundaries for 1% error for the three methods according to equations (2.19), (2.20), and (2.8). Comparing these three methods, the Eichhorn method (2.8) is seen to have the largest area of validity in the η-Z plane, followed by the "phase" method (2.20). The Eichhorn method, of course, has the drawback that the thermal properties of the pressure medium must be known. This drawback is eliminated in the two-frequency method based on equation (2.16). No error calculations have been made for this method, but if the frequencies are chosen so that η is kept above the curve of 1% error for the Eichhorn method in figure 2.VI for both frequencies the resulting error should certainly be below 1% for this method, too.

We can therefore conclude that the most useful of the simplified methods described in section 2.5.2 appears to be the two-frequency Eichhorn method, equation (2.16), followed by the methods of equations (2.20) and (2.19), in that order. The Eichhorn method and the amplitude method of equation (2.22) are less suitable for measurements under pressure, since they cannot be used unless the thermal properties of the surrounding medium are known.

2.6 Tests of new methods

To test the new methods several measurements were made on copper samples of different sizes and in different environments. The results were in most cases very satisfactory. However, none of the methods tested was able to give accurate results for η when the sample was placed in a liquid medium. This was, of course, to be expected, since none of the methods was capable of taking into account heat losses by convection.

All tests were carried out on copper samples cut from ordinary commercial copper wire of unknown purity. The wire diameters varied from 0.5 mm to 3 mm and sample lengths were in the range 70 to 150 mm. All samples were constructed as described in section 5.1.1. We shall show experimental results here for two samples, 3 and 0.7 mm in diameter. These results show clearly most of the interesting features
Fig. 2.VI  Error map, giving the boundaries for 1% error for three of the simplified methods. The error is less than 1% above the curves.
Full line: Eichhorn method (2.8)
Dashed line: Phase method (2.20)
Dot-dash line: Method of equation (2.19)
of the results obtained.

Since the purity of the samples were not known, we did not expect the results for $a$ to be very close to the TPRC recommended value $a = 1.17 \text{ cm}^2/\text{s}$ (Touloukian et al., 1973). However, if the solutions are correct the measured values of $a$ should be independent of $\omega$, at least for the "exact" radial heat loss method (2.15). For the other simplified methods the experimental results should at least tend to the "correct" value given by this method at high values of $\omega$. Also, the measurements of $a$ by Angström's method in air should give results that are independent of $\omega$. This serves as a good test on the experimental equipment (see section 3.5) and also on the validity of the assumption of a semi-infinite sample (see section 2.7.1).

Fig. 2.VII Thermal diffusivity of two copper samples, measured by the Angström method. The dashed line denotes the value $a = 1.17 \text{ cm}^2/\text{s}$ recommended by Touloukian et al. (1973).
A: Sample A, 3 mm in diameter
B: Sample B, 0.7 mm in diameter
Figure 2.VII shows measured results for $\alpha$ for sample A (3 mm in diameter) and sample B (0.7 mm in diameter) as functions of $T = 2\pi/\omega$. These results were obtained by the Angström method with sample A in air at atmospheric pressure and sample B in air at 0.01 torr. The thermal diffusivity is clearly independent of $\omega$ over the 20:1 range in $T$ covered. However, while the results for specimen A are close to the value $\alpha = 1.17 \text{ cm}^2/\text{s}$ recommended by Touloukian (1973), the results for specimen B are low by about 12%. The cause of this discrepancy has been traced to the constantan wires, 0.15 mm in diameter, used for the thermocouples. For the relatively massive sample A heat losses through the thermocouples are negligible, but for sample B there are disturbances in the heat flow due to extra heat losses through the constantan wires. This gives rise to two effects: The first is an extra phase shift, and an increased attenuation of the wave, which would show up as a frequency dependent increase in $\alpha$; the second is the appearance of a small reflected wave travelling backwards from the second measurement point and interfering with the main wave travelling forwards. Depending on the properties of the sample and the surrounding medium, and on the distance between the measurement points, this reflected wave could give rise either to an increase or to a further decrease in $\alpha$. A simple calculation of the reflected wave intensity using the transmission-line analogy (Howling et al., 1955; Horch, 1975) shows that this effect is probably responsible for a large part of the error in $\alpha$. Since the main interest in this work was not on the original Angström method, but on a modification of this, no attempt was made to explain this discrepancy in detail.

After measurements in air a cylindrical epoxy block was cast around each sample. Several types of epoxy were used, and in some experiments fillers were used. These were carbon black, to eliminate all possibilities of heat transport by infra-red radiation, and quartz powder, to enhance heat losses by conduction. The results obtained for $\alpha$ by the radial heat loss method were in all cases the same, within the experimental errors. It was therefore decided to use Araldite AW 106 with hardener HV 953 U as pressure transmitting medium in the high pressure experiments, since this material was already extensively used by our workshop as an adhesive.

Figures 2.VIII and 2.IX show the results for $\alpha$ obtained for specimens A and B, respectively, after they had been encased in Araldite. The
Fig. 2.VIII Thermal diffusivity of sample A, 3 mm in diameter, in Araldite. The arrow denotes the recommended value \( \alpha = 1.17 \text{ cm}^2/\text{s} \). Dashed line indicates the results obtained by Angström's method in air. The equations used when calculating \( \alpha \) were: \( \bullet \)-(2.19), \( \times \)-(2.20), \( \square \)-(2.16), \( \circ \)-(2.15), and \( \blacksquare \)-(2.5).

Fig. 2.IX Thermal diffusivity of sample B, 0.7 mm in diameter. All symbols are the same as above.
results are plotted as a function of $T$. For the two-frequency methods, 
$a$ is plotted versus $T_m = (T_1^2 - T_2^2)^{1/2}$. Results are given for several methods, 
and as a comparison the results from the measurements in air by the 
Angström method are shown by the dashed lines. As was expected, all 
methods give fairly accurate results for specimen A, and the absolute 
value of $a$ is close to the "handbook" value of $a = 1.17 \text{ cm}^2/\text{s}$. Surprisingly enough this is also true for specimen B, at least for the 
radial heat loss method. The other methods in this case give results 
that deviate strongly from the correct value, but for low values of 
$T$ the agreement between the different methods becomes better, as would 
be expected. The good agreement of the absolute value of $a$ for sample 
B with the accepted standard value is probably due to the fact that 
heat losses through the thermocouple leads are now completely negligible 
compared to the heavy radial conduction losses, even for this specimen.

The deviations of the results of the simplified methods from those of 
the "exact" method can, of course, be compared to the theoretical 
errors found from the "error maps" of section 2.5.3. As an example, 
we can check the results for the "phase" method on sample B. In the 
case of a copper sample in Araldite $\log Z = -0.35$. The radius of 
sample B is 0.35 mm and $a_m = 1.4 \times 10^{-3}\text{cm}^2/\text{s}$ (see section 6). From 
figure 2.VI, therefore, we should have $1\%$ error for $\log \eta = 0.635$, 
that is, for $\omega = 21 \text{ s}^{-1}$ or $T = 0.3 \text{ s}$. Comparing this to the actual 
experimental results in figure 2.IX, we find that the agreement is 
good. In this case we are close to the error "valley" of figure 2.V. 
Studying this figure we find that, as $\omega$ decreases, the error should 
first increase to about $10\%$ at $T = 14 \text{ s}$ and then decrease again, 
reaching zero at about $T = 60 \text{ s}$. Again, the experimental results of 
figure 2.IX are in good agreement with this prediction: The error in­
creases with $T$, reaching a maximum of about $15\%$ at $T = 12 \text{ s}$, and then 
decreases.

From the experiments described it can be concluded that the modified 
Angström methods developed above do indeed give accurate results for $a$, 
and therefore can be used for measurements of $a$ at high pressures using 
a solid pressure transmitting medium. Also, the "error maps" given in 
section 2.5.3 give a very good description of the validity of the simpli­
fied methods in different experimental situations.
2.7 Some further modifications of the method

2.7.1 Reflected waves

In sections 2.2 and 2.5.1 it was shown that the time-dependent part of the temperature distribution in the sample could be described by the function

\[ T(x, t) = B \exp(-\gamma x + i\omega t). \]

In this expression we have chosen to write the complex coefficient \( \gamma \) as a positive number. The function above describes a temperature wave travelling in the direction of the positive \( x \)-axis, and it was derived under the implicit assumption that the sample was semi-infinite, so that we must have \( T(\infty, t) = 0 \). For a finite sample, extending from \( x = 0 \) to \( x = x_0 \), however, there is instead some other boundary condition for \( T(x_0, t) \). In most cases this boundary condition must be taken into account by introducing a reflected temperature wave \( T_1(x, t) \) travelling in the direction of the negative \( x \)-axis. Such a reflection is analogous to the reflection of an electromagnetic wave in a transmission line not terminated by its characteristic impedance (Howling et al., 1955; Horch, 1975). The propagation constant \( \gamma \) is of course the same for both waves, and thus we have

\[ T_1(x, t) = R B \exp(\gamma x + i\omega t). \]

Here \( R \) is a reflection coefficient. For a short sample the effect of such reflections can be clearly seen if \( a \) is measured as a function of \( \omega \). For \( \omega \) larger than some characteristic \( \omega_0 \) the damping of the reflected wave is large enough, so that no reflected wave is observed, and \( a \) is a constant. For \( \omega < \omega_0 \), however, the reflected wave is larger and interferes with the wave travelling forward. This gives rise to a change in \( a \). A typical result for a short sample is shown in figure 2.X, where the reflected wave causes a rise in \( a \) for \( T > T_0 \), corresponding to \( \omega < \omega_0 \).
Fig. 2.X  \( a(T) \) for a short copper sample, showing the effect of a reflected heat wave. Assuming \( T(x, t) = -T(x, t) \) at the end of the sample, the amplitude of \( T \) should be about 1% of \( T \) at the second measuring point for \( T = 10 \) s.

Suppose now that we measure \( T(t) \) at three points on the sample. These points are \( x = x_1, x_2 \) and \( x_3 \). The total temperature wave is \( T(x, t) + T_1(x, t) \). At time \( t \) we have

\[
Y_{21} = \frac{T(x_2, t) + T_1(x_2, t)}{T(x_1, t) + T_1(x_1, t)} = \frac{\exp(-\gamma x_2) + R \exp(\gamma x_2)}{\exp(-\gamma x_1) + R \exp(\gamma x_1)}
\]  

(2.25)

and, with \( Y_{31} \) defined in an analogous way,

\[
Y_{31} = \frac{\exp(-\gamma x_3) + R \exp(\gamma x_3)}{\exp(-\gamma x_1) + R \exp(\gamma x_1)}
\]  

(2.26)

By eliminating \( R \) between the equations (2.25) and (2.26) and introducing \( \ell_{ij} = x_i - x_j \) is possible to write an expression for \( \gamma \ell_{21} \):

\[
\exp(\gamma \ell_{21}) = \frac{1 - Y_{31} \exp(-\gamma \ell_{12}) - \exp(-2\gamma \ell_{32}) + Y_{21} \exp[\gamma(\ell_{12} - \ell_{32})]}{Y_{21} [1 - \exp(-2\gamma \ell_{31})]}
\]

(2.27)

In an experimental situation we measure \( q \) and \( \phi \), as defined in section 2.2, between two points. The values \( q_{21} \) and \( \phi_{21} \) measured between the points \( x = x_1 \) and \( x = x_2 \) can be identified with the modulus and argument of the complex function \( Y_{21} \). For simplicity
assume \( R = 0 \) in (2.25); we then have
\[
Y_{21} = \exp (-\gamma \ell_{21}) = \exp (-\gamma \ell_{121})
\]
\[
\exp (-i\gamma \ell_{21}) = q_{21} \exp i\phi_{21}.
\]
However, when \( R \neq 0 \) we do not obtain the correct value of \( \gamma \) from \( Y_{21} \), and thus the values \( q_{21} \) and \( \phi_{21} \) obtained are in error due to the reflected wave. In this case it is necessary to use equation (2.27) to calculate the true \( \gamma \) by an iterative procedure. First, \( Y_{21} \) is inserted instead of \( \gamma \) on the right side of (2.27) and a first \( \gamma \) is calculated. This \( \gamma \) is then inserted into the right side again and a new \( \gamma \) is calculated. The procedure is repeated until a constant \( \gamma \) is obtained, which usually requires 5 - 20 iterations.

This procedure has been used mainly for obtaining accurate results for \( a \) at high pressures using the belt apparatus (see section 4.1), where fairly short specimens had to be used. The main drawback of this method is that the statistical spread in the measured values of \( a \) increases, since the statistical errors in the measured \( q \) and \( \phi \) are increased by the mathematical operations necessary. A further drawback is that the correction procedure makes it necessary to make twice as many measurements, since \( \phi \) and \( q \) must be measured between two pairs of points. The measurement time is therefore doubled, which makes it more difficult to keep both \( T \) and \( P \) constant during a complete measurement sequence. Also, it is possible that the act of introducing an extra thermocouple might in itself give rise to an extra reflected wave.

In the actual measurement situation it was found that although the absolute value of \( a \) was sometimes changed by several per cent by the correction procedure, the pressure derivative was seldom changed appreciably. In fact, the increased scatter in the data was mostly responsible for an additional uncertainty in \( \partial a / \partial P \) which was of the same order of magnitude as the change brought about by the correction. When the piston-cylinder apparatus was brought into operation (see section 4.2) it was found that the correction was no longer necessary, due to the availability of enough space in the pressure cell to accommodate an effectively semi-infinite sample. The correction procedure was therefore abandoned.
2.7.2 Measuring the thermal properties of the pressure transmitting medium.

It was shown above in section 2.5.1 that the actual heat losses from the sample can be calculated from equation (2.9), provided that $\lambda_m$ and $a_m$ are known. Conversely, it is possible to calculate the thermal properties of the pressure transmitting medium from a measurement of the heat losses.

It is a simple matter to find the heat loss coefficients $\mu_1$ and $\mu_2$ from the measurements of $\phi$ and $q$. Once $a$ has been found by any of the methods above, $\mu_1$ and $\mu_2$ are given directly by equations (2.11a) and (2.11b). However, to find $\lambda_m$ and $a_m$ from these values for $\mu_1$ and $\mu_2$, using equation (2.9), is very difficult due to the mathematical complexity of the modified Bessel functions $K_0$ and $K_1$.

There is a simpler way to do this, however. The function $Q$, defined from (2.13), does not contain $\lambda_m$ but only $a_m$, $\omega_1$, $\omega_2$, and $R$. For a constant value of $\omega_2/\omega_1$ it is possible to calculate $Q$ as a function of $R(\omega_2/a_m)^{1/2} = \eta_2$, or, equivalently, $\eta_2$ as a function of $Q$. Both $R$ and $\omega_2$ are known and $Q$ can be calculated from the measured $\phi_1$ and $q_1$. It is therefore possible to obtain the thermal properties of both the pressure medium and the sample from one single set of measurements, by proceeding as follows:

The two quantities $\phi$ and $q$ are measured in the usual way for two values of $\omega_2$ and $Q$, and $a$ are calculated in the manner described in section 2.5.1. The value of $\eta_2$ corresponding to the measured $Q$ is then found from a table or a polynomial approximation, and from this $\eta_2$ it is possible to find $a_m$, since $R$ and $\omega_2$ are known. Once $a_m$ is known, it is fairly easy to calculate $\lambda_m$ from equation (2.9) since $\mu_1$ and $\mu_2$ can be found from equations (2.11a) and (2.11b), respectively. The last step requires a knowledge of $\rho$ and $c_p$, but fortunately these quantities can be assumed to be known as functions of $P$ (see section 7).

The method outlined above thus gives a large amount of information on the thermal properties of the pressure medium without any large increase in the amount of calculations necessary to find $a$. Unfortunately,
the accuracy of the method is rather low. This is due to the large sensitivity of $a_m$ on the value of $Q_1$, and on the low accuracy obtainable for $Q_1$. As can be seen from equation (2.13), $Q_1$ is calculated as the ratio between two numbers, both of which are obtained as the difference between two other numbers which are of the same order of magnitude. The possible error in $Q_1$ is therefore large even if $q_i$ and $\phi_i$ are measured very accurately. It was seen above that $a_m = \omega R^2/\eta^2$, and $a_m$ is therefore very sensitive to errors in $\eta_2$. As can be seen from figure 2.XI, $\eta_2$ is furthermore very sensitive to errors in $Q_1$, since $Q_1$ is normally greater than 1.5 for the combinations of metals and Araldite used in the present experiments.

Although the accuracy of this method can be expected to be quite low, an attempt has been made to calculate $a_m$ and $\lambda_m$ as functions of pressure using measured values of $\phi$ and $q$ from one experiment on gold. The results for $a_m$ are shown in figure 2.XII. As a comparison, the results from a measurement using the "hot wire" method are also shown (see sections 2.9 and 6). The statistical scatter in the results for $a_m$ is large, and the absolute values differ from the directly measured values by 15-30%. Also, the pressure coefficient of $a$ measured in this way is in error by about 20%. The results for $\lambda_m$ are similar; in this case the scatter in the data is less, but the absolute value is in error by 25-40%. The pressure coefficient of $\lambda_m$ is in good agreement with the "hot wire" value above 1 GPa, but below this pressure the error increases. In view of the large scatter in the results, and the errors in the values of $\lambda_m$ and $a_m$ obtained, this method must be considered unsuitable for accurate measurements. It is probable that the method could be improved by an optimization of the geometrical parameters of the experiment. No attempt to do this has been made, however, since other accurate methods to measure $a$ and $\lambda$ for insulating solids already exist.

2.8 Some comments on Yukutake's method

The measurements by Yukutake (1974) have been mentioned several times above. Yukutake used a variation of the Ångström method to measure $a$ for quartz under pressure and obtained fairly accurate results, despite the fact that he took radial heat losses into account using
Fig. 2.XI  $Q_1$ versus $\eta_2$ for $\omega_1/\omega_2 = 4$.

Fig. 2.XII  The thermal diffusivity of Araldite as a function of pressure. Dashed line-measured by the "hot wire" method. Points-calculated from heat losses by the method described in section 2.7.2.
a real $\mu$ only. Yukutake's method can be traced back to Starr (1937), who obtained $a$ from measurements of $q$ at two different values of $\omega$. Yukutake instead measured $q$ for several values of $\omega$. Using the theory of Angström's original method, it can be found from equation (2.4a) that

$$\frac{\omega^2}{4a^2} = \dot{a}^2 - a\mu. \quad (2.28)$$

Yukutake calculated $a^2 \equiv (\ln q)^2/\ell^2$ and $\omega^2/4a^2$ from measured values of $q$ at several values of $\omega$. He then fitted a straight line to the results, and from the slope of this line $a$ was calculated, using equation (2.28). Unfortunately, since all heat losses in Yukutake's experiments were by conduction, this theory is not valid. This can also be seen from Yukutake's original plots of $\omega^2/4a^2$ versus $a^2$ (Yukutake, 1974; figure 1), where the experimental points do not fall on straight lines. Assuming that $\alpha \gg a^2$ in Yukutake's experiment we can instead use the theory developed in section 2.5.1 to derive an alternative expression for $\omega^2/4a^2$.

For the actual experimental situation $\ln q = \ell \cdot \gamma$, with $\gamma$ given by equation (2.12a). From this equation $\omega = \omega(\mu_1, \mu_2, a, \gamma_1)$ is found. Using the fact that $\omega > 0$, $\omega^2$ can be written as

$$\omega^2 = 4a^2\gamma_{1}^4 - 4a\mu_{1}\gamma_{1}^2 + \mu_{2}^2 + 2\mu_{2}(4a^2\gamma_{1}^4 - 4a\mu_{1}\gamma_{1}^2).$$

What Yukutake plotted is, in this notation, $\omega^2/4\gamma_{1}^2$ versus $\gamma_{1}^2$. Using the expression above for $\omega^2$ it is easily found that

$$\frac{\omega^2}{4\gamma_{1}^2} = \dot{a}^2\gamma_{1}^2 - a\mu_{1} + \mu_{2}^2/4\gamma_{1}^2 + \mu_{2}(a^2 - a\mu_{1}\gamma_{1}^2)^{1/2} \quad (2.29)$$

Comparing this expression to Yukutake's equation (2.28) it is easily seen that $a$ can no longer be found by simply calculating the slope of $\omega^2/4\gamma_{1}^2$ versus $\gamma_{1}^2$. However, using equations (2.17) and (2.22) it can be shown that the third term in (2.29) is a constant at high values of $\omega$, while the fourth is a slowly varying function of $\omega$ in the same region. Therefore, the simple equation (2.28) could probably be used to calculate $a$ if sufficiently high values of $\omega$ were used.
Since the experimental points obtained by Yukutake evidently do not lie on straight lines when plotted as $\omega^2/4\gamma^2$ versus $\gamma^2$, the values of $\alpha$ calculated by him should not be expected to be very accurate. The agreement found with other experiments, however, suggests that at the highest frequencies used (~1 Hz) the last two terms in (2.29) might not be very important, and thus that the value of $\alpha$ found from (2.28) is not very much in error. This must be regarded as a fortunate coincidence only. Since heat losses generally increase under pressure it would also be expected that the accuracy of equation (2.28) decreases with increasing pressure, and for this reason the values found by Yukutake for the pressure coefficient of $\alpha$ for quartz might not be very accurate. However, it should also be pointed out that the assumption $\alpha >> \alpha_m$ made above might not be true in this case. Yukutake used talc and pyrophyllite as pressure media, and these materials have high thermal diffusivities. Therefore equation (2.29) might not be much better than equation (2.28) in estimating the influence of the pressure transmitting medium on the measurement.

2.9 "Hot wire" method

In this section a very brief account will be given of another method of the dynamic type. In this method a long heat pulse is applied to a medium, and the temperature is studied during the pulse. The method is usually called the thermal conductivity probe method or the "hot wire" method, for reasons to be found below.

The principle of this method is to use a thin metal wire encased in the sample to be measured. The wire is heated by an electric current, and the temperature rise in the wire is measured as a function of time. Since heat losses from the wire are determined by the thermal properties of the surrounding medium, these properties can be calculated from the temperature rise in the wire.

The geometry of this experiment is almost the same as for the methods studied above in sections 2.3 and 2.5, but the boundary conditions differ. It can be shown that, if a constant power $P$ is applied to the wire, the temperature of this varies with time as
\[ T - T_0 = \left( \frac{P}{4\pi \lambda_m L} \right) \left[ \ln \left( 4\alpha_m t / R^2 \right) + \delta'_0(t) \right] \] (2.30)

(Carslaw and Jaeger, 1959; p. 345) where \( T_0 \) is the initial wire temperature, \( L \) is the length of the wire and \( \delta'_0(t) \) is a function which approaches zero as \( t \) increases. By finding the slope of \( T - T_0 \) versus \( \ln t \) it is thus possible to find \( \lambda_m \).

This method will not be studied in detail here, since it cannot be used to measure the thermal properties of electrical conductors. A measurement system using this method has been developed by Andersson and Bäckström (1976) and improved by Sandberg et al. (1977). The system consists in principle of a constant power generator and an associated data acquisition system, which can be used with either a PDP-11 computer or the Wang 600 programmable calculator. The temperature rise in the wire during the experiment is calculated from the change in its resistance, and from these temperature data both \( \lambda_m \), \( \alpha_m \) and \( \rho_mC_m \) can be calculated.

This measurement system was used to measure the thermal properties of the pressure transmitting medium, Araldite AW 106, over a wide range of temperatures and pressures. These measurements will be described further in section 6. Unfortunately, it has recently been found (Sandberg, 1978) that the measurements of \( \alpha_m \) made with this system are in error by approximately 40% in the case of Araldite. The error is probably fairly independent of \( P \) and \( T \), however, and thus more accurate values of \( \alpha_m \) and \( \rho_mC_m \) can be obtained by simply multiplying the results previously obtained by a constant correction factor. This correction has been carried out on all results presented in this work.
3 MEASUREMENT SYSTEM

3.1 Introduction

In section 2 several practical methods to measure $a$ for metals under pressure were developed. The use of any of these methods necessitates the measurement of the relative amplitudes of two periodic signals and their phase difference. In this section some problems associated with such measurements will be mentioned. The electronic equipment used in this work will then be described in some detail.

A measurement of the amplitude of an AC signal is not, in principle, a serious problem, especially since this amplitude in the present case can be expected to be as large as 10 to 400 $\mu$V, peak-to-peak. This corresponds to an amplitude of between 0.1 and 5 K for the temperature wave. If the frequency is high enough a lock-in amplifier can be used to obtain an accurate reading. Such an amplifier might also be able to give a measurement of the phase angle relative to some reference signal. If the frequency is too low for a lock-in amplifier to be used, it is still possible to measure the amplitude accurately by passing the signal through a narrow band-pass filter, to remove noise, and applying it to a sensitive voltmeter.

The measurement of the phase difference between two signals of the same frequency is more difficult. If the frequency is high enough, this can in principle be done with a lock-in amplifier; however, the accuracy in this case is usually not very good, being in most cases about $1^\circ$ for commercially available models. Some workers have recorded the temperature variations at the measurement points as functions of time on a two-channel recorder and measured the phase difference directly. Danielson and Sidles (1969) describe a method to calculate the phase difference from a Lissajous figure obtained in a similar way on an X-Y recorder. This method was also used by Andersson and Bäckström (1972). Several related methods, using for instance null detectors together with variable phase shift networks, are described in the literature. All of these methods are difficult and time-consuming and not always very accurate. Also it is almost impossible to carry out automatic calculations of the phase difference. In view of the complicated mathematical
calculations already necessary for the measurement of $a$ by our modified method it was decided to try to find a simple method which made possible an automatic, accurate measurement of the phase difference using a programmable calculator and a small data acquisition system.

There are several other possible methods which can be used to measure phase differences. Commercially available phasemeters mostly use the zero cross-over detection method. In this method, the point at which each signal crosses zero is detected. The detection circuitry produces a trigger pulse for each zero crossing, and the trigger pulses from the two signal channels are used to drive the two inputs of a bistable flip-flop. The duty cycle of the square wave output signal from the flip-flop is then proportional to the phase difference between the input signals. By averaging the square wave a DC signal is obtained which can directly drive a meter circuit. This technique is quite accurate if noise and distortion levels are low enough. However, serious problems can be introduced by noisy or distorted signals, and therefore this method was rejected.

A second method, known as the vector addition method, calculates the phase difference from trigonometric equations. The amplitudes $S_1$ and $S_2$ of the two input signals are measured. A differential amplifier is used to find the vector difference $S_3$ between the signals, and the amplitude of this difference signal is measured. The phase difference $\phi$ can then be found from the trigonometric identity

$$\phi = \arccos \frac{S_1^2 + S_2^2 + S_3^2}{2S_1 S_2}$$

(3.1)

This method is very simple and has several advantages: For instance, after the differential amplifier has been used to find $S_3$, all three signal channels can be heavily filtered without concern about phase changes, as all information is contained in signal amplitudes. However, the differential amplifier has to be of very high quality, as it sometimes has to cope with high noise levels in addition to the wanted signals. Also, the accuracy is not very high for distorted signals, or for small values of $\phi$, since $\cos \phi = 1 - \phi^2$ in this range. Middlebrook (1975, 1976) has described a similar method which eliminates the last difficulty. In this method, variable gain
amplifiers are used to make $S_1 = S_2$. After this, the sum or the difference between the signals is found, and the phase difference can be calculated from either of two simple expressions, similar to (3.1).

For the measurements reported in this work a third method was devised. In this method, the temperature at a point of the sample is measured at certain time intervals, using a sampling circuit. A digital voltmeter is used to convert the temperature data to digital form. All data are then fed into a programmable calculator, which fits the data to a function of the form $T(x, t) = F + G \cos(\omega t + \psi)$. From the results of this calculation $q$ and $\phi$ can easily be found. The rest of this section will be devoted to a more detailed description of this method and of the electronic equipment used.

### 3.2 Signal generation

Figure 3.I shows a block diagram of the experimental set-up. This will be described in some detail in this and the following section.

The heart of the equipment is the "step sine generator". This generator has two tasks. The most obvious of these is to generate the waveform of the heater signal. The second task is to carry out the synchronization of the measurement, that is, to tell the rest of the equipment when it is time to make a measurement. A block diagram of the generator is shown in figure 3.II.

The step sine generator is governed by a 1 MHz crystal controlled clock, which gives the output frequency a stability of a few parts per million. Since this frequency is much too high to be used directly, a digital counter is used to divide the clock signal by a variable factor to obtain a suitable output frequency. This counter is set by thumb-wheel switches, calibrated directly in terms of $T = 2\pi/\omega$. The clock pulses are then applied to a sequence generator, consisting of five 8-bit parallel-out serial shift registers, connected in series. This sequence generator thus has 40 outputs. At any time, only one of these outputs is active and gives an output which is "high" (that is, +5 V). This "high" state
Fig. 3.1 Block diagram of the electronic equipment used.

Fig. 3.11 Block diagram of the step sine generator.
is shifted between the outputs in a given order, at a frequency given by the clock frequency.

One of the tasks for this sequence generator is the generation of the waveform of the heater voltage in the experiment. We want the applied power to vary as \( P = P_0 + P_1 \cos \omega t \), where \( \omega \) is about 1 rad s\(^{-1}\). A sine generator operating at this frequency is quite difficult to build by conventional methods, especially since we require the frequency to be variable. We also want a very good amplitude and frequency stability. One way to obtain this is to use a piece-wise linear approximation of a sine wave. This can be obtained by applying a triangular wave to a non-linear amplifier. Such an arrangement has been described by Andersson (1972). In the present case, however, a different approach has been chosen, in that the output waveform is generated digitally by the sequency generator. The outputs of this generator are connected via a diode logic decoder to 15 FET switches, as shown in figure 3.III. These switches are each connected to a resistive voltage divider.

![Diagram](image)

**Fig. 3.III** Generation of heater waveform digitally with 15 FET switches. D denotes a special drive circuit. All FETs are type 2N 3819.
When a certain generator output is "high" only one FET is "on", and the output voltage corresponding to this specific voltage divider is applied to a high input impedance buffer amplifier, using a Teledyne Philbrick Nexus 100901 operational amplifier. All other FET switches are "off", and the corresponding voltage dividers are effectively removed from the circuit. The output voltages are dimensioned so that this circuit gives an output signal corresponding to a 40 step staircase approximation of the function $|\sin \omega t/2|$. This corresponds to an output power having the functional dependence $|\sin \omega t/2|^2 = \frac{1}{2} (1 - \cos \omega t)$, which is of the desired form.

The output signal from the step sine generator is then applied to a Kepco 36-1.5 M Bipolar Operational Power Supply/Amplifier, which supplies the necessary power to the heater on the sample.

This technique has several important advantages. The amplitude stability of the applied voltage is excellent, since it is only determined by the stability of the supply to the voltage divider network. The frequency $\omega$ can be changed by any factor in seconds, as it is set digitally by thumb-wheel switches. Once set, $\omega$ is controlled by a crystal oscillator and thus has excellent stability and accuracy. The harmonic content of the temperature waveform can be made very low by adjustment of the individual voltage dividers. The dominant harmonic, theoretically, is the $40^{th}$, which arises from the step nature of the waveform. Due to the strong dispersion of the temperature wave in the sample (see equations 2.12), such a high harmonic is very efficiently damped relative to the desired wave, and is thus of no consequence. Therefore no problems should arise from distortion of the wave from a pure sine function.

The second task carried out by the sequence generator is the synchronization of the measurements. This will be discussed further in next section.
3.3 Signal analysis

3.3.1 Signal analyzer

The signals to be measured and analyzed in this experiment are produced by thermocouples, welded to the sample. The output voltages from these thermocouples are applied to a combined amplifier/data acquisition system, called the "thermal diffusivity analyzer" in figure 3.I. This analyzer is controlled by the step sine generator and performs most of the actual measurements.

The input signals to the analyzer are first amplified in a low noise, low drift preamplifier. Originally this amplifier was a Teledyne Philbrick Nexus chopper-stabilized operational amplifier, type 1701. It was later discovered, however, that this amplifier gave a certain amount of "chopper" noise in its output signal, and that this noise interfered with the measurements to give an unnecessarily large scatter in the data. A new preamplifier was therefore constructed using several operational amplifiers, type OP-07 from Precision Monolithics, Inc., connected in parallel. The design of this amplifier is presented in appendix B. The amplifier has a gain of 20000 X, and is provided with an adjustable offset voltage control to balance out any DC input voltages. The original version of the analyzer also contained a simple switched RC low pass filter, built around a type 741 operational amplifier. This was removed from the later version for two reasons: Firstly, because it introduced an unwanted phase shift into the signal path; and secondly, because adequate filtering was found to be provided by the subsequent integration and sampling procedures.

The input amplifier is followed by a sampling integrator built around a Teledyne Philbrick type 102601 FET input operational amplifier. This integrator is controlled by the step sine generator, and works as follows: The 40 steps of the sequence generator in the step sine generator are divided into five groups of eight steps each. One signal sample is taken during each such group. The first step
of each group resets the integrator to zero, with the help of FET switches. During the next four steps the input signal is integrated, and the sixth step stops the integration and stores the output voltage of the integrator in an analog memory, consisting of a bank of capacitors. To obtain the best possible insulation the capacitors are connected via reed relays, thus reducing leakage to a minimum. From the description above, we see that the integrator integrates the input signal over one tenth (4/40) of the period of the signal. This is repeated five times each period. The analyzer has two channels, so that input signals from two thermoelements can be analyzed simultaneously to obtain \( \phi \) and \( q \), as defined above. Since all measurements are carried out in synchronism with the applied heater signal, the measurement system could, in fact, be described as a kind of lock-in amplifier.

\[ E_{kj} \]

At the end of each period of the signal, ten voltage samples \( E_{kj} \) have been stored in the memory. Subscript \( k = 1,2 \) here denotes the channel, while \( j = 1, \ldots, 5 \) indicates the order of measurement. To read these samples, a trigger pulse is delivered to the read-out circuit. This circuit connects sequentially the ten voltages \( E_{kj} \) via a high impedance buffer amplifier (Teledyne Philbrick Nexus 100901) to a digital voltmeter (Hewlett-Packard 3480 B). The values of \( E_{kj} \) are read by the voltmeter and converted to a BCD-coded output, which is applied to a Wang 600 programmable calculator via a Wang 605-1 interface. The calculator then automatically performs the calculations necessary to find \( a \), and the results are printed out. These calculations will be described in some detail in section 3.4.

### 3.3.2 Noise filtering

The sampling integrator described above also carries out most of the necessary filtering of the input signal. To understand how this filtering works, we consider an integrator such as the one shown in figure 3.IV. The input signal can be written as \( E_i = E \cos(\omega t + \psi) \). Any periodic disturbance can be expressed as a Fourier series and written as a sum of signals of this form. The input signal is integrated during the time \( t = 0 \) to \( t = t_0 \), and we obtain (Tobey et al., 1971) the output
Fig. 3.IV Operational amplifier integrator

$$E_0 = -\frac{1}{RC} \int_{0}^{t_0} E \cos(\omega t + \psi) \, dt = -\frac{E}{\omega RC} \left[ \sin(\omega t_0 + \psi) - \sin \psi \right].$$

By using a simple trigonometric formula this can be put on the form

$$E_0 = -\frac{2E}{\omega RC} \sin \frac{\omega t_0}{2} \cos \left( \frac{\omega t_0}{2} + \psi \right)$$

It is interesting to look at the zeros of this function. Putting $E_0 = 0$ two possible solutions are found:

1) $\frac{\omega t_0}{2} = n \pi$; \hspace{0.5cm} $\omega = n \cdot 2\pi/t_0$

2) $\frac{\omega t_0}{2} + \psi = \frac{\pi}{2} + n \cdot \pi$; \hspace{0.5cm} $\omega = \frac{2\pi}{t_0} \left( n + \frac{1}{2} - \frac{\psi}{\pi} \right)$

In the first case we find that the integration always gives zero provided the input signal frequency is a multiple of $t_0^{-1}$. The second solution depends on the value of $\psi$ and this zero is thus of less interest from the filtering point of view.
The maximum value possible for $|E_0|$ for an arbitrary $\psi$, can be found from (3.2) as

$$|E_0|_{\text{max}} = \frac{2E}{\omega RC} \left| \sin \frac{\omega t_0}{2} \right|.$$ (3.3)

This means that $|E_0|_{\text{max}} \leq 2E/(\omega RC)$. We also see that

$$|E_0|_{\text{max}} \rightarrow E_0/RC \text{ as } \omega \rightarrow 0.$$

From the description of the apparatus above we know that $t_0 = 2\pi/10\omega_T$, since we integrate over one tenth of the period of the temperature wave, the angular frequency of which is $\omega_T$. The output from the integrator for the wanted signal is thus, according to (3.2),

$$E_0 = -\frac{2E}{\omega RC} \sin(\pi/10)\cos(\psi + \pi/10).$$

This value depends on $\psi$ and $E$ only, except for some constants. Noise, hum, and other unwanted signals of frequency $\omega_N$ and amplitude $E_N$ give contributions which are less than $|E_0|_{\text{max}} \leq 2E_N/\omega_N RC$. Also, all components of frequency $\omega_N = n \cdot 2\pi/t_0$ give $E_0 = 0$. Figure 3.V shows a plot of $|E_0|_{\text{max}}$ versus frequency. The figure has been plotted to show $20 \cdot \log \left( |E_0|_{\text{max}}/(E_0/RC) \right)$ versus normalized frequency $f_0$. Here $f = \omega/2\pi$. The measurement frequency $\omega_T$, of course, correspond to $f_0 = \omega t_0/2\pi = 0.1$.

As can be seen from the figure, the sampling integrator is equivalent to a combination of a simple RC low-pass filter, with a slope of $-6 \text{ dB/octave}$, and a "comb" type of notch filter, giving in theory an infinite rejection of all frequencies $f = n/t_0$. The cut-off frequency, $f_c$, of the low-pass filter is very close to the signal frequency $f_T = \omega_T/2\pi$ ($f_c/f_T = 3.5$), which provides good filtering. A very large advantage of this method is that we obtain a fairly efficient filter without introducing any differential phase shifts between the signal channels. A simple RC filter with the same value of $f_c/f_T$ would introduce a phase shift of about $-15.9^\circ$. Using one such filter per channel makes it necessary either to match the filters very closely or to introduce a correction factor, which might amount to several degrees, into the measurement. This was one of the reasons why the use of separate filters was abandoned. Another advantage with the sampling filter is that $f_c/f_T$ is a constant, and thus changing $f_T$ automatically changes $f_c$. This provides the same amount of filtering for all values of $f_T$. 
Fig. 3.V Frequency response of the sampling filter, as described in the text. The figure shows the minimum attenuation obtained.

Fig. 3.VI Frequency response of the sampling filter. Full line shows minimum attenuation, independent of $\psi$. Dashed line shows attenuation for $\psi = 0$, while dash-dot line corresponds to $\psi = \pi/4$. 
As was seen above there are two possible solutions for the equation $E_0 = 0$. In figure 3.VI three curves are plotted. First, we have plotted $|E_0|_{\text{max}}$, in the same way as in figure 3.V. This gives the minimum attenuation obtainable by this filtering technique. We have also plotted $|E_0|$ from equation (3.2) for $\psi = 0$ and $\psi = \pi/4$ radians, to show that the actual attenuation generally is better than this. All functions are plotted as attenuations relative to $E_0/RC$ in the same way as in figure 3.V.

The largest source of noise in the present measurements is mains hum pick-up. Due to the construction of the high pressure cell and the sample it is necessary to use rather long unshielded wires which pick up several microvolts of hum, probably originating mainly from fluorescent tubes and the press pump motor. By choosing $\omega_1$ correctly, however, these signals can be almost completely eliminated by the "comb" filter. The hum signals have frequencies that are multiples of 50 Hz. Thus, $t_0$ should be a multiple of 20 ms for complete cancellation, and this is easily accomplished by making $f_T = 5/n$ Hz. In fact, even in the case where the signal-to-hum ratio is about 1, the precision in the determination of $\psi$ has been found to be about 1%.

To increase the accuracy even further the measured values of $E_{kj}$ are usually summed over 3 - 10 periods by the calculator, before the calculation of $\alpha$ is performed. In this way small random errors in $E_{kj}$ due to noise are further reduced. Due to the combined effects of this procedure, the use of the very low noise and drift pre-amplifier described in appendix B, and the automatic elimination of constant terms in $E_{kj}$ described in next section, no high-pass filtering has been found necessary. This eliminates another potential source of phase errors, as well as problems with long time constants at switch-on.

3.4 Determination of amplitude and phase angle

The output signal from the thermal diffusivity analyzer described in section 3.3.1 consists of ten voltage values $E_{kj}$. The temperature variations at a point on the sample can be described by $T(t) = F + G \cos (\omega t + \psi)$, where the phase angle $\psi$ is measured relative
to some arbitrary reference. We shall first verify that the integrated voltage values $E_{kj}$ are, in fact, proportional to the temperature of the sample at a well defined instant of time.

Suppose that we have a function $F = \cos(\omega t + \psi)$. This function is integrated from $t = t_1$ to $t = t_1 + \Delta t$:

$$\int_{t_1}^{t_1+\Delta t} F \, dt = \int_{t_1}^{t_1+\Delta t} \cos(\omega t + \psi) \, dt = \{\sin[(\omega(t_1 + \Delta t) + \psi) - \sin(\omega t_1 + \psi)]\omega^{-1}$$

By using a simple trigonometric formula we find

$$\int_{t_1}^{t_1+\Delta t} F \, dt = \frac{2}{\omega} \sin(\Delta t/2) \cos[(\omega t_1 + \Delta t/2) + \psi]$$

This expression shows that the value of the integral is directly proportional to the value of $F$ at time $t_1 + \Delta t/2$. Since the output voltages of the thermoelements are proportional to temperature, it follows that $E_{kj}$ is directly proportional to the temperature at measurement point $k$ on the sample at a time corresponding to the middle of integration interval $j$. We can therefore write $E_{kj}$ as

$$E_{kj} = A_k + B_k \cos(\omega t_j + \psi_k)$$

where $A_k$ and $B_k$ are linear functions of $F$ and $G$, respectively. Since most of the DC voltage from the thermoelement is removed by the offset control in the preamplifier, $A_k$ should be small and ideally $B_k >> A_k$.

To find $\alpha$ it is necessary to find $B_k$ and $\psi_k$ from the measured values of $E_{kj}$. $A_k$ can easily be eliminated from $E_{kj}$. Dropping subscript $k$ for the moment we have, for $j = 1, \ldots, N$, and with $t_j = t_0 + 2\pi(j - 1)/N$

$$\sum_{j=1}^{N} E_j = NA + B \Re\left\{ \sum_{j=1}^{N} \exp[i(\omega t_0 + 2\pi(j - 1)/N + \psi)] \right\}.$$  

The last $N$ terms contain three constants, which can be taken out. The sum is a geometric series and can be summed to obtain

$$\sum_{j=1}^{N} \exp(2\pi ij/N) = \exp(2\pi i/N) \left[ 1 - \exp(2\pi i N/N) \right] / \left[ 1 - \exp(2\pi i/N) \right]$$
For $N > 1$ this sum is zero, and thus

$$\sum_{j=1}^{N} E_j = NA$$

or, reintroducing subscript $k$,

$$A_k = \left( \frac{\sum_{j=1}^{N} E_{kj}}{N} \right)$$

The constants $B_k$ can be found in a similar way as

$$B_k^2 = 2 \left( \frac{\sum_{j=1}^{N} (E_{kj}^2 - A_k) / N}{N} \right)$$

or, equivalently

$$B_k^2 = 2 \left( \frac{\sum_{j=1}^{N} E_{kj}^2 / N - 2 A_k^2}{N} \right)$$

We are not really interested in the value of $\psi_k$; we are more interested in the phase difference $\phi = \psi_1 - \psi_2$, which can be found from

$$\cos \phi = 2 \left[ \sum_{j=1}^{N} (E_{1j}^1 - A_1)(E_{2j}^2 - A_2) / N \right] / N B_1 B_2$$

or, equivalently

$$\cos \phi = 2 \left[ \sum_{j=1}^{N} (E_{1j}^1 E_{2j}^2 - NA_1 A_2) / N B_1 B_2 \right]$$

The derivations of (3.6) – (3.9) are given in appendix C.

In the actual experiment, the calculator reads the values of $E_{kj}$ from the digital voltmeter. These values are summed over a predetermined number of periods to minimize noise. The values for $E_{kj}$ thus obtained are used to calculate $\phi$ and $q = B_1 / B_2$ using equations (3.5), (3.6), and (3.8). As a check of the accuracy of the fit, new values $E_{kj}'$ are calculated from (3.4) using the values of $A_k$, $B_k$ and $\psi_k$ found by the previous calculation. The root mean square deviation $\left( (E_{kj}^1 - E_{kj}^2)^2 / 5 \right)^{1/2}$ is then compared to $B_k$; if this deviation is larger than 1% the calculator stops and awaits further instructions.
After $\phi$ and $q$ have been found, $\alpha$ is calculated using equation (2.15). The function $Q_2 = Q_2(Q_1)$ is stored in the program in the form of a series of polynomials, each valid over a certain range in $Q_1$. The results of the calculation are printed out by the calculator's printer.

3.5 Tests of the measurement system

The analyzer was first calibrated by applying identical input signals to both channels. Due mainly to tolerances in the value of the integrator capacitors the amplitude ratio, $q$, thus obtained differed from 1. This difference was measured as a function of frequency for the different integrator capacitors used and corresponding correction factors were calculated. The correction factors were found to be almost independent of frequency and to be of the order of 10%. In the same experiments correction factors for the phase difference $\phi$ were measured. For the original version, which included switched low-pass filters, these corrections were appreciable, amounting to 1 - 5 degrees. They also depended strongly on frequency. However, after removing the filters these correction factors were reduced to less than 0.1 degree, typically about 0.02 degrees. This is of the same order of magnitude as the statistical spread in the measured values. All these correction factors have been included into the calculator program. A selector switch on the thermal diffusion analyzer allows the user to apply the same signal to both channels at any time, so that a quick check of the calibration can be made.

When the equipment had been calibrated, it was tested on actual heat signals. These tests were carried out as a series of comparisons between the present method and that used by Andersson (1972), involving Lissajous figures on an XY-recorder (see section 3.1). The results for $q$ and $\phi$ obtained by the two methods were always equal within the experimental errors. After this, the experiments shown in section 2.4 were performed using the original Angström method. Since both $q$ and $\phi$ change with $\omega$, the fact that $\alpha(\omega)$ was found to be constant over a range of 20:1 in $\omega$ was taken to confirm further that the measuring equipment was working properly.

The equipment was also tested in a series of measurements of $\alpha$ and $\lambda$ for some polymers under pressure in collaboration with Dr. Per Andersson.
(Andersson and Sundqvist, 1975). Since this investigation was not in the general line of this work, the results are only very briefly described in appendix A. These measurements again showed that the equipment was capable of giving highly accurate readings of $\phi$ and $q$, and was highly reliable in spite of its complexity. In this investigation the radial heat wave method was used (section 2.3). The fact that $a$ as calculated from $\phi$ only was in good agreement with the values calculated from $q$ served as a further check on the accuracy of the measurements.

The results of the above three tests, together with the experimental results of section 2.6, all indicated that the measurement system works as intended, and that it has a very high accuracy.
4.1 Belt apparatus

High pressure experiments have been carried out in two different types of apparatus. One of these is the belt type, to be described briefly in this section, and the other is the piston and cylinder type, which shall be described in next section.

The earliest experiments were carried out in a belt or girdle type of apparatus of the kind previously used by several other workers in this laboratory (Lundberg, 1973; Andersson, 1973; Alm, 1976). A general view of the experimental arrangement of this type of apparatus is shown in figure 4.1. Since the construction and use of this type of apparatus has been described before by the workers mentioned above and others (Bradley, 1969), only a few further technical details will be mentioned here.

Fig. 4.1 General view of the experimental arrangement of the belt high pressure apparatus.
The belt used had a tungsten carbide die, prestressed by winding stretched steel bands on the outside. This construction makes the belt very light and easy to handle. The sample cavity had an inside diameter of 12.7 mm and a length of 24 mm at atmospheric pressure. The lower gaskets were always made of pyrophyllite. Grooves were made for the wires in one gasket, and the wires and the second gasket were secured by a small amount of fast-setting epoxy. This procedure resulted in a very high reliability, making wire breakage a rare incident. One of the upper gaskets was usually also made from pyrophyllite, while the second one was made of a more compressible material, usually a compacted mixture of talc and pyrophyllite powder. To facilitate removal of the pressure cell after a run, and to minimize pressure gradients, a lubricating coating of MoS\textsubscript{2} was usually applied to the outside of the pressure cell. The construction of the pressure cells will be described in section 5.2. The load necessary for the generation of high pressures was in all experiments supplied by a 5 MN press, made by Amsler. Pressures up to 4 GPa can easily be obtained in this apparatus.

The main drawbacks of the belt apparatus are the small volume of the pressure cell and the large pressure gradients obtained when using a solid pressure medium. The experiments in this apparatus were therefore abandoned as soon as the 45 mm in diameter piston and cylinder apparatus described in next section was ready for use.

4.2 Piston and cylinder apparatus

Several types of piston and cylinder apparatus have been tried in this laboratory previously, but mostly without success (see, for instance, Alm, 1976; appendix C). The main difficulty has mostly been to obtain reliable seals at the pistons.

In some early experiments on copper a 20 mm in diameter cylinder was used with a liquid pressure medium. These experiments invariably ended by catastrophic failure of the bottom seal. A series of experiments was therefore undertaken to find a more reliable construction. Figure 4.11 shows the bottom seal used in the experiments just mentioned, and also by Alm (1976; appendix C). These seals usually failed because the
Al₂O₃ tube broke when shear stresses increased. Some modifications of this seal were first tried, but all failed in similar ways. It was noted, however, that experiments in the belt apparatus seldom failed because of gasket failure. A sealing method similar to that used in the belt was therefore tried in the cylinder. An exploded view of this seal is shown in figure 4.III. The bottom piston has a conical end, like the pistons used in the belt apparatus. A triangular steel ring and two pyrophyllite gaskets are used as seal, and wires are brought out between the pyrophyllite gaskets in the same way as in a belt apparatus. The bottom piston has grooves to allow wires to pass out of the cylinder. The Teflon plate shown at top of the figure is part of the Teflon pressure cell. This seal proved to be very reliable, and has since been used in several cylinders.

The piston and cylinder apparatus used in most of the present experiments is shown in figure 4.IV. The cylinder is of the composite type with an inside diameter of 45 mm. The bottom piston uses the seal shown in figure 4.III, and the apparatus has proved to be extremely reliable. The sample is usually enclosed in a Teflon pressure cell. This will be further described in section 5.2.2. The upper piston has a simple cadmium-coated
triangular steel ring as seal. This apparatus has a maximum working pressure of 3 GPa. A similar, larger cylinder with an internal diameter of 70 mm, capable of reaching 1 GPa, has also been used in some experiments. This is a massive steel cylinder, using the same type of bottom seal as the smaller one, but using fibre reinforced bakelite instead of steel and pyrophyllite.

The large internal volumes of these cylinders made construction and handling of the pressure cells much easier than in the belt apparatus. Moreover, pressure gradients were smaller, improving the accuracy of the measured data. Most experiments for pure metals were therefore carried out in this type of apparatus, as were also the measurements on Araldite described in section 6.

Fig. 4.IV The 45 mm in diameter piston and cylinder apparatus used for the high pressure experiments.
A-Top piston, B-Bottom piston, C-Cylinder, D-Sample cavity.
EXPERIMENTAL DETAILS

Sample construction for measurements at atmospheric pressure

Measurements at room temperature

All the early measurements for testing the methods and the experimental equipment took place at atmospheric pressure. The results of these measurements have been presented earlier, in sections 2.4 and 2.6. In all these measurements the samples were made from ordinary commercial copper wire from different sources. If the wires were originally insulated, the insulation (PVC, enamel) was removed and the surfaces were cleaned. Some of the samples were annealed. The samples were then prepared for the measurements in the following way:

First, thermocouple wires were welded to the samples at two points a distance \( \ell \) apart, using a Hughes resistance welder, model HRW 250 B, with head VTA-70. The distance \( \ell \) was accurately measured with a travelling microscope. In a few cases three thermoelements were used (see section 2.7.1). The thermocouple wires used were constantan, 0.15 mm in diameter. After this, a heater was wound on to the upper end of the sample, using 0.1 mm in diameter insulated manganin wire, and secured with Araldite. Finally, the cold end of the assembled sample was soldered to a massive copper rod with cooling fins, acting as a heat sink. This was kept in a water bath. A constantan wire was welded to the heat sink. In this way two differential thermoelements were formed, and the temperatures at the two measuring points were measured relative to the heat sink temperature. Figure 5.1 shows the construction of the sample. It should be noted that in most cases the sample was kept vertically during the experiment.

The whole experimental assembly was always placed in a Dewar vessel with an expanded polystyrene cover during an experiment in air, to avoid irregular heat losses due to draughts.

A vacuum-tight aluminium cup could be attached to the upper end of the heat sink. This was used for the measurement of \( \alpha \) for samples in a vacuum or in various liquids. When measurements in a solid medium (epoxy) were to be performed, the sample was removed from the
5.1.2 Measurements below room temperature

The thermal diffusivity of aluminium has been measured as a function of temperature between 80 and 400 K at atmospheric pressure. These measurements are presented in section 7.4.2.

In these measurements the simple arrangement shown in figure 5.II was used. The sample itself is constructed as shown in figure 5.I, with the only modification that a chromel-alumel thermocouple is used to measure the temperature at the hot end. The lower end of the sample is screwed on to a massive brass block, 80 mm in diameter and 65 mm high. The temperature of this block is measured by a second chromel-alumel element close to the sample. An aluminium heat shield encloses the sample.

Fig. 5.1 Schematic drawing of sample for measurements at atmospheric pressure. H-heater, S-sample, T-thermocouple wire, R-reference thermocouple wire, HS-heat sink.

heat sink and put in a cylindrical paper mould. This was then filled with epoxy. After the epoxy had hardened, the sample was resoldered to the heat sink.
Fig. 5.II

Apparatus for measurements of $a$ at low temperatures.

Fig. 5.III

Vertical cut through belt high pressure cell, showing positions of sample $S$ and calibration wire $C$. 
In use, the whole assembly is placed in a Dewar vessel and liquid nitrogen is poured over the brass block and the heat shield to cool them. During the cooling procedure the heater on the sample is used to keep the sample fairly hot, so that any water vapour inside the heat shield condenses first on this and not on the sample. When the brass block has reached 77 K measurements are begun at the lowest temperatures obtained. The temperature is then allowed to drift slowly upwards. An electrical heater on the brass block can be used to increase the heating rate or to obtain temperatures above room temperature. The high thermal conductivity of the aluminium heat shield means that the temperatures at all points inside this are kept near the temperature of the brass heat sink, while the large heat capacity of the latter precludes any fast temperature changes. In fact, using the normal input power of about 0.1 W to the sample heater, and with the assembly placed in a Dewar vessel closed at the top with mineral wool, the temperature of the sample drifted by only about 0.5 K/min at an absolute sample temperature of 85 K.

5.2 High pressure measurements

5.2.1 Belt cells

As has been mentioned above, several early measurements on copper under pressure were made using a belt apparatus. The main problems in the use of such apparatus arise from the fact that the available volume of the high pressure cell is very small, only about 2.5 cm³. The theory developed in section 2 always assumes the sample to be a straight, semi-infinite wire. This condition clearly cannot be fulfilled in a belt cell. The first problem in constructing a pressure cell for this geometry is therefore to obtain an acceptable approximation of the straight sample geometry. The second serious problem is that large pressure gradients exist in a belt cell under pressure. A way must therefore be found to position the sample so that the effects of such gradients are minimized.

Several possible cell geometries were explored. Some early samples were positioned as shown in figure 5.III. This gives a good straight wire approximation over about 10 mm of the sample, and by using the
reflection correction procedure of section 2.7.1 accurate measurements should be possible. It was found, however, that in this geometry large pressure gradients developed along the sample. This led to distortions of the sample and to difficulties in estimating the effective pressure at the measuring points.

Later, the sample was positioned as shown in figure 5.IV. In this figure, an outer cylindrical pyrophyllite sheath has been removed to show clearly the inner part of the cell. The sample itself is bent in a circle with a tail going off in the vertical direction. This tail is made so long that the temperature at the end can be regarded as a constant. The reference thermocouple is welded on here. The sample is not positioned in the center plane of the cell, but is slightly offset, and the pressure calibration wire (section 5.3) is positioned on the other side of the center with an equal offset. In this way the pressure at the sample and at the calibration point are approximately equal. Putting a circular sample on a constant radius in the cell minimizes pressure differences over the length of the sample. However, one further problem arises: The heater is now fairly close to the cold end of the sample, and temperature waves propagating
directly through the pressure transmitting medium might disturb the
wave in the sample at the cold end. The minimum distance $\Delta r$, as defined
in figure 5.V, must be large enough so that heat waves directly from
the heater have disappeared. The heater can be regarded as a periodic
point source, dissipating heat in all directions through the surrounding
medium. Such a case is studied by Carslaw and Jaeger (1959; p. 263). The
solution for $T(r, t)$ in this case is

$$T(r, t) = (4\pi a_m r)^{-1} \exp\left[-r(1 + i)(\omega/2a_m)^{1/2}\right]\exp(i\omega t)$$

where $r$ is the distance from the point source. In the cases considered,
the radius of the heater can be taken as 0.4 mm. In this case we find
that for $T = 5$ s and with $a_m = 2 \cdot 10^{-7}$m$^2$/s (worst case) the heat wave
is damped by a factor 5900 at $\Delta r = 4$ mm and a factor 750 at $\Delta r = 3$ mm.
The pressure cells were therefore always built so that this distance
was $\geq 4$ mm.

This type of pressure cell minimizes pressure gradients in the sample
by sacrificing the ideal straight line geometry. However, bending the
sample in the form of a loop should not be too serious, provided the
radius of the loop is much larger than the radius of the sample. In
this case, the ratio between the radii was about 10.

The sample itself was constructed in the same way as described in
section 5.1.1. The only difference was the addition of an extra
copper wire, welded to the sample at the hot end, near the heater.
This wire served as a current lead in a measurement of the resistance
of the sample (see section 5.4).
The pressure cells were quite simple to assemble. The different parts shown in figure 5.IV were first machined separately. The assembled sample and the calibration wire were then fitted into grooves in the central epoxy slab and fastened with epoxy. Care was taken that all cavities were filled. All parts were then assembled into a cylindrical pyrophyllite shell using an epoxy adhesive. At the ends, the pyrophyllite shell had double walls to allow wires to pass out past the steel end slabs. The function of these slabs was only to decrease the effective compressibility of the cell to obtain higher pressures at lower loads.

5.2.2 Piston and cylinder cells

Two general types of pressure cells were used in this type of apparatus. In some early experiments of copper, a 20 mm in diameter Teflon cell was used with a liquid pressure medium, which in all cases was n-pentane. The cell consisted of a Teflon tube, 100 mm long and with walls 2 mm thick. The lower end was sealed as shown in figure 4.II,
and the upper end was sealed by a simple Teflon lid. All leads were taken out through the bottom seal. Since none of these experiments was very successful no more need be said about these cells.

The second type of cell has been used in most of the high pressure measurements reported in this work. Such cells, with suitable diameters, have been used in both the 70 mm and the 45 mm in diameter vessels described in section 4.2. The cell consists simply of a shallow Teflon cup as shown in figure 5.VI. In the first measurements using this type of cell the sample was positioned diagonally across the cell. Since radial pressure gradients were found to be troublesome, the sample was later put on a constant radius in the cell, in the same way as in the belt cell in figure 5.IV. For these cells, however, the ratio between the sample radius and the radius of the sample loop was always larger than 30, and therefore the straight wire approximation should be much better in this case. All wires were brought out through the bottom of the cell as shown in figure 5.VI.

The samples were designed as before, but with some slight modifications. No third thermoelement for reflection corrections was used. The connections to the sample were the following, starting from the hot end (see figure 5.VII):  
1) A current lead for four-probe resistivity measurements.  
2) Heater.  
3) Two constantan wires, at the measuring points.  
4) At the cold end, one copper and one constantan wire.

---

Fig. 5.VII Sample for measurements at high pressure. For clarity the sample is drawn straight. For an explanation of numbers, see text.
The last connection made possible a measurement of the temperature at the cold end of the sample; since there were also differential thermoelements between this point and the measurement points, the temperatures at the latter could be measured. The cell further contained a calibration wire, which was positioned on the same radius and in the same horizontal plane as the sample to give an accurate indication of the true pressure.

When assembling a cell, the sample itself was assembled first. The Teflon cup was then placed on a flat table, and lead-out wires were introduced through holes in the bottom of the cup. The assembled sample and the calibration wire were then soldered to the lead-out wires. A suitable amount of epoxy resin was mixed carefully, by stirring from below in a special mixing tool, and heated to about 30 - 50°C. Stirring from below lessens the possibilities of introducing air bubbles in the epoxy, and by heating the mixture the viscosity is lowered, so that any gas bubbles present can escape. The epoxy was then poured into the Teflon cup. Since hot, liquid epoxy is clear and transparent before hardening, it was easy to check the cell for any air pockets around the sample. Any cavity in the cell arising from such a bubble will collapse under pressure creating unnecessary strains in the cell. Also, it is necessary for the validity of the theory of section 2.5.1 that heat losses are the same on all surfaces of the sample; clearly, this is not so if air pockets exist on the sample surface.

From the description above it is seen that all outgoing wires, both copper and constantan, have soldered joints at some point inside the cell. This has no effect on the measurement proper, since the temperature of the joints are constant and the measurements are carried out at a frequency \( \omega \). However, the accuracy of the measurements of absolute temperature might suffer. In all cases, however, the joints are between two wires of the same material and we should expect any effects of temperature or pressure gradients to be small. Also, the accuracy required is not very large (see section 5.4), since we are only interested in relative temperature changes under pressure. For these reasons it was considered that the soldered joints should have no adverse effects on the measurement accuracy.
In the measurements on copper, constantan wire 0.15 mm in diameter was used for thermocouple wires. When measurements on aluminium were first attempted, however, it was found that this wire sunk deeply into the soft sample during the welding procedure. To avoid excessive distortions in the sample, the constantan wire was therefore flattened by rolling to a thickness of about 0.1 mm before welding. This was found to be a very efficient way to prevent the constantan wire from sinking into the sample, and all measurements on aluminium, silver and gold were made using such constantan bands for thermocouples.

5.3 Pressure calibration

In order to find the pressure in the high pressure apparatus some kind of pressure calibration must be used. A convenient way of doing this is to use a material having an easily observed phase transition in the pressure range in question, and to use these phase transitions to obtain fixed points on a pressure scale for the experiment.

In the present experiments, pressure calibration has been effected by using the cerium α - γ transition at 0.75 GPa (Jayaraman, 1965) and the bismuth I-II transition at 2.55 GPa (Decker et al., 1972). Both these transitions give large, easily detected changes in the resistivity of the materials. The two metals were extruded together in the form a single coaxial wire (Alm et al., 1974) with bismuth as an outer protective sheath around the reactive cerium core. Bismuth is also very easily soldered, in contrast to cerium. As described in the last sections, the pressure calibration wire was always positioned so as to give a reliable reading of the pressure at the position of the sample. In the belt apparatus, six calibration runs were made on two cells containing two pressure calibration wires each, one of them replacing the sample. It was found that the difference in pressure between the two positions was 0.05 - 0.15 GPa, with the "sample" always having a lower pressure. The pressure scale was adjusted according to these findings. In the experiments on polymers described in appendix A a triple coaxial wire was used, containing also thallium which has a phase transition at 3.7 GPa (Decker et al., 1972).

The phase transitions were detected by measurements of the resistance
of the calibration wire. This resistance could be registered either as a function of time, using an Y-T recorder, or as a function of press load, using an X-Y recorder with a press load signal derived from a potentiometer attached to the press load indicator.

Since it was easy to obtain fixed points on the pressure scale, the main problem in pressure calibration was to obtain a reliable interpolation scale between these fixed points. The resistance of the manganin heater on the sample could, in principle, be used for this purpose (Decker et al., 1972). However, the resistance of the manganin wire was found not to be a linear function of pressure in a solid pressure transmitting medium, a fact which has been observed earlier by other workers (Kozuka and Yamamoto, 1974). For the belt apparatus, therefore, the interpolation curve of pressure versus press load was obtained by a simple graphical interpolation procedure. The errors in the pressure calibration, using this procedure, could probably amount to ± 0.2 GPa at points intermediate between the fixed points.

In the piston and cylinder apparatus it was found that pressure was a linear function of the applied load for increasing pressures, and an interpolation scale was easily made. The strain measured on the outside of the vessel was also used as an interpolation scale in some experiments. This strain was, however, also found to be a linear function of load.

On decreasing the load a large hysteresis in pressure was always observed. Also, the fixed points in this case were less accurately determined than for increasing load, due to hysteresis phenomena in the transitions. During most of the decrease, however, the strain on the outside of the vessel decreased linearly with load. This was taken to mean that the pressure also decreased in the same way. A calibration curve for decreasing pressures was constructed from these strain measurements. Fewer points, however, were always measured during a pressure decrease than during a pressure increase, due to the lower accuracy in pressure calibration in the former case.

In principle it would have been possible to construct a general pressure calibration curve for all piston and cylinder cells, since
The repeatability of the load/pressure points was very high. In fact, for identical pressure cells, and using the same pistons in all cases, the load necessary to find the bismuth transition in the 45 mm vessel was $457 \pm 1$ ton ($4.48 \pm 0.01$ MN). This corresponds to a repeatability of 0.2 %. The repeatability in the load necessary for the cerium transition was not as good as this, due to the sluggishness and temperature dependence of this transition. When the effect of temperature changes was allowed for, however, this transition had a repeatability of about 1 %.

The accuracy in the pressure calibration of the piston and cylinder apparatus can be estimated to be about 50 MPa for increasing pressures. For decreasing pressures, however, the calibration was less accurate. At pressures above 1 GPa the pressure might be in error by up to 0.1 - 0.2 GPa, depending on hysteresis phenomena. Below 1 GPa the error should be less than 0.1 GPa.

5.4 Corrections to measured values

The "raw" experimental data in the experiment sometimes contained errors. In several cases, however, the magnitude of the error was more or less well known, and the error could be corrected. Two correction procedures have already been described and will only be mentioned here: The correction factors for $q$ and $\phi$ used in the calculator program, and mentioned in section 3.5, and the reflection correction routine used in the belt experiments and described in section 2.7.1.

When the value of $\alpha$ had been found in an experiment under pressure, two further corrections were applied. The value of $\alpha$ was corrected for changes in temperature and for changes in the distance $\ell$ between the measurement points. The first of these corrections was small; the second was generally 20 - 40 % of the total observed effect, and in some cases in the belt apparatus even changed the sign of the pressure coefficient of $\alpha$.

For the temperature correction, the approximate temperature changes at the measurement points were measured. The temperature coefficient of $\alpha$ at atmospheric pressure, as given by Touloukian et al. (1973)
was then used to obtain a correction factor. This temperature coefficient should not change much with pressure, since the pressure coefficient of \( a \) is not expected to change much with temperature (see sections 8.4 and 9). Since temperature changes during an experiment rarely exceeded 10 K, this correction was small.

The second correction is more difficult to make. During a pressure run, using a solid pressure transmitting medium, there is inevitably some deformation of the sample. In all the methods developed in section 2, \( a \) is proportional to \( \ell^2 \). The measured values of \( a \) are therefore very sensitive to changes in sample dimensions. Fortunately, as long as the deformations are small and homogeneous over a certain distance, they can be corrected for by measuring the resistance of the sample and comparing the resistance value obtained to that obtained before the deformation. The procedure used to make such a correction has been described by Andersson and Bäckström (1976).

In the present case, the resistance of the sample was measured during the experiment by a four-probe technique. A stabilized AC current of typically 0.5 A at 70 Hz was passed through the sample via the reference thermoelement at the cold end and a special current lead at the heater end. The current was measured with a Data Technology digital multimeter. The voltage drop between the measurement points was measured with an Ithaco Dynatrac 391 lock-in voltmeter, using the thermocouples as potential leads. This voltage was typically about 100 \( \mu \)V, which is large enough to be easily measured.

The initial value of the sample resistance at room temperature and atmospheric pressure is known and pressure and temperature are measured. A theoretical value for the resistance at the measured \( P \) and \( T \) can then be calculated, using the known pressure and temperature coefficients of resistivity. From the ratio of the theoretical and experimental values thus found, the changes in \( \ell \) can be calculated.

Normally the correction was small, less than 0.1 %, up to about 1 GPa, but above this pressure the correction increased as plastic deformations of the pressure medium became more important. At 2.5 GPa the corrections in \( a \) was of the order of 1 to 5 %, which is about 10 to 40 % of the total effect observed. This correction was thus
very important. In most cases a small permanent change in resistance could be observed after each cycle. This is believed to be due to permanent plastic deformations of the sample, giving changes in sample dimensions. Some of these resistance changes, however, might be due to an increase in residual resistance of the sample because of cold-working of the material under pressure, especially in the annealed samples.

In principle, the change in $I$ under pressure could be calculated theoretically from a knowledge of the relative compressibilities of the Teflon cell wall and the Araldite pressure transmitting medium. The compressibility of the latter, however, is not well known, and since there is always an initial air gap between the walls of the pressure vessel and the pressure cell, the accuracy of such a calculation would not be sufficient. The measured variations of $I$ with pressure are, however, compatible with available compressibility data for Teflon (Bridgman, 1948) and typical epoxy resins (Munson and May, 1972; Warfield, 1968).

5.5 Experimental procedure

The experiments were carried out in the following way: After the pressure cell had been assembled and mounted in the high pressure apparatus a functional check was made and power was applied to the heater. When the temperature had stabilized a measurement of $a$ was made at atmospheric pressure. Load was then applied in steps and measurements were made at higher pressures. Usually the load steps were adjusted to give 10 – 15 measurement points between atmospheric pressure and the maximum pressure obtained, which of course varied between the different pressure vessels. To complete the pressure cycle the load was then decreased stepwise down to 10 – 30 tons. Larger steps were taken during the pressure decrease, since the pressure calibration in this case was less accurate.

The load was rarely decreased to zero after the first pressure cycle, since this in most cases caused the wires to break in the gaskets. A second pressure cycle was then made if the leads were still intact. Sometimes a third pressure cycle was possible, but this was not very common. Measurements were usually concluded during the second cycle when the gasket material had been extruded so much that heater or
thermocouple wires broke. Only in a couple of cases did breakage occur inside the cell, and in these cases it was probably the soldered or welded joints that broke. It was empirically found, for the 45 mm in diameter vessel, that limiting the first cycle maximum pressure to 2.0 GPa generally made possible a complete second cycle with a maximum pressure above 2.5 GPa. Trying to reach this pressure during the first cycle usually resulted either in broken leads at about 2.2 GPa during this cycle, or in a very restricted pressure range being attainable in the second cycle. Using nickel or alloy wires (usually Chromel or constantan) through the gaskets improved the situation, since these wires are mechanically stronger than copper wires.

At each load the temperature in the cell was first allowed to stabilize before any measurement was made. The temperature changes due to adiabatic heating were rather large due to the high compressibility of the pressure medium. When a steady state was obtained measurements were made. In most cases $\phi$ and $q$ were measured for two pairs of frequencies $\omega$. The periods $T = 2\pi/\omega$ commonly used were 8 and 2 s and 4.8 and 1.2 s. In this way it was possible to discover effects of reflected waves or pressure inhomogeneities which might otherwise have passed unnoticed. Using periods above 8 s increased the risk for reflections, since the attenuation of the wave diminished, and also lessened the accuracy in the measurement of $\phi$. For $T < 1$ s the signal amplitude was generally too low for accurate measurements to be possible. For each pair of measurements a value of $a$ was calculated as described in section 3.4. If a reflection correction was desired, the measurements were then repeated for a second set of thermocouples with a different spacing $\ell$.

When $a$ had been found the thermal diffusion analyzer was disconnected and the resistance of the sample was measured, as described in section 5.4. The approximate absolute temperatures at the measuring points were also measured. Finally, the resistance of the manganin heater was measured as was also the strain on the vessel, if a strain gauge was used. During pressure changes the resistivity of the calibration wire was monitored by a pen recorder. At the transitions both the applied load and the temperature were noted, since at least the cerium transition pressure is strongly dependent on temperature.

In most cases a final pressure calibration was made only after the
completion of the pressure runs, and all values of $a$ obtained were corrected, as described in section 5.4, in a separate calculation.

5.6 Error analysis

5.6.1 Absolute value of thermal diffusivity

All measurements on metals under pressure were performed using the most exact method developed (equation (2.15)). An exact, general error analysis of this equation is very difficult to make, since the expression for $a$ is a ratio between two factors, each consisting of the difference between two terms which are of the same order of magnitude.

Equation (2.15) can be divided into two parts and written as

$$a = \frac{\omega_2 \ell^2}{2} \cdot \frac{Q_2 - \omega_1/\omega_2}{Q_2 \phi_2 \ln q_2 - \phi_1 \ln q_1}$$  (2.15a)

The possible errors in the first part are easily evaluated. Since $\omega_2$ is known to within better than 10 ppm, the error is simply twice the possible error in $\ell$.

The second part of (2.15) is more difficult to evaluate. To obtain a realistic estimate of the random errors possible, the spread in the experimentally found values for $\phi$ and $q$ was studied for three high pressure runs on three different samples, one gold, one silver, and one aluminium. All samples were chosen to show a "typical" scatter in the data for $a$; in no case was the "best" sample for that particular metal chosen. The values for $\phi(P)$ and $q(P)$ for $T = 8$ and $2^s$ found in each experiment were plotted and fitted to 12 second degree polynomials in $P$. The deviations of the experimental points from these polynomials were then assumed to represent the random scatter in the measurements of $\phi$ and $q$. Of the 146 experimental points studied, only five deviated by more than 0.5% from the polynomials in $P$, and only nine deviated by more than 0.3%. Typically, the scatter was found to be less than 0.1%, and to be approximately the same for both $\phi$ and $q$.

The influence of the scatter in $\phi$ and $q$ on the measured value of $a$ was then determined. Typical values for $\phi$ and $q$ were obtained from the
experiment on silver studied earlier. These values were used to calculate \( \alpha \). The values of \( \phi \) and \( q \) were then changed by \( \pm 0.2 \% \), and new values of \( \alpha \) were found. All possible combinations of errors were tried. These calculations showed that errors of \( \pm 0.2 \% \) in \( q \) and \( \phi \) typically resulted in an error of about \( 0.7 \% \) in \( \alpha \). The maximum error obtained was \( 1.5 \% \).

Using these results it is possible to estimate the random error in a measurement of \( \alpha \) with the new method. From the figures given above, it is reasonable to expect the maximum error in \( \phi \) and \( q \) to be \( 0.3 \% \), and the typical error to be \( 0.1 \% \) or less. Assuming the error in \( \alpha \) to be linearly dependent on the errors in \( \phi \) and \( q \), this would mean that the maximum scatter in \( \alpha \) would be about \( \pm 2 \% \), and the typical random error should be approximately \( \pm 0.75 \% \). These figures are in good agreement with the actual scatter found in the experiments. This is not surprising, since the errors in \( \phi \) and \( q \) were estimated from the experimental results. It should be pointed out, however, that in many of the later high pressure experiments the scatter in the data was a factor 2 less than the values given above.

Since many measurements were made on each sample, systematic errors are much more important than random errors. Systematic errors can be introduced in many ways. An error in \( \ell \) clearly gives a systematic error in \( \alpha \) for a given sample; there might be systematic errors in the measurements of \( \phi \) and \( q \); or reflected heat waves might give rise to systematic errors. In most of the later samples \( \ell \) was chosen to be about 10 mm. This distance was accurately measured with a travelling microscope. Since each weld has a finite width, however, the actual position of each thermocouple might not be known to better than \( 0.1 \) mm. This would give a maximum error of \( 4 \% \) in \( \alpha \), while the probable error would be closer to \( 2 \% \).

Systematic errors in \( \phi \) and \( q \), if present, must necessarily be small. This is clear from the tests described in section 2.6, which showed that the modified Angström method always gave results that were in good agreement with accepted values. The results were furthermore independent of both \( \omega \) and \( R \), and also of the thermal properties of the medium, within the range tested. Since the experimental value of \( \alpha \) depends on \( \phi \cdot \ln q \), it could possibly be argued that a small constant
relative error in $\phi$ or $\ln q$ would not be detected in a measurement of $a(\omega)$. In view of the good agreement between measured values and literature values of $a$ such errors are improbable.

The influence of heat losses through thermocouples, and of reflected heat waves, on the measurements are more difficult to assess. Reflected heat waves are in most cases easily detected by measuring $a$ as a function of $\omega$ (see figure 2.X). Also, they can be eliminated by making the sample long enough. Heat losses through thermocouples proved to be quite important for thin samples in air, as shown in section 2.6. Also, the measured results for such samples were in many cases almost independent of $\omega$ (see figure 2.VII). This, however, is believed to be due to the combined effects of several mechanisms working in different directions; for other thin samples the measured values of $a$ were clearly dependent on $\omega$. As seen in figure 2.VIII, this effect disappeared when the sample was encased in Araldite, since heat losses from other parts of the sample surface were then increased to a similar level. Systematic errors from these mechanisms can not, however, always be completely ruled out.

In conclusion, it is believed that the error in the absolute value of $a$ measured by the present method is less than 3 %, if the experiment is carefully made. Of these 3 %, 2 % come from the possible error in $\ell$, while 1 % error is estimated to arise from reflected waves etc. The maximum error is estimated to be 6 %.

Measurements have in all cases been carried out on several samples of the same metal. The average value of $a$ was found for each sample from measurements at different values of $\omega$. These average values were then used to calculate a grand average over all samples of the same material. The error in this value is then given as either the mean deviation of the average results for each sample from the grand average, or as 3 %, whichever is greater.
5.6.2 Pressure dependence of the thermal diffusivity

In the measurements of the pressure dependence of \( \alpha \) the error in the absolute value is of little importance, as long as it is constant. As before, the random scatter in \( \alpha \) is also of minor importance, since many experimental points are obtained. The most important possible sources of error are therefore changes in \( \ell \), systematic errors in the measurements of \( \phi \) and \( q \), and errors arising from heat loss inhomogeneities and heat wave reflections.

Systematic errors in the measurements of \( \phi \) and \( q \) can probably be neglected, since the total change in these quantities under pressure is generally very small, less than 5% for \( \phi \) and about 15% for \( q \). Any systematic errors should therefore be approximately constant. The same is true for errors arising from heat losses through thermocouples. Heat wave reflections might be troublesome. However, the effect of such reflections depends through \( \gamma \) on the thermal properties of the pressure medium. This means that such effects vary with pressure. The variations have been found to be cyclical, and can thus easily be identified. A typical example of such an effect is shown in figure 7.II.

The most serious source of error in the determination of \( \partial \alpha / \partial P \) is the variation in \( \ell \) under pressure. As stated in section 5.4, such variations can be corrected for by a measurement of the resistance of the sample. However, this is true only for homogeneous distortions, and in a solid pressure medium all distortions are not always homogeneous. Systematic errors in \( \partial \alpha / \partial P \) can also be introduced through this correction by the use of incorrect pressure (or temperature) coefficients of the electrical conductivity \( \sigma \). Since both these coefficients are probably known to within 10%, the error introduced in this way should be small. There is, however, no way to estimate how large any inhomogeneous deformations of the sample might be, and this is thus the largest and most unpredictable source of error in \( \partial \alpha / \partial P \). It has sometimes been found that the absolute value of \( \alpha \) suddenly has changed by 1-2% in the pressure range where Araldite has been found to have a phase transition (see section 6). This is probably due to deformations of the sample; the correction factor, however, has mostly changed too little to compensate fully for this step change in \( \alpha \). In general, however, the pressure coefficients of \( \alpha \) found for different pressure cycles on the same sample
are in excellent agreement; this shows that if inhomogeneous distortions are present they have a very high repeatability.

For all metals investigated it has been found that the value of $\alpha a/\alpha P$ varies strongly between different samples. This has been attributed to inhomogeneous deformations of the samples under pressure. Since there is no way to estimate these, the error in the value of $\alpha a/\alpha P$ must be found in some other way. The procedure to find $\alpha a/\alpha P$ from the measurements has been as follows: The mean value of $\alpha a/\alpha P$ was first found for each sample, and the grand average over all samples was calculated. The results were weighted in such a way that pressure runs showing lower scatter in the data, or extending over a larger range in pressure, received a greater weight. This was achieved by simply including some results several times in the calculation. The mean deviation of the values from the individual runs from the grand average was then taken as a measure of the error. Since the deviations observed were appreciable, it was felt that any systematic errors would be too small to be significant, and were therefore neglected.
THERMAL PROPERTIES OF AN EPOXY RESIN

6.1 Experimental details

As indicated in section 2.5.2, the thermal diffusivity of a metal can be accurately determined from the simple equations (2.11a) or (2.11b), or from Eichhorns equation (2.8), if only the thermal properties of the pressure transmitting medium in the experiment are well enough known as functions of pressure. For this reason an attempt was made to measure these properties, using the "hot wire" measurement system described in section 2.9. These measurements were carried out in collaboration with Mr. Olov Sandberg, whose interest in Araldite arose from his work on the temperature and pressure dependence of the glass transition temperature $T_g$ for polymers.

The epoxy resin used was Araldite AW 106 with hardener HV 953 U, mixed in the proportions 1:1 by volume. This material is manufactured by CIBA-GEIGY, Switzerland. All samples were made from the same batch of epoxy resin as used for pressure transmitting medium, and the preparation of a sample closely followed the casting procedure described in section 5.2.2. All pressure experiments were carried out in the piston and cylinder type of apparatus. The pressure cells used were very similar to those used in the experiments on metals (figure 5.VI). The nickel wire probe was placed on a constant radius in the cell to minimize pressure gradients. Apart from the nickel wire probe, the cell contained only a Chromel-Alumel thermocouple, to measure temperature, and a pressure calibration wire. Pressure calibration was carried out as described in section 5.3. During measurements at atmospheric pressure the pressure cell was placed in an aluminium cylinder which could be heated electrically. In the high pressure experiments temperature variations were effected by heating the pressure vessel itself. The heating and cooling rates were about 15 K/hour.

6.2 Results

The results of the measurements are presented in figures 6.1 and 6.11. In the first experiments, $\lambda$ and $a$ were measured for six samples at room temperature and at pressures up to 2.5 GPa. The results for
one of these samples is shown in figure 6.1. The phase transition occurring at about 1.2 GPa was very accurately repeatable on pressure cycling this specimen. However, this transition was not seen in all samples. The existence of this transition might therefore possibly be very sensitive to the composition of the sample and the curing procedure. One other possible explanation is that we are observing a phase transition in one phase of an incompletely cured mixture. The

![Diagram](image-url)

Fig. 6.1 $\lambda(P)$ and $\alpha(P)$ for one Araldite sample. Circles denote $\lambda$ and squares $\alpha$; open symbols denote increasing $P$, filled symbols decreasing $P$. 
phenomenon has not, however, been investigated further.

The pressure dependence of $\lambda$ and $\alpha$ for Araldite was found to be well described by the polynomials

$$
\frac{\lambda(P)}{\lambda(0)} = 1 + 0.56 P - 0.07 P^2
$$

$$
\frac{\alpha(P)}{\alpha(0)} = 1 + 0.38 P - 0.07 P^2
$$

where $P$ is in GPa. These expressions are valid up to 2.5 GPa for those samples not showing any phase transitions. For those samples that undergo a transition, the same quantities above the transition are well described by the linear relations

$$
\lambda = (0.255 + 0.078 P) \text{ W m}^{-1}\text{K}^{-1}
$$

$$
\alpha = (1.53 \pm 0.44 P) \times 10^{-7} \text{ m}^2\text{s}^{-1}
$$

All numerical results in this section have been corrected for an error in the original calculations, as indicated in section 2.9. The figures given therefore do not coincide with those previously published (Sundqvist et al., 1977).

The results given in (6.1) for $\lambda$ are in good agreement with the results of Andersson and Bäckström (1973a) up to about 0.7 GPa, but above this pressure the discrepancy gradually becomes larger. At 2.5 GPa they found $\lambda(2.5)/\lambda(0) = 1.75$ while (6.1) gives 1.96. This discrepancy could possibly arise from differences in the curing procedures used, since their samples were always cured at 340 K. The difference could also be due to errors in their radial heat flow experiments, since these were carried out in a belt apparatus. Unknown variations in sample length and thermocouple distance under pressure could easily explain the differences between the results. Some part of this difference might, of course, be due to the error in the original hot wire method. It is improbable, however, that this error should depend so strongly on pressure as to explain the whole of the difference between the results.

The temperature variations of $\lambda$ and $\alpha$ were studied in a separate experiment. For samples produced by the procedure described earlier, $\lambda$ and $\alpha$ were found to be linear functions of $T$ in the range 275 - 350 K. In this
\[ \lambda(T) = (0.116 + 3.2 \times 10^{-4} T) \text{ W m}^{-1}\text{K}^{-1} \]
\[ \alpha(T) = (1.46 - 2.9 \times 10^{-3} T) \times 10^{-7} \text{ m}^2\text{s}^{-1} \]  

(6.2)

with \( T \) in K. These results have been recalculated from the original measurements using correction factors found by Sandberg (1978), who remeasured \( \lambda \) and \( \alpha \) for one Araldite sample at 300 K using a new, modified version of the "hot wire" system. Sandberg found the following results in his experiment: \( \lambda = (0.211 \pm 0.003) \text{ W m}^{-1}\text{K}^{-1} \) and \( \alpha = (1.37 \pm 0.09) \times 10^{-7} \text{ m}^2\text{s}^{-1} \). The errors given correspond approximately to the error limits found previously, since the new method should be at least as accurate as the old method. From the results above, \( \rho c_p \) can be calculated to be \( \rho c_p = 1.54 \times 10^6 \text{ J m}^{-3}\text{K}^{-1} \). Since \( \rho = 1.06 \times 10^3 \text{ kg m}^{-3} \), according to the manufacturer, it is found that \( c_p = 1.45 \text{ kJ kg}^{-1}\text{K}^{-1} \).

Curing the specimen at higher temperatures was found to limit the applicability of equations (6.2) to temperatures below 325 K. Figure 6.II shows the temperature dependence of \( \lambda \) found for one sample (A) cured at 440 K (triangles). Above 350 K, the difference in thermal expansion coefficients between sample and probe wire caused a loss of thermal contact, and the results here were discarded. To increase the temperature range, pressure was applied. A new sample (B) was used for measurements of \( \lambda \) and \( \alpha \) in the temperature range 300 - 450 K at pressures of 0.11 GPa and 0.27 GPa. These results are also shown in figure 6.II. From these measurements the temperature dependence of the pressure coefficient of \( \lambda \) could be calculated, and this is also shown. In going through the glass transition the pressure coefficient changed by a factor of about 1.75. Below the glass transition, the pressure coefficient obtained in this experiment agreed well with that given by equation (6.1) (shown as a point in figure 6.II). The absolute value of \( \lambda \) for sample B, as extrapolated to atmospheric pressure, is in very good agreement with that for sample A.

The glass transition temperature \( T_g \) was found to have a pressure dependence \( T_g(P) = (322 + 1.4 \times 10^2 P) \text{ K} \). \( T_g \) at atmospheric pressure was also determined by a dilatometric method, with the result \( T_g = 321 \text{ K} \). These results are in good agreement with the value \( T_g = 323 \text{ K} \) obtained from sound velocity measurements (Krishnamurty et al., 1973).
Fig. 6.11 Below: $\lambda(T)$ for Araldite. Triangles: Sample A at atmospheric pressure. Circles: Sample B at 0.11 GPa. Squares: Sample B at 0.27 GPa. Filled symbols denote decreasing $T$, open increasing $T$. The dashed line shows $\lambda$ for sample B as extrapolated to atmospheric pressure.

Above: $[\lambda(0)]^{-1} \partial \lambda / \partial P$ for sample B. The point denotes the value given by equation (6.1).
The positive pressure coefficient obtained for $T_g$ shows that the phase transition observed earlier could not be the glass transition.

In the present work, the main interest in these measurements lies in the measured values of $\lambda$ and $a$ and their possible application as an aid in the measurement of $a$ for metals. The rest of this chapter will therefore be devoted to this application.

6.3 Calculation of heat loss coefficients for a metal sample.

The measured values of $a$ and $\lambda$ for Araldite were used in an attempt to measure $a$ for copper under pressure, using some of the simplified methods developed in section 2.5.2. (For the rest of this section the thermal properties of the Araldite will be denoted by subscript $m$, to avoid confusion.)

The first attempts were made using equations (2.11a) and (2.11b). The second of these equations is, in principle, similar to (2.8), only more exact. It should also be more exact than (2.11a), since it contains $\gamma_1 \gamma_2$ instead of $(\gamma_2^2 - \gamma_1^2)$; also, $\mu_2^2$ is here only a correction to be added to $\omega$. The heat loss coefficients $\mu_2$ and $\mu_1$ were calculated from equation (2.9), using the original data for $\lambda_m$ and $a_m$ given by Sundqvist et al. (1977). These heat loss coefficients were then used together with experimental values of $\phi$ and $q$ to calculate $a$ as a function of pressure. The results from this calculation are shown in figure 6.III, together with the corresponding results found using equation (2.15).

As expected, the agreement with (2.15) is better using (2.11b) than using (2.11a), but in neither case is the agreement acceptable. The pressure coefficient, for instance, is in both cases larger by a factor of two than that found using equation (2.15). It could be expected that using the new corrected values for $\lambda_m$ and $a_m$ might improve the agreement. This was tried, but the results obtained were in no better agreement with (2.15) than those shown. The absolute value of $a$ decreased by about 5%, and the pressure coefficient, in the case of $\mu_1$, increased slightly.

A second approach was then tried, in that equation (2.15) was still used but $Q_2$ was calculated theoretically from the measured $a_m$. $Q_2$ is a function of $\eta_2 = R(\omega_2 / a_m)^{1/2}$. This function is similar to the function
Fig. 6.III  Thermal diffusivity for one copper sample as a function of pressure. Dashed line: Measured using equation (2.15). Dots: Measured using (2.11b). Squares: Measured using (2.11a).

Fig. 6.IV  $Q_2$ as a function of $P$ for a typical copper sample. The dashed line was calculated using experimental values for $\lambda_p$ and $\alpha_p$, while the dots indicate values of $Q_2$ found in an actual experiment on copper.
$Q_1 = Q_1(n_2)$ shown in Figure 2.XI. An error in $a_m$ then gives only a small error in $n$; furthermore, $Q_2$ is almost independent of $n_2$ over a large range in $n_2$. It should thus be possible to calculate $Q_2$ quite accurately as a function of pressure. Figure 6.IV shows a comparison between the theoretical $Q_2$ calculated for a copper sample and the corresponding values of $Q_2$ obtained in an actual experiment. The agreement is very good. It should be pointed out that the agreement becomes neither much better nor much worse if the new, corrected values for $a_m$ are used. In fact, for this specific experiment, a change in $a_m$ of 40% will give a change in $Q_2$ of less than 0.5%.

The results for $a$ for several copper specimens were recalculated, using theoretical values for $Q_2$. No significant changes in either absolute value or pressure coefficient of $a$ was found relative to the previous values using equation (2.15) and the experimental $Q_2$, and the scatter in the data was approximately the same for both methods. Since the use of a theoretical $Q_2$ was not any large simplification of the experiments, no further use was made of any of these methods. Also, since the thermal properties of Araldite were not always well defined at high pressure, due to the phase transition sometimes occurring, it was felt that using theoretical values for $u$ or $Q_2$ might introduce an unnecessary source of possible systematic errors.
7 THERMAL CONDUCTIVITY OF METALS: EXPERIMENTAL RESULTS

7.1 Copper

7.1.1 Commercial copper wire

Copper was chosen as the first metal to be investigated, since the thermal properties of this metal were believed to be well known. The measurements would thus also serve as a check on the accuracy of the method and of the instrumentation. The results of the preliminary measurements at atmospheric pressure, using the Ångström method and the new modified methods, have been described earlier in section 2.4 and section 2.6, respectively. In these investigations ordinary commercial copper wire was used, with wire diameters ranging from 0.5 to 3 mm. The purity of these wires was unknown.

The same material was then used for measurements under pressure. The first measurements were made using the "belt" type of apparatus. As mentioned in section 5.2.1, several different geometrical arrangements of the sample in the pressure cell were tried. The final arrangement chosen was that shown in figure 5.IV.

The results obtained in these experiments were rather uncertain, however. The scatter of the individual data points from the mean during a single pressure cycle could amount to ±10%, and the pressure coefficient of a varied strongly even between different pressure runs on the same specimen. The values of the "raw" pressure coefficient of a varied between \(-4 \times 10^{-2}\) GPa\(^{-1}\) and \(+6 \times 10^{-2}\) GPa\(^{-1}\). Application of the correction for length changes, described in section 5.4, and the elimination of reflected waves by the method described in section 2.7.1 almost always resulted in a final positive value for the pressure coefficient of a. This gave rise to some doubts on the validity of the method, since the only results known to us at that stage were those of Bridgman (1922) and Averkin et al. (1972), both of which obtained negative pressure coefficients. It was found, however, that in most cases the corrections worked in such a direction as to shift the pressure coefficient of a towards the average value over all samples. This was taken to mean that the corrections were probably working correctly. A total of 11 samples were used in the belt apparatus. Several of these, however, broke during the first pressure cycle, or gave results that had to be discarded. Also,
since distortions of the samples were largest during the first pressure cycle for each sample, all data from these runs were discarded. Consequently, only the results from six runs on the eleven samples were considered in the final calculation of \( \frac{\partial a}{\partial P} \). A typical result from a run in the belt apparatus is shown in figure 7.1. The large scatter in the data is obvious. The dashed line has been fitted by the method of least squares.

In view of the large difficulties found in making measurements in the belt apparatus, with its large internal pressure gradients, other types of high pressure apparatus were then tried. A 20 mm in diameter piston and cylinder vessel was available, and it was first decided to try using this in an experiment. The pressure cell used was described in section 5.2.2. A 50 mm long copper sample, 0.7 mm in diameter, was mounted vertically in the cell. The lower part of the cell was filled with Teflon powder up to the level of the heater, to minimize convection. The experiment was not very successful. In the only

![Graph](image)

**Fig. 7.1** Thermal diffusivity versus pressure for one copper sample in the belt apparatus.
relatively successful run the influence of convection was very apparent, and the value of \( \alpha \) measured at atmospheric pressure was a factor of 5 too large. The situation improved as the pressure increased, and at about 0.3 GPa the value of \( \alpha \) obtained corresponded very well to the normal value of \( \alpha \) at atmospheric pressure. Above this pressure \( \alpha \) was found to be approximately constant, within the experimental error. Due to leakage the maximum pressure obtained was about 1 GPa; however, no measurements could be done above 0.8 GPa since the thermocouple wires broke, probably because of failure of the Al 0. tube in the bottom seal.

The same vessel, with a similar pressure cell, was used in an attempt to measure \( \lambda \) directly by a static radial heat flow method, similar to that used by Bridgman (1922) for measurements on lead and tin. Unfortunately, this experiment was also unsuccessful. No usable data were obtained. At atmospheric pressure convection was heavy and no accurate value of \( \lambda \) could be obtained. No heating was applied during pressurizing, to avoid unnecessary heating of the pressure calibration wire, and before heating was applied again the pressure run was terminated by catastrophic failure of the bottom seal.

Finally, two commercial copper samples were measured in the 1.0 GPa, 70 mm in diameter piston-cylinder apparatus. The first of these samples was simply placed between two solid plates of silver chloride, sandwiched between Teflon plates in the cylinder. The silver chloride plates served as a semi-hydrostatic pressure medium when load was applied. These plates were made by compressing silver chloride pulver at 0.3 GPa in a simple cylinder. Unfortunately this material is sensitive to light. When the salt is exposed to daylight it changes colour from white to dark red, and the electrical conductivity increases, probably due to precipitation of metallic silver. Thus, as the pressure increased, electrical contact was established between the sample and the heater and further measurements were made impossible.

The second sample was placed diagonally across a Teflon cell similar to that shown in figure 5.VI. This run was quite successful, and the results are shown in figure 7.II. The slight oscillations of the data points about the straight line obtained by a least squares analysis are probably effects of the finite length of the sample, giving rise to reflections of the heat wave. The damping of the wave depends on the thermal properties
Fig. 7.11 Thermal diffusivity versus pressure for one copper sample in the piston-cylinder apparatus. Triangles: $T = 2$ and 8 s. Circles: $T = 1.2$ and 4.8 s.

of the pressure transmitting medium. Thus, as the pressure increases, the interference effects vary and give rise to this cyclical effect. It should be noted that different wavelengths, that is, different values of $T$, give different pressure periods of the oscillations in $a$.

The accuracy of the pressure dependence of $a$ obtained from these experiments is not very high. To find the most probable value, the results from pressure runs where the sample had suffered heavy distortions, or where the results differed very much from the average result of all the other runs, were first discarded. The average value for $\frac{\partial a}{\partial P}$ was then obtained by the procedure described in section 5.6.2. The result obtained in this way was $[a(0)]^{-1} \frac{\partial a}{\partial P} = (2.2 \pm 0.6) \cdot 10^{-2}$ GPa$^{-1}$, where the error given is the mean deviation of the results for the individual samples from the grand average over all samples. This result was obtained from runs in the belt apparatus only. However, the result is in excellent agreement with the value $2.1 \times 10^{-2}$ GPa$^{-1}$ found for the run in the piston-cylinder apparatus.

From the results for $a(P)$ given above the pressure dependence of $\lambda = \frac{a \rho c}{P}$ can be calculated. The pressure dependence of $\rho$ for copper
has been measured by Vaidya and Kennedy (1970), and the pressure dependence of $c_p$ has been measured by Bastide and Loriers-Susse (1975). Using values for $\rho(P)$ and $c_p(P)$ given by these workers the pressure dependence of $\lambda$ was calculated to be $|\lambda(0)|^{-1} \partial \lambda / \partial P = (2.6 \pm 0.6) \times 10^{-2} \text{GPa}^{-1}$. The errors in $\rho(P)$ and $c_p(P)$ can be assumed to be negligible. The accuracy in the pressure coefficient of $\lambda$ is obviously quite low. However, since the material used was of unknown purity, the exact value obtained for $\partial \lambda / \partial P$ was not really considered very important. The physical interpretation of the results would in any case be somewhat uncertain. The important things found in these measurements were instead the following:

1) The method used was working as intended. All problems occurring originated in the high pressure technology, not in the measuring system.

2) While the actual value of $\partial \lambda / \partial P$ was rather uncertain, there was no doubt that $\partial \lambda / \partial P$ was actually positive, as found also by Starr (1938), and not negative, as found by Bridgman (1922) and Averkin et al. (1972).

3) The value found for $\partial \lambda / \partial P$ was reasonably close to the pressure coefficient of resistivity. This was reasonable, since the Wiedemann-Franz law should be fairly well obeyed by copper at this temperature.

To obtain physically more interesting results, measurements were then initiated on copper samples of higher purity.

7.1.2 High purity copper

Pure copper was obtained in the form of "ultra pure" wire, 0.76 mm (0.030") in diameter, from the RESEARCH Organic/Inorganic Chemical Corp., Sun Valley, California. The purity of this copper wire was stated to be 99.999 + %. No analysis of the material has been made. Measurements have been made both on annealed samples and on samples in the "as received" condition. The latter samples had been appreciably cold worked in the drawing process.

All annealed samples were bent to their desired shape prior to annealing to avoid unnecessary coldworking afterwards. To preserve the purity of the materials no welding was performed on the specimens until after the anneal. Annealing was done in air at about 0.1 torr at different tempe-
ratures, ranging from 1 hour at 1100 K to 5 hours at 800 K. The anneal was made in air to minimize further the impurity contents of the material. As is well known, an air anneal can improve the residual resistance ratio $\sigma(4 \text{ K})/\sigma(300 \text{ K})$ by about a factor of ten (Fickett, 1974) for the noble metals. This improvement is probably brought about by oxidation of magnetic impurities. The metal oxides formed are precipitated as macroscopic particles in the noble metal matrix (Yaeli and Lipson, 1976). The relatively large and few oxide particles scatter electrons much less efficiently than the many original magnetic ions, and thus both thermal and electrical conductivities at low temperatures are increased by this treatment.

After annealing the grain sizes in the samples were in the range 0.1 to 0.2 mm, measured by the intercept method. No difference in grain size were found between samples, subjected to pressure runs in the cylinder apparatus, and control samples cut from the same wire and annealed at the same time, but kept at atmospheric pressure. Some cold working, however, was observed in micrographs of annealed samples directly under the welds, where the metal was deformed during welding, but the amount was very small.

Six attempts were first made to measure $\alpha$ in the belt apparatus, using the pressure cells described earlier. All results from these runs were discarded due to the large scatter in the data. The distortions of the samples were quite large, probably due to the softness of the very pure material. Seven samples were then measured in the piston-cylinder apparatus. In three cases the 70 mm in diameter vessel was used and in four the 2.5 GPa 45 mm in diameter cylinder. One sample from each group was unannealed. The pressure coefficients of these did not significantly differ from those of the others. Only one pressure run was made on each sample, and a typical run is shown in figure 7.III. An average pressure coefficient of $\alpha$ was obtained for each sample, and a weighted average over all samples was then calculated as described in section 5.6.2. The pressure coefficient of $\alpha$ obtained in this way was $[\alpha(0)]^{-1} \partial \alpha / \partial P = (2.7 \pm 0.6) \times 10^{-2} \text{ GPa}^{-1}$. The error given is the mean deviation in the weighted data. All measurements were made at $T = 310 \text{ K}$. The absolute value of $\alpha$ found at atmospheric pressure at this temperature was $\alpha = (1.17 \pm 0.03) \text{ cm}^2/\text{s}$. This value is in excellent agreement with the value $\alpha = (1.17 \pm 0.05) \text{ cm}^2/\text{s}$ recommended by Touloukian et al. (1973).
The values for the electrical conductivity \( \sigma(T) \) necessary for the length correction were taken from Moore et al. (1967), while \( \sigma(P) \) was taken from Bridgman (1938).

To compute the pressure coefficient of \( \lambda \) values of \( \rho(P) \) from Vaidya and Kennedy (1970) and \( c_p(P) \) from Bastide and Loriers-Susse (1975) were used. The pressure coefficient of \( \lambda \) was found to be \( |\lambda(0)|^{-1} \frac{\partial \lambda}{\partial P} = (3.1 \pm 0.6) \times 10^{-2} \text{ GPa}^{-1} \). Once again errors in \( \rho(P) \) and \( c_p(P) \) are assumed to be negligible, since the pressure dependencies of these quantities are much less than that of \( \alpha \).

As mentioned earlier in section 1, the pressure coefficient of \( \lambda \) for copper has been measured previously by several workers, with widely differing results. Lussana (1918) found the coefficient to be positive and to have the value \( |\lambda(0)|^{-1} \frac{\partial \lambda}{\partial P} = 1 \times 10^{-2} \text{ GPa}^{-1} \), while Bridgman (1922) found a negative coefficient \( |\lambda(0)|^{-1} \frac{\partial \lambda}{\partial P} = -7.5 \times 10^{-2} \text{ GPa}^{-1} \). Bridgman's results were later criticized by Starr (1938), who remeasured \( \frac{\partial \lambda}{\partial P} \) (in Bridgman's laboratory) and found instead \( |\lambda(0)|^{-1} \frac{\partial \lambda}{\partial P} = 2.9 \times 10^{-2} \text{ GPa}^{-1} \), which is in good agreement with the present results. Quite recently, however, Averkin et al. (1972) found the result
\[ \lambda(0)^{-1} \frac{\partial \lambda}{\partial P} = -6.4 \cdot 10^{-2} \text{ GPa}^{-1}, \]
which would thus seem to support Bridgman's results. All of these workers have used similar methods, namely variations of the longitudinal heat flow technique with the sample surrounded by a liquid medium (see section 2.1). As shown by Starr (1938), this technique is very difficult to apply correctly, since heat losses by convection are very strong. It seems likely that the results by Lussana, Bridgman, and Averkin et al. are all troubled by heat convection problems. Starr, however, paid special attention to the convection problem and demonstrated in a convincing way that convection losses could be eliminated, and that this elimination always resulted in positive pressure coefficients for \( \lambda \) for the noble metals.

### 7.2 Silver

When the measurements on copper were completed, the two other noble metals gold and silver were an obvious choice of materials for further experiments. Pure silver was obtained from Koch-Light Laboratories Ltd, Colnbrook, England in the form of wire, 1.0 mm in diameter. The purity of this wire was stated as 99.998 %. This figure, however, only indicates that the wire was originally drawn from an ingot containing typically 0.002 % metallic impurities. No chemical analysis has been made on the material, and the actual purity is thus only known to be less than 99.998 %. The purity should be rather high, however, since the residual resistance ratios of two typical unannealed wire samples, "as received", after three pressure runs and after some rather heavy coldworking during the assembly and disassembly of the pressure cells were measured to be 140 and 210, respectively.

In all, seven silver samples were used and a total of fourteen successful runs were made. Only one sample was annealed. The anneal was carried out for two hours at 1000 K in air at 0.1 torr. The pressure coefficient for this sample was almost exactly equal to the average pressure coefficient for all other samples. Therefore, no more annealed samples were used, since their extreme softness made welding of thermocouples and assembly of the pressure cell difficult. For most of the silver samples, the 0.15 mm constantan thermocouple wire used was flattened by rolling prior to welding, as described in section 5.2.2. All experiments on silver were done in the 45 mm in diameter vessel. The values for the electrical conductivity \( \sigma(T) \) necessary for the length correction
were taken from Matsumura and Laubitz (1970) while $\sigma(P)$ was taken from Bridgman (1938).

All measurements were done at $T = 315$ K. At this temperature the average absolute value of $\alpha$ was $\alpha = (1.75 \pm 0.05)$ cm$^2$/s for the unannealed samples. The error given is the mean deviation of the individual results from the mean value. For the annealed sample $\alpha = (1.81 \pm 0.06)$ cm$^2$/s. The values found are in good agreement with the value $\alpha = (1.73 \pm 0.07)$ cm$^2$/s recommended by Touloukian et al. (1973).

A typical pressure run is shown in figure 7.IV. The maximum pressure in the individual runs varied from 2.2 to 2.5 GPa, except for two attempts to make a third pressure run on the same specimen, when the bottom seal in both cases failed at about 1.7 GPa. Due to the fairly small deformations observed for the silver samples the results for $\alpha$ obtained for different pressure runs on the same sample generally agreed to within 0.5%. However, the spread in pressure coefficients between different samples was rather large. Taking the weighted average, as before, the mean pressure coefficient is obtained as $[\alpha(0)]^{-1} \partial \alpha/\partial P = (3.6 \pm 0.8) \times 10^{-2}$ GPa$^{-1}$.

To find the pressure coefficient of $\lambda, \rho(P)$ and $c_p(P)$ must first be found. The density as a function of pressure is given by Vaidya and Kennedy (1970). The pressure dependence of $c_p$, however, has never been measured for silver. We can calculate this pressure dependence from the thermodynamic relation (Rodionov, 1967)

$$\left(\frac{\partial c_p}{\partial P}\right)_T = - T \cdot v \left[\alpha^2 + \frac{\partial \alpha}{\partial T}\right] \quad (7.1)$$

In this expression $v$ is the specific volume and $\alpha$ is the volume expansion coefficient. Equation (7.1) gives fairly accurate results in the case of copper; using values of $\alpha$ given by Hahn (1970) we obtain in this case a theoretical value $[c_p(0)]^{-1} \partial c_p/\partial P = - 3.3 \times 10^{-3}$ GPa$^{-1}$. The more recent measurements of $\alpha$ by Kroeger and Swenson (1977) instead give $[c_p(0)]^{-1} \partial c_p/\partial P = - 2.9 \times 10^{-3}$ GPa$^{-1}$. Experimentally, the pressure coefficient of $c_p$ for copper was found by Loriers-Susse et al. (1973) to be $- 2.8 \times 10^{-3}$ GPa$^{-1}$. This figure was later corrected by Bastide and Loriers-Susse (1975) to $- 3.4 \times 10^{-3}$ GPa$^{-1}$. The good agreement between theory and experiment is obvious. We would then also expect equation
Fig. 7.IV Thermal diffusivity under pressure for a typical silver sample.
Circles: First pressure cycle. Squares: Second pressure cycle.
Open symbols denote increasing pressure, filled decreasing pressure.

(7.1) to give a similarly good accuracy in the case of silver. Using values of \( a \) given by Simmons (1970) we find for silver \( \frac{c_p(0)}{c_p'} \frac{\partial c_p}{\partial P} = -4.4 \times 10^{-3} \text{ GPa}^{-1} \). The accuracy should be about 5 - 10 %, which is satisfactory since the pressure coefficient of \( a \) is much larger than that of \( c_p' \). Using the value for the pressure coefficient of \( c_p' \) found above, the pressure coefficient of \( \lambda \) is found to be \( \frac{\lambda(0)}{\lambda'} \frac{\partial \lambda}{\partial P} = (4.0 \pm 0.8) \times 10^{-2} \text{ GPa}^{-1} \).

This pressure coefficient has also been measured previously. Bridgman (1922) found the negative coefficient \( \frac{\lambda(0)}{\lambda'} \frac{\partial \lambda}{\partial P} = -3.6 \times 10^{-2} \text{ GPa}^{-1} \), while Starr (1938) found \( \frac{\lambda(0)}{\lambda'} \frac{\partial \lambda}{\partial P} = 4.4 \times 10^{-2} \text{ GPa}^{-1} \), in good agreement with the present result.

7.3 Gold

Gold samples were obtained from Koch-Light Laboratories Ltd, Colnbrook, England. The material was in the form of wire, 1.0 mm in diameter, with a stated purity of 99.999 %. As in the case of silver this figure refers
only to metallic impurities in the ingot from which the wire was drawn. As in the previous cases, experiments were done both on samples "as received" and on annealed samples. The anneal was carried out at 1000 K for four hours, in air at 0.1 torr. The annealed samples were very soft and were handled with great care. As in the case of silver, constantan bands were used as thermocouples to avoid excessive distortions of the sample during the welding process. All pressure experiments were made using the 45 mm in diameter piston-cylinder apparatus. The values of the electrical conductivity $\sigma(T)$ necessary for the length correction were taken from Cook and van der Meer (1970) while $\sigma(P)$ was taken from Bridgman (1938).

Measurements of $\alpha$ were made on five samples, two of which were annealed. No significant difference in pressure coefficient was found between annealed and unannealed samples. The absolute values of $\alpha$ found at atmospheric pressure and at $T = 315$ K were $\alpha = (1.30 \pm 0.04) \text{ cm}^2/\text{s}$ for the unannealed samples and $\alpha = (1.33 \pm 0.04) \text{ cm}^2/\text{s}$ for the annealed ones. These values are in good agreement with the value $\alpha = (1.28 \pm 0.06) \text{ cm}^2/\text{s}$ recommended by Touloukian et al. (1973). The agreement between the pressure coefficients found for different samples was good, and the agreement between the results for different runs on the same sample was excellent, in general better than 0.5 % at 2.5 GPa. A total of ten runs were made, and a typical result is shown in figure 7.V. Weighting the results from the different samples in the same way as before the average pressure coefficient of $\alpha$ was found to be $[\alpha(0)]^{-1} \frac{\partial \alpha}{\partial P} = (3.5 \pm 0.6) \times 10^{-2} \text{ GPa}^{-1}$.

As before, the values of $\rho(P)$ can be taken from Vaidya and Kennedy (1970). The pressure dependence of $c_p$ must once again be calculated from equation (7.1). Using values of $\alpha$ given by Simmons (1970), we obtain $[c_p(0)]^{-1} \frac{\partial c_p}{\partial P} = -2.5 \times 10^{-3} \text{ GPa}^{-1}$. The pressure coefficient of $\lambda$ is then found to be $[\lambda(0)]^{-1} \frac{\partial \lambda}{\partial P} = (3.9 \pm 0.6) \times 10^{-2} \text{ GPa}^{-1}$. This value is equal to that found by Starr (1938) for a sample of commercially pure gold. No other measured values exist for $\lambda$ under pressure for this metal.
7.4 Aluminium

7.4.1 Thermal conductivity at high pressure

Aluminium was chosen as a suitable material for further experiments for several reasons. It is easily obtainable in high purity and also in wire form. Although it is a trivalent metal with a large Fermi radius, the Fermi surface is to a good approximation spherical and free-electron-like. (Segall, 1961). Aluminium is, in fact, much more free-electron-like than the monovalent noble metals with their complicated Fermi surfaces. Also, it is one of the few metals for which $c_p$ is experimentally known under pressure (Bastide and Loriers-Susse, 1975). Finally, it has a rather large compressibility and one should therefore expect to find a large and easily measureable pressure coefficient of $\alpha$, and thus also of $\lambda$. Aluminium was, in fact, the second metal to be investigated in this work. The experimental results for gold and silver have been presented earlier, however, since it is logical to discuss all the noble metals together.
High purity aluminium wire, 1.0 mm in diameter, was obtained from Alfa Europe Products, Ventron Corp., Rotterdam, the Netherlands. The purity was specified as 99.999%; the same reservations apply to this figure as it did in the cases of gold and silver. As for the other metals measurements were made on both annealed and unannealed samples. Annealing was carried out for two hours at 600 K, in air at 0.1 torr. Due to the softness of the material, especially in the annealed samples, the thermocouples consisted of thin constantan bands in the same way as for gold and silver. The values of the electrical conductivity $\sigma(T)$ for the length correction were taken from Smithells (1976) while data for $\sigma(P)$ were taken from Bridgman (1951).

All pressure measurements were carried out in the 45 mm in diameter cylinder. Ten successful pressure runs were made on six different samples, four of which were annealed. No significant difference was found between the pressure coefficients of annealed and unannealed samples. All measurements were made at about 315 K. At atmospheric pressure the absolute value of $\alpha$ was found to be $\alpha = (0.97 \pm 0.03) \text{ cm}^2/\text{s}$ for the annealed samples and $\alpha = (0.95 \pm 0.03) \text{ cm}^2/\text{s}$ for the unannealed ones. Again, the results obtained are in excellent agreement with the value $\alpha = (0.96 \pm 0.04) \text{ cm}^2/\text{s}$ recommended by Touloukian et al. (1973).

Figure 7.VI shows a typical result for a pressure run on an annealed sample. In the case of aluminium it was in most cases evident that the function $\alpha(P)$ was not a straight line. Thus, for those samples where the scatter in the data warranted this, a second degree polynomial was used to describe the results. Weighting the results in the usual way, the results found for $\alpha(P)$ were $\alpha(1)/\alpha(0) = 1.047 \pm 0.005$ and $\alpha(2.5)/\alpha(0) = 1.104 \pm 0.015$, with $P$ in GPa. The initial pressure coefficient can to a good approximation be taken as $[\alpha(0)]^{-1} \frac{\alpha}{\partial P} = 4.7 \times 10^{-2}$ GPa, since the function $\alpha(P)$ was found to be practically linear up to about 1.2 or 1.5 GPa.

The value of $\rho(P)$ was taken from Vaidya and Kennedy (1970). The function $c_P(P)$ has been measured by Bastide and Loriers-Susse (1975). Using their results we obtain for the thermal conductivity as a function of pressure $\lambda(1)/\lambda(0) = 1.041$ and $\lambda(2.5)/\lambda(0) = 1.092$. However, the initial pressure coefficient $[c_p(0)]^{-1} \frac{c_p}{\partial P}$ found by Bastide and Loriers-Susse was $-1.8 \times 10^{-2}$ GPa$^{-1}$, which is quite large. Using instead equation (7.1)
and values of $\alpha$ from Kroeger and Swenson (1977), the coefficient is found to be $[c_p(0)]^{-1} \frac{\partial c_p}{\partial P} = -8.8 \times 10^{-3} \text{ GPa}^{-1}$, which is less than one half of the value experimentally found. Using values of $\alpha$ given by Simmons (1970) we obtain $-8.4 \times 10^{-3} \text{ GPa}^{-1}$, which is still less. In view of the good agreement between theory and experiment for copper, this discrepancy is surprisingly large. Using the theoretical value $-8.8 \times 10^{-3} \text{ GPa}^{-1}$ for the initial pressure coefficient of the specific heat, the pressure coefficient of $\lambda$ is found to be $[\lambda(0)]^{-1} \frac{\partial \lambda}{\partial P} = 5.0 \times 10^{-2} \text{ GPa}^{-1}$, which is significantly larger than the value $4.1 \times 10^{-2} \text{ GPa}^{-1}$ found using the experimental results of Bastide and Loriers-Susse.

The only known previous attempt to measure the pressure coefficient of $\lambda$ for aluminium was made by Lussana (1918). He found $[\lambda(0)]^{-1} \frac{\partial \lambda}{\partial P} = 8.5 \times 10^{-2} \text{ GPa}^{-1}$, which is of the same order of magnitude as the present result.

7.4.2 Thermal conductivity at low temperature

Aluminium is one of the few normal metals for which a minimum in $\lambda$ has been reported to occur at intermediate temperatures (Powell, 1969; see also section 8). Since the material used in the present experiments
was very pure, it was decided to investigate the temperature dependence
of $\lambda$ from 80 K to 350 K to see if it was possible to verify this be-

haviour. The very simple low temperature apparatus described in section
5.1.2 was therefore constructed.

In this measurement an unannealed piece of high purity aluminium wire,
from the same batch as used in the high pressure experiments, was used.
The original Angström method was used to measure $a$, since this method
is quick and accurate. From the measured $a$, $\lambda$ was calculated using
smoothed values of $c_p(T)$ from Giauque and Meads (1941). The density
$\rho$ was taken as $\rho = 2698$ kg m$^{-3}$ at 300 K (Hestermans and Volk, 1966).
The distance $l$ in this experiment was 7.75 mm, and values of $T$ between
1.4 and 8 s were used. The main source of error in these measurements
lies probably in the temperature measurements. The absolute temperature
was not measured at the points of measurement, but only at the hot and
cold ends of the sample. The differential aluminium-constantan elements
on the sample then gave the temperatures at the measuring points. For
this reason it is possible that the temperature measurements might be
in error by as much as 2 K at low temperatures.

The results found for $a(T)$ are shown in table 7.1. Values of $\lambda$ cal-
culated from these results are shown in figure 7.VII and table 7.1.
All data given have been corrected for thermal expansion. The thermal
diffusivity found at 300 K is about 3% lower than the value found by
the method of equation (2.15) and given in last section. This is prob-
ably due to heat losses through the thermoelements, as noted in section
2.6. The calculated values of $\lambda$ are in good agreement with the recent
measurements of Cook et al. (1976). As is clear from figure 7.VII there
is a definite, if shallow, minimum in $\lambda$ at about 150 K. The depth of
this minimum, however, is only somewhat over 1%. By assuming the lattice
thermal conductivity to be $1.9 \times 10^3/T$ W m$^{-1}$K$^{-1}$ (White, 1969) it is
possible to find the electronic thermal conductivity $\lambda_e(T)$ by subtraction
of the lattice thermal conductivity from the total $\lambda$. The results found
for $\lambda_e$ are shown in table 7.1 and also as a dashed line in figure 7.VII.
The minimum in $\lambda_e$ is about 5% deep. The components of $\lambda$ will be further
discussed in section 8.
Fig. 7.VII Thermal conductivity of an unannealed aluminium sample as a function of temperature. Full line shows the results of Cook et al. (1976). Dashed line shows the electronic thermal conductivity only, after subtraction of the lattice component.
<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\alpha$ (cm$^2$/s)</th>
<th>$\lambda$ (W/m·K)</th>
<th>$\lambda_e$ (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>2.36</td>
<td>272</td>
<td>251</td>
</tr>
<tr>
<td>100</td>
<td>1.89</td>
<td>248</td>
<td>229</td>
</tr>
<tr>
<td>150</td>
<td>1.18</td>
<td>220</td>
<td>207</td>
</tr>
<tr>
<td>200</td>
<td>1.02</td>
<td>221</td>
<td>211</td>
</tr>
<tr>
<td>250</td>
<td>0.95</td>
<td>222</td>
<td>214</td>
</tr>
<tr>
<td>300</td>
<td>0.92</td>
<td>224</td>
<td>218</td>
</tr>
<tr>
<td>350</td>
<td>0.88</td>
<td>225</td>
<td>220</td>
</tr>
</tbody>
</table>

Table 7.1 Thermal diffusivity and thermal conductivity of aluminium as a function of temperature.
8 THEORY OF THERMAL CONDUCTION IN METALS

8.1 Introduction

In a metal, heat is usually transported by two types of carriers: electrons and phonons, that is, lattice vibrations. These two carriers act effectively in parallel, and the total thermal conductivity $\lambda$ can therefore be written as $\lambda = \lambda_e + \lambda_p$, where $\lambda_e$ is the electronic thermal conductivity and $\lambda_p$ is the lattice thermal conductivity. In most metals, and at most temperatures, $\lambda_e$ is the larger component. For this reason it is often assumed that for all good conductors $\lambda = \lambda_e$, at least at high temperatures.

In the next section we shall take a brief theoretical look at $\lambda_p$ and its pressure dependence. The rest of the chapter will then be devoted to the temperature and pressure dependence of $\lambda_e$. The theoretical treatment will be simple without any large mathematical complexities. From the experimentalist's point of view, the results, and the assumptions and approximations made to find the results, are in most cases more interesting than the often difficult and tedious mathematical work necessary to get from the assumptions to the results. The reader will be assumed to be familiar with basic solid state concepts such as phonons in a crystal lattice and Fermi surfaces. For those readers who want to study further the theories of heat conduction in metals the books by Ziman (1960) and Berman (1976) are recommended.

8.2 Lattice thermal conductivity

8.2.1 Thermal conductivity at atmospheric pressure

Lattice vibrations act as heat carriers in all crystalline materials. In dielectric materials lattice vibrations always carry the dominant part of the heat current, except possibly at high temperatures where phonon heat transport might become important. In metals, electrons can easily carry large amounts of heat through the material, and in general the lattice thermal conductivity in these materials is only an insignificant fraction of the total thermal conductivity. The lattice thermal conductivity of metals is therefore mostly regarded as important only in alloys or some transition metals, in which the electron flow is re-
duced by strong scattering mechanisms. In the present measurements we are concerned only with very good electrical conductors, in which the lattice thermal conductivity does not amount to more than a few percent of the total thermal conductivity. There is, therefore, no need to explore the conduction mechanisms in detail, and only the dominant behaviour of $\lambda_p$ in different temperature regions will be described.

As is well known from elementary solid state theory (Kittel, 1971) the energy of lattice vibrations is quantized. The quanta of vibrational energy are called phonons, in analogy with photons etc. In a simple model, phonons can be regarded as particles propagating through the crystal. They are scattered by various lattice defects, such as vacancies, impurity atoms, including isotopes of the lattice atoms themselves, dislocations, and grain or sample boundaries. Since the lattice potential is not purely harmonic for large amplitude atomic vibrations, phonons can also interact and thus scatter each other. In a metal, phonons can also be scattered by conduction electrons. There are also more exotic possibilities, like phonon-exciton or phonon-magnon interactions, but they will not be considered here. The total lattice thermal resistivity $W_p = \lambda_p^{-1}$ can be written as a sum of the thermal resistivities due to the individual scattering mechanisms. In this way we obtain $W_p = W_{po} + W_{pp} + W_{pe}$, where $W_{po}$ is the lattice thermal resistivity due to phonon-impurity collisions, $W_{pp}$ is the corresponding resistivity due to phonon-phonon collisions and $W_{pe}$ is the resistivity due to phonon-electron interactions. At a given $T$, $W_p$ is generally dominated by only one of these terms. Figure 8.1 shows the theoretical general form of $\lambda_p$ for a good metal. The figure is adapted after Makinson (1938). The limiting mechanisms in different temperature intervals are indicated in the figure.

At very low temperatures, $\lambda_p$ is limited by boundary scattering of phonons. This phenomenon can be explained by some very simple arguments. To a first approximation, the phonons can be regarded as a gas of particles. It is then possible to use the kinetic theory of gases (Kittel, 1971; p. 224) to obtain the thermal conductivity, which in this case is $\lambda_p = W_{po}^{-1}$, as

$$\lambda_p = c_v \cdot v_p \cdot \Lambda/3$$

(8.1)
Fig. 8.1 General form of the lattice thermal conductivity for a typical metal. The main limiting mechanisms in different temperature intervals are shown. The dotted line shows the typical form of $\lambda_p$ for a non-metallic solid. (After Makinson, 1938)

where $c_v$ is the specific heat of the phonons, $v_p$ is some average velocity, and $\Lambda$ is the mean free path. As $T$ is lowered, the average energy of the phonons decreases, and the wavelength increases. The rate of scattering of phonons on impurities then decreases, as does the scattering of phonons by phonons. As a result, $\Lambda$ increases until it is of the same order of magnitude as some characteristic dimension of the sample. At still lower temperatures, $\Lambda$ is a constant, as is also $v_p$. At low temperatures we know that $c_v \propto T^3$ (Kittel, 1971; p. 215), and thus $\lambda_p = W_{po}^{-1} \propto T^3$. The term $W_{po}$ is thus proportional to $T^{-3}$ at low temperatures. At higher temperatures $W_{po}$ might become very small, but it is ultimately limited by impurity scattering in the crystal. This occurs when the wavelength of the phonon becomes comparable to the size of a typical impurity.

The terms $W_{po}$ and $W_{pp}$ are limiting factors for $\lambda_p$ in all materials, but the term $W_{pe}$ only exists for metals. This term, however, is only important at low temperatures, where $W_{pe} \propto T^{-2}$ (Makinson, 1938). At higher temperatures $W_{pe}$ approaches a low, constant value which is of the same order of magnitude as $\lambda_e^{-1}$.

Finally, from figure 8.1 it is seen that at high temperatures $\lambda_p$ is limited mainly by phonon-phonon scattering, that is, by the term $W_{pp}$. This
term is extremely difficult to calculate exactly. However, it has some very interesting features. As is well known, the fact that phonon-phonon interactions can give rise to any thermal resistivity at all depends on the existence of Umklapp processes (Kittel, 1971; p. 228), in which two phonons collide to form a third which is, as it were, "turned around" by a reflection in the lattice. Umklapp processes can only occur if the magnitudes of the wave vectors of the colliding phonons are large enough for the wave vector of the resulting phonon to fall in an adjacent Brillouin zone. This means that they are very rare at low temperatures. Since the mean energy of the phonons increases as $k_B T$, where $k_B$ is Boltzmann's constant, the probability of Umklapp processes increases at higher temperatures. It is found that $W_{pp} \propto \exp (-\Theta_u / T)$ at low temperatures. Here $\Theta_u$ is some characteristic temperature. At higher temperatures the probability of Umklapp processes saturates, and $W_{pp}$ increases linearly with temperature.

Contrary to what was said above, normal processes do contribute to the thermal resistivity, if only in a rather subtle way. Umklapp processes, as stated above, can only occur for phonons with some minimum value of the phonon wavevector. Since such phonons are then effectively removed from the crystal by the scattering process, the steady state distribution of phonon energies is disturbed. The normal phonon-phonon interaction ensures that the energy distribution among the phonons is always in approximate thermal equilibrium, and thus it does have an important effect on the thermal resistivity.

Exact calculations of $W_{pp}$ are very difficult, and the results can in most cases not be written as an analytical formula. Several workers, however, have obtained results of the form

$$W_{pp} = A_0 \gamma^2 \Theta^3 / Ma^3$$

where $A_0$ is a numerical constant, $\gamma$ is the Grüneisen parameter, $M$ is the atomic weight of the crystal material, $a$ is the lattice parameter, and $\Theta$ is the Debye temperature. This expression is often attributed to Leibfried and Schlömann (1954), but similar formulas have been derived by several other workers (Aim, 1976). Experimentally it is found that
equation (8.2) gives a good account of $W_{pp}$ for metals at $T > \Theta$, at least if the constant $A$ is modified by a factor 2 from the value given by Leibfried and Schlömann (White, 1969). Since it is difficult to measure $\lambda_p$ for metals, however, equation (8.2) has mainly been applied to non-metals. In general, it is found that $W_{pp}$ increases somewhat faster with temperature than $W_{pp} \propto T$. This can in most cases be explained by the temperature dependence of $\gamma$, $a$, and $\Theta$.

More refined calculations of $\lambda_p$, and especially of $W_{pp}$, have been made by many workers (Berman, 1976). However, since $\lambda_p$ in the present cases is $\lambda_p = W_{pp}^{-1}$ and can be fairly well described by equation (8.2), there is no need to go deeper into this subject. In next section the pressure dependence of $\lambda_p$ will instead be studied.

8.2.2 Pressure dependence of the lattice thermal conductivity

Very little theoretical work has been done to calculate the pressure dependence of $\lambda$. Most of the existing work, however, has been devoted to the pressure dependence of $\lambda_p$. Alm (1976) reviews the results of some calculations of $\lambda_p$ versus volume, $V$, for crystalline dielectric materials. Since $\lambda_p$ at room temperature is limited by phonon-phonon scattering both in metals and in dielectrics, we can use the same formulas in both cases. A particularly simple derivation of $\partial \lambda_p / \partial V$ has been given by Bohlin and Andersson (1974). The starting point of their analysis is equation (8.2). The Grüneisen parameter $\gamma = - [a(\ln \Theta)/a(\ln V)]$ was used to express the volume dependence of the phonon spectrum. Using $a(\ln \gamma)/a(\ln V) = 2\gamma$ they obtained

$$a(\ln W_{pp})/a(\ln V) = 3\gamma - 1/3 + 2 [a(\ln \gamma)/a(\ln V)] = 7\gamma - 1/3$$

(8.3)

From this expression the pressure dependence of $W_{pp}$ can easily be found, using measured values of the bulk modulus $B_0 \equiv - V aP/aV$.

The above analysis has recently been criticized by Averkin et al. (1977). They argue that the volume dependence of the phonon spectrum should be calculated from the measured pressure dependence of the elastic moduli instead of from $\gamma$. Also, the volume dependence of $\gamma$ should be calculated in a similar way. They calculated the volume dependence of $\lambda_p$ for a number of alkali halides, taking $a(\ln \gamma)/a(\ln V) = 1.5$ and
calculating the volume dependence of \( \Theta \) from the pressure dependence of the elastic moduli. To this result, they added an empirical correction, valid for solids with the NaCl structure, for changes in elastic anisotropy under pressure; in the case of the potassium halides this correction was 50% of the final results for \( \partial \lambda_p / \partial V \).

To compare the results of these two theoretical calculations with the experimental results, table 8.1 has been compiled. In this table are shown experimental values of \( [\lambda_p(0)]^{-1} \partial \lambda_p / \partial P \) for several alkali halides, measured by several groups of workers. These values are compared to the theoretical pressure coefficients given by Averkin et al. (1977) and to the predictions of equation (8.3). The values of \( B \) used in the calculation were taken from Vaidya and Kennedy (1971), while \( \gamma \) was taken from White (1965) and White and Collins (1973). The values of \( \gamma \) used were derived from thermal expansion measurements, since it is common

<table>
<thead>
<tr>
<th>Reference</th>
<th>KCl</th>
<th>KI</th>
<th>LiF</th>
<th>NaCl</th>
<th>NaF</th>
<th>RbBr</th>
</tr>
</thead>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridgman (1924)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alm (1976):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radial st.st. method</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>0.29</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>&quot;Hot wire&quot; method</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>Seleznev et al. (1976)</td>
<td>0.47</td>
<td>1.05</td>
<td>0.18</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Averkin et al. (1976)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.68</td>
</tr>
<tr>
<td><strong>Theoretical calc.:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equation (8.3)</td>
<td>0.54</td>
<td>0.79</td>
<td>0.17</td>
<td>0.46</td>
<td>0.21</td>
<td>0.70</td>
</tr>
<tr>
<td>Averkin et al. (1977)</td>
<td>0.48</td>
<td>0.72</td>
<td>0.18</td>
<td>0.38</td>
<td>-</td>
<td>0.69</td>
</tr>
</tbody>
</table>
practice to use such values in connection with equation (8.2) (White, 1969).

As can be seen from the table, the agreement between theory and experiment is good. The calculations by Averkin et al. are in better agreement with experiment than is equation (8.3) for NaCl and KCl; for KI none of the theoretical calculations seem to agree with experiments. The "radial steady state" measurements by Alm are systematically lower than other experimental results, while there is a good agreement between his "hot wire" results and the results by other workers. Disregarding Alm's "radial steady state" results, equation (8.3) is in very good agreement with the average of the experimentally found coefficients. The error is less than about ten percent, except for KI and NaCl, where it is 20 - 30%. Since $\lambda_\rho$ is such a small part of the total $\lambda$ in a metal, however, we conclude that equation (8.3) will probably give a satisfactory accuracy in the calculation of $\alpha W_\rho / a P$ in this case, and that there is no need to use the more complex method used by Averkin et al.

8.3 Electronic thermal conductivity

8.3.1 Thermal conductivity at atmospheric pressure

In most "good" metals, such as those investigated in this work, the electrons carry most of the heat current, and the electronic thermal conductivity $\lambda_e$ is much larger than $\lambda_\rho$. In this section $\lambda_e$ will be investigated. The discussion will concentrate on the physical ideas behind the scattering mechanisms, and the mathematical treatment will be kept at an elementary level. The reader will be assumed to be familiar with some basic solid state concepts, such as Fermi surfaces. It is necessary to make a few definitions: The electron wave vector is denoted by $k$, the Fermi momentum, that is, $|k|$ at the Fermi surface, is $k_F$, and the Fermi energy is written $E_F$.

First, it is instructive to take a brief look at the Fermi surfaces of the metals studied. A simple, monovalent free-electron metal should have a perfectly spherical Fermi surface. None of the metals studied here show such simple features. The noble metals are monovalent, and should, in the free electron approximation, have spherical Fermi sur-
faces contained fully within the first Brillouin zone. However, since these metals have the f.c.c. structure, the free electron Fermi surface would be fairly close to the Brillouin zone boundary. In reality the Fermi surfaces of the noble metals have the general shape shown in figure 8.11 (after Kittel, 1971). The Fermi surfaces in adjacent Brillouin zones are in contact with each other through short, narrow "necks", protruding in the <111> directions, from the approximately spherical "belly". Although the main part of the Fermi surface is almost spherical, it can be expected that the existence of the necks should have an influence on the transport properties of these metals.

Aluminium, on the other hand, is trivalent, and the Fermi momentum $k_F$ is so large that the Fermi surface extends into three Brillouin zones. This, clearly, could in principle complicate the Fermi surface enormously. Band structure calculations (Segal, 1961) show, however, that the Fermi surface of this metal is surprisingly spherical, that is, free-electron-like. In fact, aluminium should be much more free-electron-like than the noble metals.

Because of the conditions imposed on the electrons by the Pauli principle, only those electrons lying close to the Fermi surface can easily change their energy, and thus normally only these take part in heat or charge transport. Once an electron has acquired some extra thermal energy it
continues carrying this until it is scattered by some mechanism, thus either losing its extra thermal energy or transporting it in some other direction. Electrons can be scattered by many mechanisms, and the total electronic thermal resistivity \( W_e \) can, according to Matthiessen's rule, be considered to be the sum of several terms: \( W_e = W_{eo} + W_{ep} + W_{ee} \). The notation used is similar to that used before; \( W_{eo} \) is the electronic thermal resistivity due to impurity or boundary scattering, \( W_{ep} \) is the resistivity due to scattering of electrons by phonons, and \( W_{ee} \) is the resistivity due to collisions among the electrons themselves. As in the case of \( W_p \) we shall look at each of these terms in turn.

Starting with \( W_{ee} \), it is found that this term is very small in normal metals. One reason for this is the screening effect of the "sea" of electrons surrounding any single electron. Another reason is furnished by the Pauli principle, which states that two electrons can collide only if the resulting electron states after the collision are initially unoccupied. It can be shown (Kittel, 1971; p. 282) that this results in a further reduction of the electron-electron interaction by a factor \(- (k_B T/E_F)^2\). The actual calculation of \( W_{ee} \) is very difficult, however. Explicit expressions for \( W_{ee} \) have been given by Ziman (1960, p. 417) and Laubitz (1970); what is generally found is that \( W_{ee} \propto T\), and that it is small at room temperature. However, Laubitz (1970) explained the negative slope of \( \lambda(T) \) for the noble metals at high temperatures by the action of an electron-electron interaction term. Such a term has also been found by Cook et al. (1972) for sodium and by Cook and Laubitz (1976) for potassium. If we assume that the results of Laubitz are in fact due to electron-electron scattering, we can calculate the numerical value of \( W_{ee} \) for the noble metals from his results. However, \( W_{ee} \) proves to be quite small at room temperature, typically less than 1% of the total \( W_e \), and can thus be ignored. The same result is found for aluminium (Laubitz and Cook, 1973). In fact, \( W_{ee} \) is usually assumed to be significant only in the case of the transition metals, where electron-electron interactions might scatter highly mobile s electrons into less mobile d states and thus enhance both thermal and electrical resistivities.

The thermal resistivity \( W_e \) is usually calculated by solving Boltzmann's equation. This equation describes how an electron distribution function \( N(k, r, t) \) changes with time when an external disturbance or field is
applied to the electrons. \( N \) gives the number of electrons having the momentum \( k \) and the space coordinate \( r \) at time \( t \). If a field is applied, \( N \) will deviate from its equilibrium value \( N_0 \). This deviation will be counteracted by scattering mechanisms, which are described by a term \((\partial N/\partial t)_S\). When a steady state situation is again established, the time derivative of \( N \) must be zero, and the Boltzmann equation can be written as

\[
\frac{\partial N}{\partial t}_S = \frac{\partial N}{\partial r} \cdot \frac{\partial r}{\partial t} + \frac{\partial N}{\partial k} \cdot \frac{\partial k}{\partial t}
\]  

(8.4)

In the general case this equation is hopelessly complex and impossible to solve. In many cases, however, the equation can be simplified by introducing \( n \), the deviation of \( N \) from \( N_0 \). The resulting linearized Boltzmann equation can then sometimes be solved.

In general, one of two different methods are used to solve (8.4). The first of these is the so called relaxation time method. This method assumes that scattering processes tend to restore \( N \) to \( N_0 \) at a rate proportional to \(| N - N_0 | \), so that \((\partial N/\partial t)_S = (N_0 - N)/\tau \), where \( \tau \) is some characteristic relaxation time. The problem is then mainly to find expressions for this relaxation time, which in a real case depends on both the scattering mechanism, the temperature, and \( k \). The most useful result obtained by this method is probably the verification of Wiedemann-Franz law.

By assuming that all scattering is elastic, and that the same \( \tau \) can be assumed for both electrical and thermal resistivities it is possible to obtain an expression for \( \lambda_e \), which is (Ziman, 1960; p. 383 ff)

\[
\lambda_e = L_0 T \sigma.
\]  

(8.5)

Here \( L_0 = \pi^2 k_B^2/3e^2 = 2.443 \times 10^{-8} V^2 K^{-2} \) is the standard Lorentz number and \( e \) is the electronic charge. This law is generally valid at all times, provided the assumptions above are valid. However, this is not always so. Equation (8.5) is in reality valid only in the limits of very high or very low temperatures. At intermediate temperatures \( \lambda_e \) is governed mainly by inelastic scattering of electrons, and thus \( \lambda_e/\sigma \) is not proportional to \( T \) in this range.
It is possible, however, to use equation (8.5) to study $W_{eo}$. At very low temperatures $W_{ep}$ and $W_{ee}$ are negligible, and both $\lambda_e$ and $\sigma$ are limited by impurity scattering only. Since both quantities are limited by the same mechanism, $\tau$ is the same for both, and (8.5) is valid. Since both the number of electrons and their Fermi velocities are independent of $T$, it is easily seen that the mean free paths of the electrons should also be independent of $T$. Thus, the electrical conductivity $\sigma$ should be a constant $\sigma = \sigma_0$. This is also observed at low temperatures. From (8.5) it is then found that $W_{eo} = \lambda_e^{-1}$ is $W_{eo} = (L_0 T \sigma_0)^{-1}$.

The other method commonly used to solve (8.4) is the so called variational method. In this method a trial function solution, containing a number of adjustable parameters, is selected. The parameters are then adjusted to obtain a minimum in the desired property. While this method is very elegant, it seldom gives results that can be written down in closed form. However, using this method, and with some simplifying assumptions concerning lattice dynamics and electron distribution functions, it has been possible to derive some expressions for the phonon-limited parts of $\sigma$ and $\lambda_e$ that give, at least, an approximately correct temperature dependence of these quantities. These expressions will be given below without any attempt to derive them mathematically. To see what behaviour can be expected, however, we shall first take a look at the electron-phonon scattering processes on the Fermi surface. For simplicity, we shall assume the Fermi surface to be spherical.

If an electric field $E$ is applied to the electrons in a metal, they are accelerated. From a semi-classical consideration we would find that each electron would acquire an additional momentum at a rate $\partial k/\partial t = eE/\hbar$. If each electron is accelerated for a time $\tau$, the Fermi sphere as a whole would be shifted by an amount $k = e\tau E/\hbar$. This is shown in figure 8.III. The same result is, in fact, obtained from the relaxation time approach to the Boltzmann equation (Blatt, 1968; p. 115). The amount of shift for a given applied field determines $\sigma$, and this shift is limited by scattering processes which move electrons from one side of the Fermi surface to the other, that is, from A to B in the figure. Phonons typically have an energy of the order of $k_B T$, or, at high temperatures, $k_B^0 T$ (in the Debye approximation). Since electrons have a typical
The effect of an applied electric field $E$ on the Fermi surface of a metal. Above: Two Fermi spheres in $k$-space. The equilibrium sphere (solid line) is centered at $k_x = k_y = 0$, while the steady state conduction sphere is centered at $k_x = \frac{\tau eE}{h}$. In the steady state, there is a deficit of electrons at $B$ and a large number of extra electrons at $A$, compared to the equilibrium situation. Below: The corresponding Fermi distribution in the $k_x$ space for the two cases.

energy of $E_F = 100 k_B \theta$, the relative change in electron energy in a collision is very small. The change in direction in $k$ might be appreciable at high temperatures, but at low temperatures this, too, is small. The electrical resistivity due to electron-phonon scattering can thus be considered to arise through a diffusion of electrons on the Fermi surface from $A$ to $B$. At high temperatures this distance can be covered in fewer steps than at lower, and we would expect the low temperature electrical resistivity to be small. This resistance mechanism is often called "horizontal" scattering, since the change in electron energy is small.

So far, only normal scattering has been considered. Umklapp processes, such as that shown in figure 8.IV, are much more efficient in reducing conductivity, since they are able to take an electron from $A$ to $B$ in a single step. Umklapp processes can only occur in a monovalent free electron metal for some minimum phonon wave vector, as shown in the figure, and should thus be "frozen out" at low temperatures. Unfortunately, this simple picture is not valid for the metals studied in this work. In these, Umklapp processes are always possible since the Fermi surfaces cross the Brillouin zone boundary.
Fig. 8.IV Electron-phonon Umklapp process. Left: On the free electron sphere. Right: In the repeated-zone scheme. Z.B. denotes the Brillouin zone boundary. In this process an electron with wavevector \( k \) interacts with a phonon with wavevector \( g \). After the collision the electron has the wavevector \( k' \). In a normal process, \( k + q = k' \). In this Umklapp process, however, \( k + q = k' + g \) where \( g \) is any reciprocal lattice vector. As indicated in the right figure there exists a minimum phonon wavevector \( q_{\text{min}} \) for which the process is possible.

Fig. 8.V The electron distribution on the Fermi surface in equilibrium (solid lines) and in a steady state thermal conduction situation (dashed lines). Heat is transported in the direction of the positive \( k_x \)-axis.
Turning now to the electronic thermal conductivity, it can be shown that a temperature gradient gives rise to a more complex charge balance on the Fermi surface. This is shown in figure 8.5. In this case the electric current is zero and thus there is no net charge flow. The center of mass of the Fermi "sphere" does not move, but instead the distribution of electrons changes close to the Fermi surface. Calling electrons with an energy \( E > E_F \) "hot" and those with \( E < E_F \) "cold", we see that, in a steady state situation, there is a small extra number of hot electrons, and a corresponding deficit of cold electrons, on one side of the Fermi surface, while the reverse is true on the other side. There is thus a net energy transport in one direction even though there is no net charge transport.

The steady state electron distribution function can relax back to the equilibrium state by two rather different mechanisms. Horizontal scattering, turning hot electrons going "east" into hot electrons going "west", or cold electrons going "west" into cold electrons going "east", is of course very efficient and corresponds roughly to the electrical resistivity case. However, large angle inelastic scattering processes turning hot electrons going "east" into cold electrons going "west" are not very important, since this changes the net energy flow very little.

In the case of heat flow, scattering processes which turn hot electrons into cold ones, without changing the direction very much, is another efficient resistance mechanism. Such processes are referred to as "vertical" scattering, since they take electrons almost vertically through the Fermi surface. In the case of electrical resistivity, however, such processes are of very little importance.

The importance of vertical processes for the thermal resistivity has a large effect on the electronic Lorentz function, which is defined as \( L_e = \frac{\lambda_e}{(\sigma T)} \). At high temperature horizontal scattering dominates both electrical and thermal resistivities, since the dominant phonon wave vectors are large. Consequently both \( \sigma \) and \( \hat{\omega}_{ep} \) are determined by the same scattering mechanisms and \( L_e = L_e^0 \). As \( T \) decreases the amount of horizontal scattering decreases, and \( \sigma \) increases. Vertical processes, however, are still very efficient in limiting the electronic thermal conductivity. The result is that \( L_e \) decreases sharply. At the very lowest temperatures both \( \lambda_e \) and \( \sigma \) depend on impurity scattering. Here
both quantities are once again limited by the same mechanism, and we have again $L_e = L_u$.

We now return to the theoretical calculations of $\lambda_e$. Since the Boltzmann equation is very difficult to solve, a lot of approximations are usually made. To obtain solutions in a closed form, a Debye model is usually used for the phonon spectrum, and all Umklapp processes are neglected. The Fermi surface is assumed to be spherical. The strength of the electron-phonon interaction is usually assumed to be a constant, $G$, irrespective of the relative motion. These simplifications might seem too many for a reasonable result to be obtainable from the calculations, but nevertheless the final results give a fairly good account of the true temperature behaviour of the transport properties.

Under the simplifying assumptions above, the following formulas can be obtained for $\sigma$ and $W_{ep}$ (Ziman, 1960; pp. 364, 391):

$$\sigma^{-1} = A(T^5/\theta^6) J_5(\theta/T)$$ \hspace{1cm} (8.6)

$$W_{ep} = (A/L \theta_0)((T/\theta)^5[J_5(\theta/T) - (2\pi)^{-1} J_7(\theta/T)] + (3/\pi^2)(k_F/q_D)^2). \cdot (T/\theta)^3 J_5(\theta/T).$$ \hspace{1cm} (8.7)

where

$$A = \frac{3\pi q_D^6 G^2}{4e^2 \pi n_c k_B k_F^2 V_F}$$ \hspace{1cm} (8.8)

and

$$J_n(y) = \int_0^y x^n e^x \left(\frac{e^x - 1}{x} \right)^2 \, dx$$

The integrals $J_n(y)$ are called the Debye integrals. In the expressions above $q_D$ denotes the largest phonon wave vector in the Debye model, $v_F$ is the electron velocity on the Fermi surface, and $n_c$ is the number of unit cells per unit volume. Subscript $p$ on $\sigma_p$ is used to indicate that this is the phonon-limited part of $\sigma$.

The expressions (8.6) and (8.7) are in fair agreement with experimental results, at least regarding the temperature dependence. Equation (8.6)
is in better agreement with experiments than (8.7); this is to be expected since the thermal conductivity is a more complicated phenomenon. At high temperatures, (8.6) simplifies to \( \sigma^{-1} = AT/4\Theta^2 \), while (8.7) can be written as \( W_{ep} = (A/L_0 T\Theta)(\Theta/T)^5 J_5(\Theta/T) = A/4\Theta^2 L_0 = (\sigma P_T L_0)^{-1} \). Thus, \( \sigma \propto T^{-1} \), \( W_{ep} \) is constant, and the Wiedemann-Franz law is obeyed. This is in good agreement with experiment.

At low temperatures \( \sigma^{-1} = 125 AT^5/\Theta^6 \), while \( W_{ep} = (A/L_0 \Theta)(3/\pi^2)(k_F/q_D)^2 (T/\Theta)^3 J_6(\Theta/T) = (375/\pi^2)(A/L_0 \Theta^4)(k_F/q_D)^2 T^2 \). This is also in general agreement with experiment. The Wiedemann-Franz law breaks down, since \( W = T^2 \) and \( \sigma = T^{-5} \). The cause of this breakdown is, of course, the influence of vertical processes on \( W_{ep} \). A closer examination of the terms in (8.7) reveals that the first term corresponds to (8.6) (with allowance for the Wiedemann-Franz law), and thus to horizontal scattering. The third term, which is dominant at low temperatures, corresponds to vertical scattering, while the second corrects for the fact mentioned above that large angle inelastic scattering is not very efficient in reducing thermal conductivity. A plot of \( W_{ep}^{-1}(T/\Theta) \), as given by (8.7), is shown in figure 8. VI for \( n_a \), the number of conduction electrons per atom, equal to 1, 2, and 3.

While equations (8.6) and (8.7) give, approximately, the correct temperature dependence of \( \sigma \) and \( W_{ep} \) at high and low temperatures, there are still serious errors at intermediate temperatures. As can be seen from figure 8. VI, equation (8.7) predicts a pronounced maximum in \( W_{ep} \) at about \( T/\Theta = 0.2 \). Such a maximum is not observed experimentally. Also, the absolute value of \( W_{ep} \) is in error by a large factor. Even the ratio between \( W_{ep} \) at high and low temperatures is in error. Most of these discrepancies can be traced to the neglect of Umklapp scattering. Umklapp scattering would increase \( W_{ep} \), mostly at high temperatures. This would then tend to remove or diminish the maximum in \( W_{ep} \), and also to shift it towards higher temperatures. This is indicated by the dashed line in figure 8. VI. Ziman (1954) improved on the results of (8.7) by including Umklapp processes in a calculation of \( W_{ep} \), and obtained a result which had only a small maximum of about 9 %, occurring at about 0.45 \( \Theta \). In fact, both sodium (Cook et al., 1972) and aluminium (Powell, 1969; Cook et al., 1976; see also section 7.4.2) show small minima in \( \lambda_e \), of about 1 - 5 %, at temperatures of 0.4 - 0.5 \( \Theta \). This indicates that Umklapp processes in these metals are not sufficiently efficient to
Fig. 8.VI  Plot of the normalized electronic thermal conductivity $A/(L_0 \Theta^2 W_{ep})$, as given by equation (8.7), versus $T/\Theta$. Curves are given for $n_a = 1, 2,$ and $3$. At high $T$, all curves tend towards the asymptote shown by the dot-dashed line. The dashed line indicates the approximate result expected when including Umklapp processes in the calculation for $n_a = 1$.

fully eliminate the maximum in $W_{ep}$. Shallow minima in $\lambda_e$ are also observed for zinc (Powell, 1969) and for calcium (Cook et al., 1975). Minima in $\lambda(T)$ are also observed for many transition metals. In these metals, however, the minima arise from the effect of temperature on the band structures and result from the fact that $\lambda$ increases with $T$ at high temperatures. In general, it can be concluded that for simple metals, equation (8.7) gives a fair picture of the behaviour of $W_{ep}(T)$, and that the deviations of the experimental results from this equation can be qualitatively explained.

After large-scale computers became available, many attempts have been made to calculate $W_{ep}(T)$ more accurately by solving the transport equations numerically. Collins and Ziman (1961) calculated $W_{ep}$ for the alkali metals, taking into account Umklapp scattering, and using more realistic models for the electron-phonon interaction parameter.
and the Fermi surfaces. They were able to correlate the temperature dependence of $W_{ep}$ with differing degrees of distortion of the Fermi surfaces of the metals studied.

Later work by for instance Sangal and Sharma (1969), Hayman and Carbotte (1971), and Srivastava (1975) on the alkali metals and by Semwal et al. (1971), Pal (1973), and Prakash et al. (1975) on the noble metals have not, in general, improved much on the calculated values of $W_{ep}$. In most cases these workers have used spherical Fermi surfaces and abandoned the Debye model, using instead more realistic models of the lattice dynamics. Generally the results have been rather disappointing, since they either show large, experimentally non-existent maxima in $W_{ep}$, or have an absolute value that is an order of magnitude wrong. Recently, however, Leavens (1977) calculated $W_{ep}$ for sodium and potassium, using very realistic models for the lattice dynamics and the electron-phonon interaction. Leavens also calculated $W_{ep}$ at constant pressure instead of at constant volume, and obtained excellent agreement with experimental results over the temperature range 1 - 300 K. It would thus seem that it is now possible to calculate $W_{ep}$ accurately as a function of both volume and temperature. So far, however, no attempt has been made to calculate the volume dependence of $W_{ep}$ for any metal in this way.

Before finishing this section, it should be noted that a different approach to the analysis of $\lambda_e$ has been used by Laubitz and Cook (1972, 1973). They noted that a large part of $W_{ep}$ is due to horizontal scattering of electrons on the Fermi surface. This part can then be calculated from the electrical resistivity by the Wiedemann-Franz law, equation (8.5). In this way, that part of $W_{ep}$ which is due to inelastic electron scattering only can be obtained. This "vertical" part, $W_v$, is then $W_v = W_{ep} - (\sigma L T)^{-1}$, and corresponds to the second and third terms in (8.7). Since the temperature and pressure dependence of $\sigma$ can be fairly well described by theory, Laubitz and Cook considered $W_v$ to be the only really interesting part of $W_{ep}$. As was seen above, $W_v$ is the dominant part of $W_{ep}$ at low temperatures. At higher temperatures, however, $W_v$ goes through a maximum. From (8.7) we see that at sufficiently high temperatures

$$M_v = (A/4L_0)[(3/\pi^2)(k_F/q_D)^2 - (3\pi)^{-1}]T^{-2}$$

(8.9)
and thus goes rapidly towards zero as \( T \) increases. In the high temperature limit \( W_v \) should furthermore be independent of the lattice dynamics. This is verified by (8.9), which does not contain \( \Theta \). Laubitz and Cook (1972) derived a more exact expression for \( W_v \), taking Umklapp processes into account but assuming the Fermi surface to be spherical. This expression was then used to calculate \( W_v \) for the alkali and noble metals (Laubitz and Cook, 1972) and for aluminium and lead (Laubitz and Cook, 1973). The calculated values of \( W_v \) were compared to the values found from experiment, and the agreement between theory and experiment was found to be good.

It can be noted that in this model the existence or non-existence of the minimum in \( \lambda_e \) depends on the relative strength of \( W_v \) and \( (W_e - W_v) \). Umklapp processes are more probable in the latter case, and thus they tend to increase the amount of horizontal scattering relative to vertical scattering, and thus to remove the minimum in \( \lambda_e \).

8.3.2 Pressure dependence of the electronic thermal conductivity

Very little theoretical work has been done on the volume dependence of \( \lambda_e \). In fact, the only available calculation of \( \lambda_e(V) \) is that of Bohlin (1976). Since \( \lambda_e = W_{ep}^{-1} \) at room temperature, Bohlin used equation (8.7) for \( W_{ep} \) as his starting point. Since this expression gives \( W_{ep} \) as a function of \( \Theta \), it is possible to use the same technique as in the case of \( W_{pp} \) to find the volume dependence. Thus, the expression \( \gamma = - \left[ a(\ln \Theta)/a(\ln V) \right] \) is used to obtain the volume dependence of the phonon spectrum. The constant \( A \) in (8.7) is almost independent of volume in the free electron approximation. In this case we have \( v_F = \hbar k_F/m^* \), where \( m^* \) is the effective mass of the electron. Also, \( k_F/q_D = (n_a/2)^{1/3} \), where \( n_a \) is the number of conduction electrons per atom. It is thus possible to rewrite \( A \) from (8.8) as

\[
A = \frac{3\pi(m^*)^2G^2}{(e^2k_B\mu n^2/h)}.
\]

In the simple model used by Ziman (1960; p. 364) to derive (8.7), \( G = n/N(E_F) \), where \( n \) is the number of electrons per unit volume. On the other hand, \( m^* = \hbar^2k_F^2/3n \) (Ziman, 1960; p. 101), so that \( m^*G = \hbar^2k_F^2/3 \), and
where the left factor is independent of volume. Introducing $x \equiv \Theta/T$, the volume dependence of $W_{ep}$ is found to be (Bohlin, 1976)

$$\frac{\partial (\ln W_{ep})}{\partial (\ln V)} = -\frac{1}{3} + \gamma \left( 2 - \frac{3}{\Theta} \frac{\partial}{\partial x} \left( \ln(x^{-4}J_5(x) - \frac{1}{2\pi^2} J_7(x)) + \frac{3}{\pi^2} x^{-2} \right) \right).$$

(8.10)

The most interesting part of this expression is of course the logarithmic derivative in the parenthesis. This derivative is shown in figure 8.VII, where the expression $\Delta \equiv \left[ \frac{\partial (\ln W_{ep})}{\partial (\ln V)} + 1/3 \right]/\gamma$ is plotted versus $T/\Theta$ for $n_a$ equal to 1, 2, and 3. It should be pointed out that Bohlin's original curve (Bohlin, 1976) corresponds to $n_a = 2$, due to an error on his part.

![Graph showing the behavior of $\Delta$ versus $T/\Theta$ for different values of $n_a$.](image)
From the figure it is seen that $\Delta$ has a limiting value $\Delta = 2$ at high temperatures. This is to be expected, since $W_{ep}(T/\Theta) = A/4L_0 \Theta^2$ in this range. At low temperatures $W_{ep}(T/\Theta) < \Theta^{-4}$, and thus $\Delta = 4$. The minimum in the curves of $\Delta$ versus $T/\Theta$ in the figure is of course connected with the maximum in $W_{ep}(T/\Theta)$ as given by equation (8.7). At temperatures above this maximum the temperature derivative of $W_{ep}$ is negative, and consequently $\Delta < 2$. At about $T/\Theta = 0.2$ to 0.23, depending on $n_a$, the maximum occurs in $W_{ep}(T)$ and $\Delta = 2$, and below this temperature $\Delta > 2$. This, of course, points to the weaknesses of this analysis.

No account is taken of Umklapp processes, which probably form the major part of $W_{ep}$ at room temperature. Also, no effects of the distortion of the Fermi surface under pressure are taken into account, since equations (8.7) and (8.10) both assume spherical Fermi surfaces. Furthermore, the electron-phonon interaction parameter $G$ is very much simplified.

The effect on equation (8.10) of including Umklapp processes in the analysis can be estimated. Due to the logarithmic derivative in the parenthesis, only the functional dependence of $W_{ep}$ on $(T/\Theta)$ is of interest. We know that the inclusion of Umklapp processes will tend to increase $W_{ep}$, obliterating the maximum or, at least, diminishing it and shifting it towards higher temperatures. Thus $W_{ep}$ would tend to rise smoothly to a constant high temperature value. The effect of this on $\Delta$ would be to remove the minimum at about 0.5 $\Theta$. For those metals where no maximum in $W_{ep}(T/\Theta)$ is observed, $\Delta$ would be expected to fall smoothly from 4 at low $T$ to slightly over 2 at about 0.5 $\Theta$, and then to stay closely above 2 at higher $T$. For those cases where a small maximum in $W_{ep}(T/\Theta)$ is indeed found a similar curve would be expected, only now $\Delta$ would fall below 2 above $T/\Theta = 0.45$, have a very shallow minimum, and once again approach 2 at high $T$. As mentioned in last section, Ziman (1954) calculated $W_{ep}$, including Umklapp processes, for a free electron model. He found an expression of the same form as equation (8.7), that is, $W_{ep} = A f(\Theta/T)/a_0^2$, where $A$ is independent of volume and $f(\Theta/T)$ is a temperature dependent function. By graphically differentiating Ziman's result for $f(\Theta/T)$ the dashed curve for $\Delta$ in figure 8.VII can be found by an analysis similar to that leading to equation (8.10).

The effects of volume changes on $G$ are more difficult to evaluate, and no attempt will be made, since $G$ depends on the actual lattice structure of the metal.
Regarding the effects of Fermi surface distortions, we can only speculate that these should not affect vertical transitions in the same way as horizontal transitions. To see this we look at equation (8.7), where the third term corresponds to vertical scattering. This term contains a factor \((k_F/q_D)^2\) not present in the other terms. Above it was stated that \((k_F/q_D) = (n_a/2)^{1/3}\), independent of volume. However, if the Fermi surface distorts we would not expect this to be true, and thus the proportions of vertical and horizontal scattering would change with pressure. For aluminium there are experimental data on \(k_F\) as a function of pressure to 10 GPa (Burton and Jura, 1968). These results show that the pressure dependence of the average \(k_F\) can be described to within 0.1\% by the free electron model over this pressure range, even though the actual change in \(k_F\) depends strongly on the position on the Fermi surface (Melz, 1966). Fermi surface distortion should thus not be very important in the case of aluminium. For the noble metals, on the other hand, the distortions of the Fermi surfaces from a sphere increases under pressure. Templeton (1974) has shown that the value of \(k_F\) on the Fermi surface "belly" for these metals increases under pressure somewhat slower than predicted by free-electron theory. On the other hand, the areas of the "necks" increase five to ten times as fast as simple volume scaling would suggest. It would thus be reasonable to expect that the increasing distortion of the Fermi surface under pressure would have some effect on the transport properties for these metals.

All calculations of the volume dependence of \(W_{ep}\) discussed above are, of course, built on very simple models. It would certainly be very interesting if these calculations could be compared to some calculation of \(W_{ep}(V)\) directly from first principles, taking into account the details of Umklapp processes, the electron-phonon interaction parameter, the volume dependence of the actual phonon spectrum and the Fermi surface, and so on. However, no such calculation has been made so far, and thus no such comparison can be made.

Since \(\lambda_e = W_{ep}^{-1}\), it is not really necessary to calculate the pressure dependencies of the other terms of \(W_e\). However, it might be interesting to have at least an idea about what to expect for \(W_{eo}\), since this might amount to a few percent of \(W_{ep}\) for an impure sample. It was shown in last section that \(W_{eo} = (L_0 \sigma T)^{-1}\), and thus \(\partial (\ln W_{eo})/\partial (\ln V) = -\partial (\ln \sigma)/\partial (\ln V)\). The pressure coefficient of \(\sigma\) has been measured for several
metals by, for instance, Dugdale and Gugan (1957) and Goree and Scott (1965). What is found is usually that $a(\ln \sigma_0)/a(\ln V)$ is small, but that it can be either positive or negative. Also, as discussed by Lawson (1956), alloys almost always have a weaker pressure dependence of $\sigma$ than have pure metals. This leads to the conclusion that $a(\ln W_{eq})/a(\ln V)$ should be numerically small compared to $a(\ln W_{ep})/a(\ln V)$, and thus that an impure sample should have a smaller pressure dependence of $\lambda_e$ than a pure sample.

For completeness, the pressure dependence of $W_v$, as defined above, should also be investigated. In the free electron model, $W_v$ corresponds to the last two terms in equation (8.7). The low temperature behaviour of $W_v$ is the same as for the total $W_{ep}$, since then $W_v = W_{ep}$. Therefore, $a(\ln W_v)/a(\ln V) = 4\gamma - 1/3$ when $T$ is small. At high temperatures, however, $W_v$ is independent of $\Theta$, as shown in equation (8.9), and therefore $a(\ln W_v)/a(\ln V) = -1/3$. We would thus expect $W_v$ to have only a very small pressure dependence in the metals investigated, since for all these metals we have $T > \Theta$ at room temperature.
9 DISCUSSION

9.1 Lattice thermal conductivity

All metals investigated in the present work are "good" metals, in which the main part of the heat flow is carried by electrons. It is thus reasonable to expect that the pressure dependence of \( \lambda \) will also be dominated by \( \lambda_e \). Since the lattice thermal conductivity can be regarded as a small perturbation only, the discussion of the experimental results will be started by an elimination of the effect of \( \lambda_p \) from the measured results for \( \partial \lambda / \partial P \). The rest of the chapter will then be devoted to a study of the pressure dependence of \( \lambda_e \).

The magnitude of the lattice thermal conductivity of the metals studied is not precisely known, due to experimental difficulties in separating out such a small component from the total \( \lambda \). White (1969) suggested that the Leibfried-Schlömann equation (8.2) should give results that are correct except for a factor 2, and gave values for \( \lambda_p \) for several good metals. In table 9.1 values of \( \lambda_p / \lambda \) (at 310 K) are shown for the metals investigated. These values were taken from White (1969). The values

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \lambda_p / \lambda )</th>
<th>( \gamma )</th>
<th>( B^0 ) (GPa)</th>
<th>( \Theta ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>( 1.1 \times 10^{-2} )</td>
<td>2.46</td>
<td>110.7</td>
<td>221</td>
</tr>
<tr>
<td>Al</td>
<td>2.9</td>
<td>2.18</td>
<td>78.9</td>
<td>390</td>
</tr>
<tr>
<td>Au</td>
<td>0.9</td>
<td>3.09</td>
<td>150.8</td>
<td>178</td>
</tr>
<tr>
<td>Cu</td>
<td>3.1</td>
<td>1.97</td>
<td>151.0</td>
<td>310</td>
</tr>
<tr>
<td>Pb</td>
<td>2.2</td>
<td>2.84</td>
<td>42.4</td>
<td>87</td>
</tr>
<tr>
<td>Sn</td>
<td>1.5</td>
<td>2.27</td>
<td>55.1</td>
<td>170</td>
</tr>
</tbody>
</table>
shown are, of course, to some extent arbitrary. For instance, for copper $\lambda_p/\lambda$ is given as $3.1 \times 10^{-2}$ at 310 K (White 1960, 1969). Larikov et al. (1973) found $\lambda_p/\lambda = 2.5 \times 10^{-2}$, while Kierspe (1967) found $\lambda_p/\lambda = 4.5 \times 10^{-2}$. The figures given are, however, believed to be correct to within a factor 2. In the same table values are given for the Grüneisen parameter $\gamma$ (Gschneider, 1964), the bulk modulus $B$ (Vaidya and Kennedy, 1970) and the Debye temperature $\theta$ (Gschneider, 1964). The same constants are also given for lead and tin. These metals were investigated by Bridgman (1922) by a radial heat flow method. Since this method should not be very sensitive to the effect of convection in the pressure medium his results for these metals should be fairly accurate, and can thus be included in this discussion. The value of $\lambda_p/\lambda$ for lead is taken from Moore and Graves (1973), while that for tin is estimated from the experimental results of Karamargin et al. (1972).

Table 9.11 Pressure dependence of $\lambda$, $\lambda_p$, and $\lambda_e$ for the metals investigated.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$[\lambda(0)]^{-1} \partial \lambda / \partial P$ (GPa$^{-1}$)</th>
<th>$[\lambda_p(0)]^{-1} \partial \lambda_p / \partial P$ (GPa$^{-1}$)</th>
<th>$[\lambda_e(0)]^{-1} \partial \lambda_e / \partial P$ (GPa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$4.0 \times 10^{-2}$</td>
<td>$15.3 \times 10^{-2}$</td>
<td>$3.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>Au</td>
<td>3.9</td>
<td>14.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Cu</td>
<td>3.1</td>
<td>8.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Al</td>
<td>4.1</td>
<td>18.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Al (teor. $\partial c_P / \partial P$)</td>
<td>5.0</td>
<td>18.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Equation (8.3) can be used, together with the data in Table 9.1, to separate the pressure dependence of $\lambda_p$ from that of $\lambda_e$. Table 9.2 shows the measured pressure coefficients $[\chi(0)]^{-1} \partial \chi / \partial P$, the pressure coefficients of $\lambda_p$, as calculated from equation (8.3), and, finally, the calculated values of the pressure coefficients of the electronic thermal conductivity $\lambda_e$. For aluminium two values are shown, corresponding to the two values of the pressure coefficient of $\lambda$ obtained using the theoretical and the experimental results for the pressure coefficient of the specific heat capacity, respectively. It is seen that the effect of $\lambda_p$ is significant in spite of its small absolute value, due to the strong volume dependence of this term.

9.2 Electronic thermal conductivity

In last section the pressure coefficients of $\chi_e$ were obtained for the metals investigated. These coefficients can now be compared to the theoretical results obtained in section 8.3.2. As noted in section 8, it is possible to write $\chi_e^{-1} = W_e = W_{eo} + W_{ee} + W_{ep}$. In the temperature range investigated in the present work, two of these three terms are almost completely negligible. According to Laubitz (1970), $W_{ee}$ should be only 0.5%, 0.6%, and 0.8% of the total $W_e$ for copper, silver, and gold, respectively, while for aluminium any such term is too small to be observed experimentally (Laubitz and Cook, 1973). Thus, unless this term shows an exceptionally strong pressure dependence, no influence from this term would be seen in $W_e$. However, it might be interesting to look for the pressure dependence of this term in the high temperature regime.

The term $W_{eo}$ is probably also very small in our experiments. This term can be calculated from a measurement of the low temperature limiting resistivity $\sigma_0$. Such measurements have been made on two gold samples and two silver samples. The measurements were made on "worst case" samples, that is, on unannealed samples, which had been subjected to high pressure runs in the piston-cylinder apparatus. The samples were further cold worked during the removal from the pressure cells, and were finally bent into a narrow "hairpin" shape to fit into the helium Dewar. In spite of this rough handling, the residual resistance ratios (RRR) were found to be 140 and 210 for the silver samples, and 110 and 50 for the gold samples. Thus, even for samples handled in this way,
$W_{eo}$ should not be more than 2% of $W_e$, and was probably typically less than 1%. It is therefore improbable that this term should have any significant effect on the pressure coefficient of the total $W_e$ for the pure metals studied, even if the pressure coefficients of $W_{eo}$ and $W_e$ differ by an appreciable amount.

It would of course be possible to remove much of the influence of $W_{ep}$ on $W_e$ by measuring the RRR of each sample in turn and correct the measured pressure coefficient of $W_e$ by an amount given by the proportions of $W_{eo}$ and $W_{ep}$, using an approximate pressure coefficient for $W_{eo}$. As mentioned in section 8.3.2, however, the pressure coefficient of $W_{eo}$ is not well known, and thus such a procedure would introduce further errors in the calculations. It should be noted that the pressure coefficient of $W_{ep}$ can be expected to be numerically small (section 8.3.2), and that impure samples therefore should have a smaller pressure coefficient than pure samples. This is in general agreement with the results for copper reported in sections 7.1.1 and 7.1.2, even if the difference between the pressure coefficients found is unexpectedly large.

In view of the fact that the experimental accuracy was not large enough to permit us to distinguish between the pressure coefficients of $\lambda$ for annealed and unannealed samples, it is reasonable to assume that any effects of $W_{eo}$ on the pressure coefficients of $W_e$ for the pure samples are too small to be important. Therefore it will be assumed in the following that $W_{eo}$ and $W_{ee}$ can be neglected, and that all of the measured pressure dependence in $W_e$ comes from the dominant term $W_{ep}$.

To facilitate a comparison between theory and experiment the experimentally found pressure coefficients of $\lambda_e$ have been recalculated to volume coefficients, using bulk moduli from table 9.1. These volume coefficients can then be compared to the predictions of equation (8.10). The comparison is made in figure 9.1, where $\Delta = \gamma^{-1} \left[ \frac{\partial (\ln W_{ep})}{\partial (\ln V)} + 1/3 \right]$ is plotted versus $T/\Theta$. In this figure $\Delta$ is shown both as calculated from equation (8.10) and as found from experiments for the pure metals studied (points). The open circles are results obtained by a corresponding calculation neglecting $\lambda_e$, that is, assuming $W_{ep} = \lambda^{-1}$. For aluminium, two sets of data are shown. Circles correspond to a calculation using the experimentally found value for $\partial c_P/\partial P$ (Bastide and Loriers-Susse, 1975) while squares denote the results
found when using a theoretical value of \( \frac{\partial c_p}{\partial P} \), as discussed in section 7.4.1.

The agreement between the theoretical values of \( \Delta \) and the values found experimentally is excellent in the case of gold and silver. The detailed agreement, however, is probably fortuitous in view of the large spread in pressure coefficients found experimentally. The agreement is also very good for aluminium, while the result for copper does not agree very well with the theoretical predictions.

![Plot of \( \Delta = \gamma^{-1} \left[ \frac{\partial (\ln W_p)}{\partial (\ln V)} + 1/3 \right] \) for \( n_e = 1, 2, \) and 3, as given by equation (8.10). Open circles denote experimental results for \( \lambda \), recalculated in terms of \( \Delta \), while points denote experimental results for \( \lambda \). For Al, the squares give the corresponding results obtained if the theoretical value of \( \frac{\partial c_p}{\partial P} \) is used in the calculation.](image)
As discussed in section 8, equation (8.10) completely neglects Umklapp scattering, and the theoretical expression for $\Delta$ thus probably underestimates $\frac{\partial W_p}{\partial V}$ at intermediate temperatures for most metals. The only metal of those investigated here showing any maximum in $W_p$ is aluminium, which is reported to have a shallow minimum in $\lambda_e$ at about 140 - 220 K (Powell, 1969; Cook et al., 1976). The measurements of $\alpha$ and $\lambda$ described in section 7.4.2 confirm the existence of this minimum. Furthermore, these measurements show that $\lambda_e$ has a positive temperature coefficient all the way from about 150 K to 350 K for the particular aluminium sample investigated. From the discussion of Umklapp scattering in section 8.3.2 it thus follows that $\Delta$ should be slightly less than 2 for aluminium over this temperature range.

In figure 9.1, two values of $\Delta$ for aluminium were shown. The value obtained using the experimental $\frac{\alpha c_p}{\alpha P}$ is in very good agreement with equation (8.10). However, from what was said above it seems unlikely that this value is correct. The value of $\Delta$ obtained using the theoretical value of $\frac{\alpha c_p}{\alpha P}$ is in much better agreement with theory, if Umklapp scattering is taken into account. It thus seems that the experimental value of $\frac{\alpha c_p}{\alpha P}$ (Bastide and Loriers-Susse, 1975) might be in error. However, this can not be stated with any certainty, since the accuracy of the present measurements is not high enough, and also the simple theory used might not be sufficiently reliable.

The noble metals have no maxima in $W_p(T/\theta)$, and $\Delta$ should thus be expected to be approximately 2 at intermediate and high temperatures. The results for gold and silver agree with this behaviour to well within the experimental error. For copper the agreement between theory and experiment improves if account is taken of Umklapp processes. However, it is still not very good, even allowing for the possible 20 % error in $\frac{\partial \lambda}{\partial P}$ specified in section 7.1.2.

In conclusion it can be stated that Bohlin's (1976) predictions of the pressure coefficients of $\lambda_e$ are in very good agreement with experimental results for the metals studied, except possibly for copper. Deviations from the pressure coefficients given by his model can mostly be explained by the neglect of Umklapp scattering.
The good agreement found is to some extent surprising. The very simple model used in the derivation of \( W (T/e) \) and \( \frac{\partial W}{\partial V} \) should be very much more successful in describing \( \alpha(T/e) \) and \( \frac{\partial \alpha}{\partial V} \). While it is true that equation (8.6) does give a fairly good account of \( \sigma(T/e) \), predictions of \( \frac{\partial \sigma}{\partial V} \) from this equation have not always been very successful. The volume dependence of \( \sigma \) can be obtained from (8.6) by an analysis similar to that of Bohlin. At room temperature and above, the result obtained is

\[
\frac{\partial \ln \sigma}{\partial \ln V} = -2\gamma - \frac{\partial \ln A}{\partial \ln V} \quad (9.1)
\]

which is very similar to equation (8.10). It is common practice to let the second term take into account any change with volume of electronic band structure, Umklapp scattering, electron-phonon interactions etc. In the simple model used by Bohlin (1976), \( \alpha(\ln A)/\alpha(\ln V) = -1/3 \). The resistivity \( \sigma(P) \) of most metals has been studied over large ranges in pressure at temperatures from 4 K to well above room temperature. A good review of earlier measurements is given by Lawson (1956). More recent measurements of particular interest are those of Dugdale and Gugan (1957, 1962) and Goree and Scott (1966). These measurements cover the noble and alkali metals from 4 to 300 K. The values of \( \frac{\partial A}{\partial V} \) obtained through equation (9.1) from the experiments are not always in good agreement with the value \(-1/3\) given above, which indicates that band structure changes etc. might also be very important in the calculation of \( \frac{\partial \sigma}{\partial V} \). There is no need to go deeper into this subject here, however, since it has been adequately reviewed by several workers (Paul, 1963; Dugdale 1961, 1969; March, 1969). It is sufficient to note that since equation (9.1) is not always very successful in predicting \( \frac{\partial \sigma}{\partial V} \), it is somewhat surprising that equation (8.10) should predict \( \frac{\partial \lambda_e}{\partial V} \) with such a high accuracy.

In connection with what has been said about \( \sigma \), it might also be interesting to look at the pressure dependence of the electronic Lorentz function \( L_e = \lambda_e/(\sigma T) \). At temperatures \( T > \Theta \) it is expected that \( L_e \) should be a constant and that \( L_e/L_0 \approx 1 \). This is in reasonable agreement with experimental results for the noble metals. From the constancy of \( L_e \), it should also be expected that \( \frac{\partial L_e}{\partial P} \) should be approximately zero. This can also be seen from equations (8.10) and (9.1), since combining these with the expression for \( L_e \) would give \( \frac{\partial \ln L_e}{\partial \ln V} = \)
\[
= \frac{\partial \ln \lambda_e}{\partial \ln V} - \frac{\partial \ln \sigma}{\partial \ln V} = - \frac{\partial \ln W_{ep}}{\partial \ln V} - \frac{\partial \ln \sigma}{\partial \ln V} = 0.
\]
Using experimental values for \(\sigma(P)\) from Bridgman (1938, 1951) the pressure coefficients of \(L_e\) for the metals investigated can easily be calculated. These pressure coefficients are shown in table 9.III. The pressure coefficients of \(L_e\) are indeed found to be close to zero for silver and aluminium (if the theoretical pressure coefficient of \(c_p\) is used). However, for gold and copper \(L_e\) increases with pressure. It can be pointed out, also, that using the results for \(\partial \lambda / \partial P\) given by Starr (1938) results in positive pressure coefficients for \(L_e\) for all of the noble metals. Since the constancy of \(L_e\) is based on very solid theoretical foundations compared to equation (8.10), this result is very interesting from a theoretical point of view.

As noted in section 8.3, the experimental results obtained can also be used in an alternative way to study inelastic scattering of electrons only, using the model of Laubitz and Cook (1972). Horizontal scattering of electrons by phonons under pressure have been extensively studied through measurements of \(\sigma(V)\) (see the reviews mentioned above). Although the simple equation (9.1) does not always give accurate values for \(\sigma(V)\), more refined calculations (Hasegawa, 1964; Bowen and Dow, 1975; Shukla and Taylor, 1976) usually give fairly accurate results. The "vertical" component \(W_v\) of \(W_e\), however, can only be studied through measurements of \(\lambda_e\).

From the measured values of \(\partial \lambda_e / \partial P\) given before it is possible to calculate the approximate pressure dependence of \(W_v\). To do this, previously published values of \(L_e\) have been used to obtain the ratio \(W_v/W_e\). The values of \(L_e\) were taken from Matsumura and Laubitz (1970) for silver, Cook et al. (1976) for aluminium, Cook and van der Meer (1970) for gold, and Moore et al. (1967) for copper. The values of \(\sigma(P)\) used in the calculation were those given earlier in table 9.III. The final results for \(\partial W_v / \partial V\) are shown in the same table together with the results previously found. Although the accuracy of these results is very low, it is clear from the table that the pressure dependence of \(W_v\) for the noble metals is large, as indeed it must be to explain the positive pressure coefficient of \(L_e\).
Table 9. III Pressure dependence of $\sigma$, $\lambda_e$, $L_e$, and $W_v$ for the metals investigated.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$[\lambda_e(0)]^{-1} \frac{\partial \lambda_e}{\partial P}$ (GPa$^{-1}$)</th>
<th>$[\sigma(0)]^{-1} \frac{\partial \sigma}{\partial P}$ (GPa$^{-1}$)</th>
<th>$[L_e(0)]^{-1} \frac{\partial L_e}{\partial P}$ (GPa$^{-1}$)</th>
<th>$-[W_v(0)]^{-1} \frac{\partial W_v}{\partial P}$ (GPa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$3.9 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
<td>$0.1 \times 10^{-2}$</td>
<td>$6.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Au</td>
<td>$3.8$</td>
<td>$2.1$</td>
<td>$0.8$</td>
<td>$13$</td>
</tr>
<tr>
<td>Cu</td>
<td>$2.9$</td>
<td>$2.1$</td>
<td>$0.8$</td>
<td>$13$</td>
</tr>
<tr>
<td>Al</td>
<td>$3.7$</td>
<td>$4.6$</td>
<td>$-0.9$</td>
<td>$-2.4$</td>
</tr>
<tr>
<td>Al</td>
<td>$4.6$ (teor. $\frac{\partial \rho}{\partial P}$)</td>
<td>$4.6$</td>
<td>$0$</td>
<td>$4.7$</td>
</tr>
</tbody>
</table>

It is possible, of course, that the high values found are due to experimental errors. However, similar results are obtained starting from the experimental results of Starr (1938), who used a quite different method to find $\lambda_e/\partial P$. The calculation of $\lambda_e/\partial P$ might also be in error due to errors in $\lambda_p/\lambda$ or $\lambda_p/\partial P$. The values of $\lambda_p$ used, however, are considered to be fairly accurate. The possibility that equation (8.3) gives erroneous results for $\lambda_p/\partial P$ must, of course, also be considered. Therefore, $\lambda_p/\partial P$ was calculated for copper and aluminium from equation (8.2), using values of $\lambda_p/\partial (\ln \nu)$ from Kor et al. (1974) and $\lambda_p/\partial (\ln \gamma)$ from Tolpadi (1974). The results obtained were in good agreement with those obtained from equation (8.3). There might, of course, also be errors in the values of $L_e/L_0$ and $\sigma(P)$ used. However, it is believed that the high values of $\partial W_v/\partial P$ for the noble metals are real, even if the accuracy of the results might be low. On the other hand, the results for aluminium indicate that $\partial W_v/\partial V$ for this metal is not very large. If the experimental results for $\partial \rho/\partial P$ are used in the calculation of $\lambda_e/\partial P$, the resulting volume dependence of $W_v$ is opposite in sign to that found for the noble metals. If a theoretical $\partial \rho/\partial P$ is used, however, the volume coefficients of $W_v$ and $W_e$ are almost identical. The results for this metal are thus rather inconclusive, showing only that the pressure coefficient of $W_v$ probably is small. This is, of course, in good agreement with the theo-
tical predictions in section 8.3.2, but the large experimental errors preclude any definite statements about the agreement with theory.

The fact that $\partial W_v / \partial V$ for aluminium is much less than for the noble metals suggests an explanation in terms of Fermi surface distortion under pressure. As mentioned in section 8.3.2, the vertical scattering term in (8.7) contains a factor $(k_F/q_D)^2$ not present in (8.6). In the free electron model this factor corresponds to the ratio between the area of the Fermi surface and the Brillouin zone. If, now, the area of the Fermi surface does not change with volume in the same way as the area of the Brillouin zone, this might lead to a volume dependence of $W_v$ which differs from that given by simple theory. This model might thus explain why aluminium, whose Fermi momentum changes with volume according to the free electron model, has a small $\partial W_v / \partial V$, while the noble metals, whose Fermi surfaces distort under pressure, have quite large values of $\partial W_v / \partial V$.

From what has been said above it would thus seem that the very good agreement between the experimentally found pressure coefficients of $\lambda_e$ for gold and silver and the theoretical predictions of equation (8.10) might, indeed, be fortuitous. The pressure dependence of the "horizontal scattering" part of $W_{ep}$, as given by $\sigma(P)$, is clearly less than that predicted by (8.10). This small pressure dependence of horizontal scattering, however, is instead offset by a large pressure dependence of $W_v$, which is possibly brought about by increasing distortions of the Fermi surface under pressure. The net result of these two effects would thus be to bring the total pressure coefficient of $W_{ep}$ into good agreement with free-electron theory. There might, of course, be an alternative explanation to the fact that (8.10) predicts the pressure dependence of $W_{ep}$ so accurately. This question could possibly be resolved by a theoretical calculation of $W_{ep}(V)$, starting from first principles. Unfortunately, no such calculation has yet been done.

To conclude this section all available accurate data for the pressure coefficients of the thermal conductivity of metals about room temperature have been collected in table 9.IV. All data have been reduced to the basic volume dependence, using $\rho(P)$ values from Vaidya and Kennedy (1970). In the table are shown measured results from this
work and from Starr (1938), and also the results for lead and tin obtained by Bridgman (1922) by a radial heat flow method. For aluminium two sets of values are shown, corresponding to using the experimental or the theoretical values for $\frac{\partial c_p}{\partial P}$ in the calculation of $\frac{\partial \lambda}{\partial P}$.

The table gives the volume dependences for $\alpha$ (for this work only), for the total $\lambda$, and for $\lambda_e$ only. As a comparison the values for the volume coefficients of $W_{ep}$ are shown computed from equation (8.10). The volume coefficients of $W_v$ are given for aluminium and the noble metals; for lead and tin the accuracy of the data was not judged large enough to warrant a calculation. Finally the volume coefficients are given for $\sigma$ and for the electronic Lorentz function $L_e$.

The table contains virtually all existing accurate data on the pressure dependence of the thermal conductivity of metals. It can thus be seen, from the size of this table, that very much work remains to be done in this field, both regarding the number of materials investigated and also the temperature range over which measurements are done.
Table 9. IV Initial pressure coefficients of the thermal and electrical conductivities of metals. References are: [1]-this work, [2]-Starr (1938), [3]-Bridgman (1922). $\sigma(P)$ is taken from Bridgman (1938, 1951). $x$ denotes that a theoretical $\sigma_c/P$ was used in the calculation.
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Finally, I would like to thank Lisbeth and Björn for their constant support during these years, and for their patience with me during these last months when we have been together far too little.

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APPENDIX A

PRESSURE DEPENDENCE OF THE THERMAL CONDUCTIVITY, THERMAL DIFFUSIVITY, AND SPECIFIC HEAT OF SOME POLYMERS.

A.1 Introduction

The equipment described in section 3 was first tested by comparing the results for $\phi$ and $q$ given by this apparatus to those obtained by applying the same input signals to an XY-recorder and analyzing the resulting Lissajous figures. Since this test was successful, the equipment was then used for testing the Ångström method. The results have been presented in section 2. After this, the measuring equipment was used in a measurement of the thermal properties of several polymers under pressure. These measurements were made in collaboration with Dr. Per Andersson. Since this work was not connected with the work on metals in any way, except that the same electronic equipment was used, the experiments will only be described very briefly in this appendix. For the present, the main interest in this work lies in the opportunity to test the equipment thoroughly. Also, this work served as an excellent introduction for the author to the field of practical high pressure physics.

A.2 Experimental details

The materials investigated in this experiments were poly(methyl methacrylate (PMMA, also known under the trade names Perspex or Plexiglas), polystyrene (PS), and atactic and isotactic polypropylene (PP). The purity of the PMMA was stated by the manufacturer to be 99.95 %, while the other materials were of commercial purity. The measurements were performed in the same belt apparatus as described in section 4.1, and a typical high pressure cell is shown in figure A.1. The sample was constructed from three cylindrical parts, stacked upon each other, for all materials except atactic PP. This was too soft to be machined, and was therefore melted and poured into the pyrophyllite cell with thermocouples and heater in position.

Thermal conductivity was measured by a steady state radial heat flow method while the thermal diffusivity was obtained by the periodic radial heat flow method described in section 2.3. From the measured $\lambda$ and $\alpha$, 
\( \rho c_p = \lambda / a \) could be found. The equipment described in section 3 was used to generate and analyze the temperature wave in the measurements of \( a \), and from the values of \( \phi \) and \( q \) obtained \( a \) could be calculated using equation (2.6).

Pressure calibration was carried out as described in section 5.3, using a coaxial cerium-bismuth-thallium wire. Fixed points on the pressure scale were thus obtained at 0.75, 2.55, and 3.7 GPa. The manganin heater wire was used to obtain a linear interpolation scale. Pressure gradients in the pressure cell were measured in a separate experiment, and the pressure scale was corrected accordingly. Furthermore, geometrical correction factors necessary for the accurate calculation of \( \lambda \) were measured in separate experiments.

A.3 Results

Figures A.II and A.III show the average results obtained for \( \lambda(P) \) and \( a(P) \) for the different materials investigated. Five samples of each material were used for the measurements, and the error bars represent the maximum variation in results between different samples. The cal-
Fig. A.II  Average results for $\lambda(P)$ for the different materials investigated. Error bars represent the maximum variation in results between different samples.

Fig. A.III  Average results for $a(P)$ for the materials investigated.
calculation of \( \lambda \) requires a knowledge of sample length. Compressibility data for PP at high pressure are not available, however, and therefore only the results for PMMA and PS could be corrected, using \( \rho(P) \) from Bridgman (1948). As can be seen from figure A.II, this correction is fairly large; since atactic PP is still more compressible, the correction should be even larger in this case.

No theoretical discussion of the results will be given here, since this work has no connection with the main line of this thesis. The results have been previously discussed by Andersson and Sundqvist (1975).

The method used to determine \( \lambda \) in this investigation has several interesting features. One of them is that \( \lambda \) can be determined separately from either \( \phi \) or \( q \). If the values of \( \lambda \) obtained by these two methods are not equal, two sources of error are possible: either the measurements of \( \phi \) and \( q \) are in error, or there are reflections of the temperature wave in the sample against the outer, cylindrical wall. Figure A.IV shows a typical result for one pressure run on one sample of PMMA. The circles indicate results obtained by the amplitude method, while the triangles indicate results given by the phase method. Both methods are in excellent agreement, and this was taken to mean both that reflections were negligible and that the equipment gave correct values for \( \phi \) and \( q \). Also, this series of experiments showed that the equipment was reliable and easy to use, and that the repeatability in the measurements was much superior to that obtained when using the method of Lissajous figures.

Fig. A.IV
Comparison between results obtained for \( \lambda(P) \) for PMMA by two different methods.
APPENDIX B

A LOW NOISE PREAMPLIFIER

B.1 Introduction and definitions

In this appendix, the low noise preamplifier mentioned in section 3.3.1 will be described in some detail.

The limiting factor in low-level measurements is in many cases thermal noise in the measuring equipment. To optimize such a measurement, it is therefore desirable that the equipment noise is as low as possible compared to the thermal noise generated by the source resistance $R_s$. The mean square noise voltage $E_n^2$ developed in this resistance is given by $E_n^2 = 4kT R_s \Delta f$ (Benedict, 1967), where $\Delta f$ is the bandwidth used in the measurement. Since electrical noise is a random phenomenon, noise voltages produced by two independent sources can not be simply added to find the total noise. On the other hand, the total noise power must be the sum of the individual noise powers. The total noise voltage $E_n$ produced by two independent noise sources with output noise voltages $E_1$ and $E_2$ is therefore given by $E_n^2 = E_1^2 + E_2^2$. This formula is, of course, only applicable if $E_1$ and $E_2$ are fully uncorrelated, that is, independent of each other.

When noise is present in a circuit, such as an amplifier, it is very important to have a way to describe how much noise is added by this circuit to the signal handled. This can be described in a variety of ways. In this section we shall use the noise figure $F$, defined as $F = \frac{P_{on}}{P_{sn}}$, for this purpose. In this expression $P_{on}$ is the total available output noise power from a circuit and $P_{sn}$ is that portion of the output noise power which is caused by the thermal noise of the source resistance.

B.2 Theory

Noise in an electronic system is in general a very complicated phenomenon. Any electrical component is a potential source of noise, and since an amplifier consists of many components a general analysis of amplifier noise can be very difficult. Therefore, in most cases a simple noise model is used to simplify the calculations. We shall not go very deep into this complex subject, and for further studies the interested reader
Fig. B.1 Amplifier noise model, including the signal source (within the dashed line).

is referred to Motchenbacher and Fitchen (1973).

The most common model of a noisy amplifier is that shown in figure B.1. The amplifier can be represented by an ideal noise-free amplifier (A) and two noise generators, located at the input: A voltage noise generator with an output voltage $E_n$ and a current noise generator with an output noise current $I_n$. In this analysis we shall assume these generators to be uncorrelated. (This is in most cases a good approximation.) In the figure the signal source is also shown. The noise voltage generated by the source resistance $R_s$ is represented by the noise generator $E_g$. From an inspection of this figure it is immediately seen that the input noise to the amplifier is $E_i^2 = E_s^2 + E_n^2 + I_n^2 R_s^2$. Since the following amplifier is ideal, no further degradation of the signal occurs, and the noise factor of the circuit is

\[ F = E_i^2 / E_s^2 = 1 + (E_n^2 + I_n^2 R_s^2) / E_s^2 = 1 + \left( E_n^2 / R_s + I_n^2 R_s / 4 k_B T \Delta f \right) / E_s^2 \]

For given values of $E_n$ and $I_n$ this expression has a minimum $F_{\text{min}} = 1 + E_n I_n / 2 k_B T \Delta f$ for $R_s = R_{\text{opt}} = E_n / I_n'$. $R_{\text{opt}}$ is generally in the range $500 \, \Omega - 100 \, k\Omega$ for amplifiers with bipolar transistor inputs and > 50 k\$ for field effect transistor inputs.

For $R_s < R_{\text{opt}}$ the dominating amplifier noise source is $E_n$. In the present work the signal source is a thermoelement, and $R_s$ is generally in the range $10 - 100 \, \Omega$. The simplest way to obtain a low noise figure from such a low-impedance source is to use a transformer between source and amplifier to provide impedance matching and voltage step-up. A transformer, however, has many drawbacks, especially regarding phase and gain linearity, at very low frequencies (Andersson, 1973; appendix B). Another way of obtaining a low $R_{\text{opt}}$ is to use several amplifiers.
connected in parallel (Faulkner, 1966; Motchenbacher and Fitchen, 1973, p. 246; Matsudaira, 1974). This is the approach used here. To see how this lowering of $R_{\text{opt}}$ is brought about, we can suppose that we have $N$ identical amplifiers, connected with their inputs in parallel (see figure B.II.). Each amplifier is, as before, represented by an ideal amplifier and two input noise sources, and has a gain $G$. The output voltages and current of the noise sources denoted by $E_{n1}$ and $I_{n1}$ is $E_n$ and $I_n$, respectively. Let the amplifier outputs be summed together in a subsequent stage. The output signal of the unity gain summing amplifier then consists of three parts:

1) The part due to $E_s$. In this case the input signal is the same to all amplifiers, and the outputs are added linearly, giving $NGE_s$.

2) The part due to $E_{n1}$. Each input amplifier receives its own input noise voltage only. Since the sources are uncorrelated, the total signal after summing is $N^{1/2}GE_n$.

3) The part due to $I_{n1}$. All these currents go through $R_s$. Since the current sources are uncorrelated, the total voltage over $R_s$ is $N^{1/2}I_nR_s$. This voltage constitutes a common input signal to all amplifiers, and a linear addition gives the output signal as $N^{3/2}GI_nR_s$.

---

Fig. B.II  Parallel connection of $N$ noisy amplifiers
Since the three different parts above are not correlated, the total output noise signal $E_{n0}^2$ is given by $E_{n0}^2 = N_2^2E_2^2 + N_3^3E_3^2 + N_4^4I_4^2R_4^2$. That part of $E_{n0}^2$ which is due to thermal noise in $R_s$ is $N_2^2E_2^2$, and thus

$$F = 1 + (NE_n^2 + N_3^3I_3^2R_3^2)N_2^2E_2^2 = 1 + (E_n^2 + N_3^3I_3^2R_3^2)/(4Nk_BTR_s\Delta f) = 1 +$$

$$+ (E_n^2/NR_s + NR_sI_3^2)/(4k_BT\Delta f).$$

The minimum noise figure is $F_{\text{min}} = 1 + E_nI_n/2k_BT\Delta f$, and this occurs when $R_s = R_{\text{opt}}' = R_{\text{opt}}/N = E_n/NI_n$. The minimum noise figure is the same as before, but occurs for a lower $R_s$. The composite amplifier can equivalently be considered to have an input noise voltage $E_n/N^{1/2}$ and an input noise current $I_nN^{1/2}$. Thus, for a low impedance ($R_s \ll R_{\text{opt}}$) signal source, where $E_n$ is the dominant noise source, the total equivalent input noise voltage can be decreased by a factor $N^{1/2}$ if $N$ amplifiers are connected in parallel.

Of course, $N$ cannot be increased indefinitely for economic reasons. Also, since the noise decreases as $N^{1/2}$ not much can be gained by increasing $N$ over perhaps 25; besides, increasing input capacitance might become a problem.

### B.3 Amplifier design and construction

When the decision had been made to replace the original chopper stabilized input amplifier by a new amplifier, commercially available operational amplifiers were first surveyed to find a suitable type. The specifications to be filled included a peak-to-peak noise less than .4 μV (equivalent to a temperature noise of 10 mK) in the frequency range 0.05 - 2 Hz, and low drift. The mono OP-07C, a monolithic integrated operational amplifier manufactured by Precision Monolithics, Inc., was found to give a very good performance. The manufacturer's data sheet indicated a typical $E_n = 0.38 \mu V_{\text{p-p}}$ for the range 0.1 - 10 Hz and a typical input offset voltage temperature drift of 0.5 μVK$^{-1}$. The input noise current was given as typically $I_n = 15 \text{ pA}_{\text{p-p}}$ and could be neglected.

This amplifier was tested and found to give much better performance than the previously used input amplifier, due to the absence of chopper noise. However, the input noise in the frequency range of interest was
still about 0.45 $\mu V_{pp}$, and an improvement was desirable.

A parallel connection of several amplifiers was tried and this proved to give the desired results. The optimum source resistance for the individual amplifiers is typically $R_{opt} = E_n/I_n = 0.38 \times 10^{-6}/15 \times 10^{-12} \Omega = 25 \, k\Omega >> R_s$, and thus a decrease in a noise voltage proportional to $N^{1/2}$ was found. Preliminary experiments on six parallel amplifiers (Sundqvist and Bäckström, 1975) showed that it was possible in this way to reduce the input noise to 0.15 $\mu V$ in the range 0.1 - 10 Hz.

The final amplifier design is shown in figure B.III (one channel only). The amplifier consists of $N$ amplifiers, each with a gain of 1000, connected in parallel, followed by a summing amplifier with gain 20. The summing amplifier is provided with an offset voltage compensating circuit. These two stages are powered with a special floating power supply to avoid ground loops and earthing problems. For the same reason the output circuit consists of a unity gain differential amplifier powered from the main power supply.

The preamplifier has two channels. The number $N$ of individual amplifiers in the preamplifiers was adjusted according to the expected input voltage levels: in the lower input level channel $N = 18$, while in the other channel $N = 4$. All the individual amplifiers were mounted in holes in a common copper block to minimize thermal drift, and the whole of the preamplifier was encased in a mu-metal shield to avoid mains-frequency hum pick-up.

B.4 Measured results

The improvements obtained by using several amplifiers in parallel should be the following: 1) Lower noise; 2) Lower offset voltage; 3) Lower thermal drift. Properties 2) and 3), of course, follow only if the values of offset voltage and thermal drift of the individual amplifier are randomly distributed.

Measured typical values for offset voltage and noise for the individual amplifiers are: Input offset voltage: 100 $\mu V$; Wide-band noise at gain 1000: 2.2 $\mu V_{pp}$; Noise in the band 0.1 - 10 Hz: 0.4 $\mu V_{pp}$ (measured through a two-pole band-pass Chebyshev filter with -3dB at 0.1 and 10 Hz, and 1 dB ripple in the passband.) All measurements were taken on a Tektronix 564
Fig. B.III Simplified input amplifier schematic. One channel only is shown. All input amplifiers are type OP-07. All circuitry to the left of the dashed line is powered by a separate floating power supply.
storage oscilloscope. Measured data agreed well with what was theoretically predicted. With \( N = 18 \) the following experimental data was found (theoretical values predicted from the individual data in parenthesis):

- **Wide-band noise voltage:** 0.57 \( \mu \text{V} \) (0.52 \( \mu \text{V}_{\text{p-p}} \))
- **Input noise 0.1 - 10 Hz:** 0.10 \( \mu \text{V}_{\text{p-p}} \) (0.09 \( \mu \text{V}_{\text{p-p}} \))
- **Input offset voltage:** 55 \( \mu \text{V} \)

(All parameters measured with the input short-circuited.)

Bandwidth (-3 dB) DC-590 Hz.

Data for the other channel (\( N = 4 \)) was in similarly good agreement with theory.

Offset voltage and thermal drift were not improved to the extent expected. In the first measurements on six parallel amplifiers (Sundqvist and Bäckström, 1975) these parameters were improved by much more than the factor \( \sqrt{6} \approx 2.5 \) expected over those of the individual amplifiers. In that case, the measured values were: Input offset voltage: 22 \( \mu \text{V} \) (80 \( \mu \text{V} \)), thermal offset voltage drift 0.16 \( \mu \text{VK}^{-1} \) (0.74 \( \mu \text{VK}^{-1} \)), where the values in parenthesis are the mean of the absolute values of the same parameter for the individual amplifiers. However, the second batch of amplifiers acquired proved to be almost identical in their input offset properties, probably due to simultaneous processing at the factory. Thus, the improvement obtained when these amplifiers were connected in parallel with the others was only marginal; temperature drift and offset voltages were both slightly worse for the amplifier with \( N = 18 \) than for that with \( N = 6 \). This is not important, however, since the input offset voltage can be eliminated in the second amplifier stage, and the large thermal mass of the mu-metal shield and the copper block, in which the amplifiers are mounted, precludes any large effects of thermal drift.

The new amplifier was found to work very satisfactory, and was a great improvement over the original input amplifier. Using this amplifier the limiting factor in the measurement was found to be mains hum, which was picked up by the thermoelements, and never amplifier noise or drift.
FORMULAS FOR CALCULATION OF $q$ AND $\phi$

In this appendix we shall show the derivation of equations (3.6) - (3.9). The notation used will be the same as that used previously in deriving equation (3.5). The starting point is equation (3.4), which gives the voltages obtained from the sampling procedures as

$$E_{kj} = A_k + B_k \cos (\omega t_j + \psi_k) \quad (3.4)$$

By rearranging the terms and squaring we obtain, after summing over all terms,

$$\sum_{j=1}^{N} (E_{kj} - A_k)^2 = B_k^2 \sum_{j=1}^{N} \cos^2 (\omega t_j + \psi_k) =$$

$$= (B_k^2/2) \sum_{j=1}^{N} [1 + \cos 2(\omega t_j + \psi_k)] =$$

$$= NB_k^2/2 + (B_k^2/2) \text{Re} \left[ \sum_{j=0}^{N-1} \exp 2i(\omega t_j + 2\pi l/N + \psi_k) \right].$$

Here $t_j = t + 2\pi l/\omega N$ where $l = j-1$. The last expression above is a geometrical series and can easily be summed:

$$\sum_{l=0}^{N-1} \exp 2i(\omega t + 2\pi l/N + \psi_k) = \left[ \exp 2i(\omega t + \psi_k) \right] \sum_{l=0}^{N-1} \exp 4\pi l/N =$$

$$= \left[ \exp 2i(\omega t + \psi_k) \right] \left[ \exp 4\pi \left( (\exp 4\pi i/N) - 1 \right) \right].$$

For $N > 2$ this expression is zero, and thus

$$\sum_{j=1}^{N} (E_{kj} - A_k)^2 = NB_k^2/2 \quad (3.6)$$

which is identical to equation (3.6). This can be further rearranged. Using equation (3.5) we obtain

$$B_k^2 = (2/N) \sum_{j=1}^{N} (E_{kj} - A_k)^2 = (2/N)(\sum_{j=1}^{N} E_{kj}^2 - 2 A_k \sum_{j=1}^{N} E_{kj} + \sum_{j=1}^{N} A_k^2) =$$

$$= (2/N) \left( \sum_{j=1}^{N} E_{kj}^2 - 2 A_k \sum_{j=1}^{N} E_{kj} + \sum_{j=1}^{N} A_k^2 \right) = (2/N)(\sum_{j=1}^{N} E_{kj}^2 - NA_k^2) \quad (3.7)$$
To obtain the expressions (3.8) and (3.9) for the phase difference between the channels we explicitly use \(k = 1\) and \(2\) and write the sum of cross-multiplied terms

\[
\sum_{j=1}^{N} (E_{1j} - A_1)(E_{2j} - A_2) = B_1B_2 \sum_{j=1}^{N} \cos(\omega t_j + \psi) \cos(\omega t_j + \psi) =
\]

\[
= (B_1B_2/2) \sum_{j=1}^{N} \left[ \cos(2\omega t_j + \psi + \psi) + \cos(\psi - \psi) \right].
\]

However, we have just shown above that for \(N > 2\)

\[
\sum_{j=1}^{N} \cos(2\omega t_j + \psi) = 0,
\]

and thus

\[
\sum_{j=1}^{N} (E_{1j} - A_1)(E_{2j} - A_2) = (NB_1B_2/2) \cos \phi
\]

(3.8)

In the same way as before the terms can be rearranged to give

\[
\cos \phi = (2/NB_1B_2) \sum_{j=1}^{N} (E_{1j} - A_1)(E_{2j} - A_2) =
\]

\[
= (2/NB_1B_2)(\sum_{j=1}^{N} E_{1j}E_{2j} - A_1 \sum_{j=1}^{N} E_{2j} - A_2 \sum_{j=1}^{N} E_{1j} + NA_1A_2).
\]

Using once again equation (3.5) we obtain

\[
\cos \phi = (2/NB_1B_2)(\sum_{j=1}^{N} E_{1j}E_{2j} - NA_1A_2).
\]

(3.9)
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