UNIVERSITY OF LONDON

THE EFFECT OF PLASTIC DEFORMATION ON THE
LATTICE THERMAL CONDUCTIVITY OF ALLOYS

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in the Faculty of Science

by

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Abstract

The thermal conductivity of a series of alpha-phase copper aluminium alloys has been measured between 1.5 and 4.2°K. Lattice thermal conductivities have been deduced by assuming the validity of the Wiedemann-Franz law. The results for the annealed specimens have been compared with the kinetic model of lattice conductivity using Callaway's theory and phonon mean free paths derived from Pippard's theory of ultrasonic attenuation. It is shown that by a choice of mean free path consistent with the absence of any detectable cubic term in temperature in the lattice conductivity, the qualitative agreement between theory and experiment is good. Comparison of the thermal conductivities of annealed polycrystals and single crystals indicates the existence of a small negative linear term in temperature due to boundary scattering.

Polycrystalline specimens were deformed in tension, and the resulting increases in lattice thermal resistivity measured. The dislocation densities introduced were measured by transmission electron microscopy, and the thermal resistivity per unit dislocation density obtained. The magnitudes for the latter are 2 to 6 times as great as those obtained experimentally for alpha-brass by Kemp et al. and Lomer and Rosenberg, and 15 to 50 times as great as the values obtained theoretically for pure copper by Klemens and Bross and Seeger; moreover, an apparent variation in dislocation phonon scattering power with aluminium content is observed. The possibility that this is due to dislocation pile-ups is considered.
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Table 7.3 page 98, figs.7.3 and 7.4 on pages 101 and 102 respectively. Values of the flow stress should be multiplied by 1.7.
Notes

1) Tables, diagrams, and plates will be found, in that order, at the ends of the relevant chapters.

2) The abbreviation \( \text{A/o} \) for atomic percent will be used throughout, and when used by itself refers specifically to copper aluminium alloys.

3) The copper aluminium alloys used in this work are in general referred to by their nominal compositions. For their actual compositions see table 2.1.
Chapter 1

1.1 Introduction.

The initial aim of the research described in this thesis was to use the measurement of the lattice thermal conductivity of alloys at low temperatures to determine dislocation density. This technique requires calibration, which means that the dislocation densities in strained specimens must be obtained by an independent method. For this, transmission electron microscopy was chosen. This calibration is as far as the experiments have progressed towards the initial aim. The reasons are twofold. Firstly the existence or otherwise of small terms linear or cubic in temperature in the lattice thermal conductivity of alloys is in question, and is of fundamental theoretical interest. To investigate this, experimental methods need to be as refined as possible, and much care was taken to improve the accuracy and reliability of the measurements. Secondly, values obtained for dislocation phonon scattering in the copper alloys used in this work did not agree with those obtained by other workers on different copper alloys; moreover, the results described in this thesis indicate that apart from a variation with solute type, there may also be a variation in dislocation phonon scattering with solute content.

1.2 Lattice thermal conductivity

In what follows, the theory of lattice thermal conductivity is presented in a simple form. It can be found discussed fully in a number of reviews, for example Klemens, 1958, and Carruthers, 1961.

It is shown in many text books, for example Ziman, 1960, Peierls, 1955, that in the harmonic approximation the vibrational energy of a lattice may be represented by a hamiltonian $H$ where

$$H = \sum_{q,j} \left( N_j(q) + \frac{1}{2} \right) \hbar \omega_j(q),$$  \hspace{1cm} (1.1)

$N_j(q)$ is the distribution function for phonons of wave number $q$ and angular frequency $\omega_j(q)$, and the sum is to be taken over all modes $j$. 

The equilibrium value of the distribution function, \( N_j(0,q) \), is given by

\[
N_j(0,q) = \left( \exp \left( \frac{\hbar \omega_j(q)}{kT} \right) - 1 \right)^{-1} \quad (1.2)
\]

where \( \hbar \) is Planck's constant, \( k \) is Boltzmann's constant, and \( T \) is the absolute temperature. At any time the heat flow \( Q \) is given by

\[
Q = \sum_{q,j} N_j(q) \hbar \omega_j(q) C_j(q) \quad (1.3)
\]

where

\[
C_j(q) = \frac{\partial \omega_j(q)}{\partial q} \quad (1.4)
\]

is the group velocity of phonons of wave number \( q \) in mode \( j \). If \( N_j(q) \) has its equilibrium value given by Eq.(1.2), \( Q \) is zero. In the harmonic approximation, for an infinite and perfect crystal, any deviation of \( N_j(q) \) from equilibrium will persist indefinitely giving an infinite thermal conductivity. In general there will be scattering processes which limit the thermal conductivity. It is assumed in the relaxation time approximation that the scattering processes define a relaxation time \( r_j \) such that

\[
\left. \frac{\partial N_j(q)}{\partial t} \right|_{\text{collisions}} = \frac{N_j(0,q) - N_j(q)}{r_j} = - \frac{N_j(q)}{r_j} \quad (1.5)
\]

In the presence of a temperature gradient a steady state will be reached when collision processes tending to decrease \( n_j(q) \) are balanced by the drift of phonons in the temperature gradient which tend to increase \( n_j(q) \). The Boltzmann equation can then be set up:

\[
\left. \frac{\partial N_j(q)}{\partial t} \right|_{\text{collisions}} + C_j(q) \cdot \nabla T \frac{dN_j(q)}{dT} = 0. \quad (1.6)
\]

It is assumed then that the deviation from equilibrium is small, so that in \( \frac{dN_j(q)}{dT} \) one may assume the relation (1.2). One then obtains
\[ n_j(q) = -r_jC_j(q) \cdot \text{grad} T \left( \hbar \omega_j(q) \right)^{-1} S_j(q) \]  

(1.7)

where \( S_j(q) \) is the specific heat associated with the mode \( j \). Substituting Eq. (1.7) into Eq. (1.3), one finds that

\[ Q = \sum_{q,j} r_j C_j(q) \cdot \text{grad} T \cdot C_j(q) S_j(q). \]  

(1.8)

Experimentally it is observed that

\[ Q_\ell = -K_{\ell m} (\text{grad} T)_m \]  

(1.9)

and in the isotropic case, comparison of Eqs. (1.8) and (1.9) gives

\[ K = \frac{1}{2} \sum_j S_j(q)C_j^2(q)r_j(q) \, dq \]  

(1.10)

where the sum over \( q \) has been replaced by an integral. This expression is very similar to that obtained in the kinetic theory of gases if one defines a mean free path \( L_j(q) \) given by

\[ L_j(q) = C_j(q)r_j(q). \]  

(1.11)

Any attempt to calculate values of thermal conductivity from Eq. (1.10) involves many further assumptions. These are discussed in detail by Carruthers, 1961. Some qualitative predictions of the temperature dependence of the lattice thermal conductivity at low temperatures can be made since then \( C_j(q) \) is usually a constant, independent of \( q \), and the specific heat has a \( T^3 \) dependence. It follows that if \( L_j(q) \) varies as \( q^{-n} \),

\[ K \propto T^{3-n}. \]  

(1.12)

This is shown by Klemens, 1958, who also lists the values of \( n \) for various scattering processes. For example, \( n \) has the value of one for electron phonon and dislocation phonon scattering, the value of two for stacking fault phonon scattering, the value of zero for boundary scattering, and the value of four for point defect scattering. These different temperature dependences afford a method of distinguishing
between the presence of different types of crystal defect, which is one reason for interest in lattice thermal conductivity at low temperatures. In metals one also has heat conduction by electrons, and in the next section the methods by which one may separate lattice and electronic contributions to the heat current are discussed.

1.3 Separation of the lattice and electronic components of the thermal conductivity.

In a pure metal, heat is carried by electrons and by lattice vibrations. It is assumed that these two mechanisms can be treated independently, that is

\[ K = K_e + K_g \]

(1.13)

where \( K \) is the total thermal conductivity, and \( K_e \) and \( K_g \) are the electronic and lattice thermal conductivities respectively. If the metal is non superconducting, \( K_e \) is usually far greater than \( K_g \) and existing experimental techniques are not accurate enough to allow even the detection of a lattice conductivity in the liquid helium range. It is well known that the thermal conductivities of dielectric crystals and pure metals are comparable at very low temperatures, and in the former heat is carried by the lattice vibrations alone. The reason why the lattice conductivity of a metal is so small compared with that of a dielectric crystal is that in the latter \( K_g \) is limited at low temperatures by boundary scattering, but in the former it is limited by electron phonon interactions which give a much smaller phonon mean free path.

Three methods of separating \( K_e \) and \( K_g \) have been proposed:

(a) \( K_e \) may be reduced by the application of a magnetic field. This method has not been used with any great success, and will be discussed no further.

(b) At temperatures of the order of \( \frac{T_0}{5} \), where \( T_0 \) is the superconducting transition temperature, the electrons in a superconductor
cannot carry a thermal current, and neither do they scatter phonons (Montgomery, 1958). It is an experimental observation that at a low enough temperature the thermal conductivity in the superconducting state has a $T^3$ dependence and is limited by boundary scattering, just as in the case of a dielectric crystal (Montgomery, 1958, and Rowell, 1960). One is, however, limited to the study of superconducting metals and alloys, and also as the effect of electron-phonon interaction is not negligible until the temperature is less than $T_0$, most measurements must be made below about 1.5°K. Nevertheless studies of $K_g$ in superconductors have yielded some interesting results which will be mentioned later.

(c) $K_e$ may be reduced by alloying, which reduces the mean free path of the electrons, while not much affecting the magnitude of $K_g$. This is the most common method to date, and is the one used in the experiments described in this thesis. In copper alloys which have a residual resistivity $\rho_0$ greater than about one microhm cm., the separation of $K_e$ and $K_g$ may be made with some certainty. The assumption is made that $K_e$ and $\rho_0$ are related by the Wiedemann-Franz law

$$K_e = \frac{LT}{\rho_0} \quad (1.14)$$

where $L$ is the Lorenz number given by

$$L = 2.445 \times 10^{-8} \text{ watt ohm/deg.}^2 \quad (1.15)$$

It then follows that

$$K_g = K - \frac{LT}{\rho_0} \quad (1.16)$$

and one combines measurements of $K$ with measurements of $\rho_0$ on the same specimen. In well annealed alloys of residual resistivity less than about 10 microhm cm. the lattice conductivity is limited by electron phonon scattering, and is predicted by the theory of Klemens, 1954, to be proportional to $T^2$. The theory of Pippard, 1955, 1960, predicts a $T^3$
term with the possibility of additional terms. At liquid helium tempera-
tures the electronic thermal conductivity should be proportional to \( T \), so that Eq. (1.13) may be written as

\[
K = AT + BT^2 + \text{other terms}
\]  

(1.17)

If there are no other terms of cubic or higher order in \( T \) then a plot of \( \frac{K}{T} \) against \( T \) will give a straight line of slope \( B \) and intercept \( A \). Differences between \( A \) and \( \frac{L}{\rho_0} \) can be interpreted either as deviations from the Wiedemann-Franz law, or as indicating the presence of a linear term in \( K_g \). Any significant curvature in the graphs of \( \frac{K}{T} \) against \( T \) would indicate the existence of terms like \( T^3 \) or higher order in \( T \) in \( K_g \).

It can be seen that the interpretation of measurements of the thermal conductivity of alloys at liquid helium temperatures depends rather critically on the validity of the Wiedemann-Franz law. Theory predicts that the law should hold when

(a) the scattering of electrons is elastic
(b) the electrons can be treated as independent of one another
(c) the Boltzmann transport equation is valid

(Wilson, 1953, Chester and Thellung, 1960). Little further can be said about conditions (b) and (c). Inelastic scattering of electrons is expected to give a temperature dependent resistivity, and at liquid helium temperatures \( \rho_0 \) is usually observed to be constant to within a fraction of a percent (Lindenfeld and Pennebaker, 1962, Jericho, 1965) so that the condition (a) is usually satisfied. Most experimental results to date on low residual resistivity alloys indicate that the Wiedemann-Franz law is obeyed to within a few percent. Indeed, some authors have used the value of \( \frac{L}{\rho_0} \) as a point at \( T = 0 \) when drawing graphs of \( \frac{K}{T} \) against \( T \) (Lomer and Rosenberg, 1959), but the accuracy possible with present experimental techniques makes this procedure unjustifiable.

Deviations from the Wiedemann-Franz law have been observed in
dilute noble metal alloys containing small amounts of transition metal as impurity, or as the alloying addition. These alloys often exhibit an electrical resistance minimum (Kjeckshus and Pearson, 1962) and anomalies in the lattice thermal conductivity below 4.2°K have been reported (Chari and de Nobel, 1959, Chari, 1962, 1964). The explanation of these deviations is believed to be the inelastic scattering of conduction electrons from the magnetic impurity atoms. The reason why inelastic scattering of electrons gives rise to deviations from the Wiedemann-Franz law is crudely that whatever the type of scattering, the electron keeps its charge, hence low angle inelastic scattering is effective in reducing $K_e$, but does not much affect the electrical conductivity. This point is discussed by Ziman, 1964.

The situation with regard to the Wiedemann-Franz law in high residual resistivity alloys is rather different, because there is reason to expect a large linear term in the lattice thermal conductivity. This point will be clarified later in this chapter.

1.4 Separation of the various contributions to the lattice thermal resistivity.

It is usually assumed that the lattice thermal resistivity $W_g$ is represented by

$$ W_g = W_e + W_d + W_p + W_b + W_u $$

(1.18)

where the terms on the right-hand side are respectively the resistivities due to electrons, dislocations, point defects, Umklapp processes and boundaries each considered separately (see for example Klemens, 1958, Mendelssohn and Rosenberg, 1961). Carruthers, 1961, has pointed out that this approximation may not be a good one. While it is valid to define a combined relaxation time if the various scattering mechanisms can be considered independently, this is not equivalent to the addition of separately derived resistivities. Fortunately, the conditions under which Eq. (1.18) may be expected to be valid are just those obtaining in
dilute alloys at liquid helium temperatures. Umklapp processes can be ignored at liquid helium temperatures, essentially because the dominant phonon wave number is very much less than the smallest reciprocal lattice vector. Point defect scattering is also negligible, because the phonon wavelength is large compared with the defect strain field. Dislocation phonon scattering and electron phonon scattering both give the same temperature dependence for the lattice thermal resistivity of dilute alloys. Under these conditions it is correct to assume that Eq.(1.18) holds provided no other scattering mechanism is present. If other mechanisms are operating, provided that the $W_e + W_d$ term dominates, Eq.(1.18) is correct to the first approximation. For example, if it is assumed that dislocations, electrons, and boundary scattering contribute to $W_g$, then

$$W_g = \frac{E}{T^2} + \frac{D}{T^2} + \frac{G}{T^2}$$

(1.19)

where the explicit temperature dependences given by Klemens, 1958, are included, and $E$, $D$ and $G$ are respectively temperature independent coefficients which describe the magnitudes of the electron, dislocation and boundary scattering. If Eq.(1.19) is inverted, one has to first order

$$K_g = (W_g)^{-1} = \frac{T^2}{E+D} - \frac{GT}{(E+D)^2}.$$  

(1.20)

Consider now the interpretation of experimental results for dilute alloys. If graphs of $\frac{K}{T}$ against $T$ are linear, and if the Wiedemann-Franz law holds, the small differences commonly observed between the extrapolated intercepts on the $\frac{K}{T}$ axis and values of $\frac{L}{\rho_0}$ indicate either the existence of other scattering processes or the incorrect assumption of a $T^{-2}$ dependence for $W_e$. However, for dilute alloys it is common practice in the literature, and one which will be followed from here on in this thesis, to write $(E+D)$ as $W_g T^2$. That is, although $W_g$ is defined as the total lattice thermal resistivity, $W_g T^2$ loosely refers only to that part
of it which varies as $T^{-2}$. Thus, differences between values of $W_g T^2$ obtained for annealed and strained alloys give values for $W_p T^2$ appropriate to the dislocation densities introduced. Consideration of the values of dislocation densities in annealed alloys, and the values of dislocation phonon scattering obtained in this thesis together with the reservations discussed earlier in this paragraph indicates that $W_g T^2$ in annealed alloys may be taken as limited by electron phonon scattering.

1.5 Experimental review.

In the following review, reference is made to theoretical work on dislocation phonon scattering, and electron phonon scattering, but any full discussion is postponed until Chapters 5 and 8 of this thesis. Pippard's theory of ultrasonic attenuation by electrons can be applied to low temperature thermal conductivity measurements in alloys, and predicts a different behaviour for low residual resistivity and high residual resistivity alloys (Pippard, 1955, 1960). To clarify the presentation, the following classifications have been made:

A Annealed low residual resistivity alloys
B Strained low residual resistivity alloys
C Superconductors and insulators
D High residual resistivity alloys.

The divisions into A, B and D are to some extent arbitrary in that results relevant to all three may be reported in one paper.

1.5A Annealed low residual resistivity alloys.

Interest in the lattice conductivity of alloys at low temperatures arose in part because a knowledge of $W_g T^2$ for a pure metal enables one to distinguish between the Bloch and Makinson coupling schemes for electron phonon interactions. These two coupling schemes are discussed in section 5.2 of this thesis. Kemp et al., 1955, measured the thermal conductivity of a series of silver cadmium and silver palladium alloys. They plotted values of $W_g T^2$, obtained in the manner previously explained,
against impurity concentration, and by extrapolation back to the pure metal obtained a value for $W_gT^2$ for silver. (For an example of the kind of plot used see fig. 4.6.) This value compared well with that obtained by Klemens, 1954, assuming the Makinson scheme, that is assuming equal interaction between electrons and phonons of all polarizations. They also observed that the lattice thermal conductivity of a strained alloy had a $T^2$ dependence, but with a smaller coefficient than for an annealed alloy. This confirmed the temperature dependence of the lattice thermal resistivity introduced by dislocations predicted by Klemens. However, an unexpected rise in $W_gT^2$ with increased cadmium or palladium content was observed. It was thought that this might be due to the change in the electron atom ratio, and changes in the Fermi surface caused by alloying. Therefore Kemp et al., 1957, added a monovalent solute, gold, to copper. This does not change the electron atom ratio, and is unlikely to much affect the Fermi surface. Nevertheless, increases in $W_gT^2$ with added gold in copper were found to be similar in magnitude to those observed for added zinc. As an alternative explanation, they suggested that since dislocations give the same temperature variation as electron-phonon scattering, increases in $W_gT^2$ with impurity content were due to the increased locking in of dislocations by segregation of impurity atoms to them. As support for this hypothesis they gave results for specimens of copper zinc for which $W_gT^2$ was first measured after an anneal at 500°C, and then after an anneal at 850°C. A considerable decrease of $W_gT^2$ in the second case was observed. This was probably due to the annealing out of dislocations not removed by the first heat treatment, and just indicates the inadequacy of a 500°C anneal. Prolonged anneals very close to the melting point were carried out with no substantial decrease in $W_gT^2$ by Birch et al., 1959, for some dilute gold alloys; nevertheless, the idea of locked in dislocations persisted up until 1962 (see for example Kemp and Klemens, 1960). This was in spite of the fact that the magnitudes of the locked in dislocation densities calculated from Klemens' 1958 value of $W_gT^2/N_0$, where $N_0$
is the dislocation density, were typical of those found in highly deformed pure metals; and also in spite of the measurements of White and Woods, 1954, of the lattice conductivity of copper iron alloys. They found that half an atomic percent of iron in copper gives an increase of $W_g T^2$ equivalent to a locked in dislocation density of $5 \times 10^{11}/\text{cm}^2$.

Lindenfeld and Pennebaker, 1962, measured the thermal conductivity of a series of copper germanium alloys at liquid helium temperatures. Their method of measurement was similar to that described in this thesis and gave an accuracy surpassing that of most previous measurements. In obtaining values of $K_g$, they assumed that $K_g$ was given by $\frac{LT}{\rho_0}$, and found that changes in $K_g$ with increased germanium content could be correlated with changes in $\rho_0$. They claim that their results all lie close to a universal curve of $\frac{K_g}{\rho_0}$ against $\frac{T}{\rho_0}$. This was compared with a similar curve calculated from the kinetic formula

$$K_g = \frac{1}{\hbar} \sum_j \int C_j(q) L_j(q) S_j(q) dq$$

which may be obtained from Eq. (1.10) and Eq. (1.11). For $S_j(q) dq$ they used the Debye specific heat function, and the values of $L_j(q)$ for both transverse and longitudinal waves were obtained from Pippard's 1955 theory of ultrasonic attenuation by free electrons. The significant parameter in these calculations is $q_f$, where $f$ is the electron mean free path. At liquid helium temperatures this is physically equivalent to $\frac{T}{\rho_0}$, since then the dominant phonon wave number is proportional to $T$, and $f$ is proportional to $\rho_0^{-1}$. In the calculation of $K_g$ it was assumed that the transverse and longitudinal modes could be treated independently, and that $K_g$ could be obtained by adding the separate contributions. It is significant that agreement between theoretically and experimentally derived curves of $\frac{K_g}{\rho_0}$ against $\frac{T}{\rho_0}$ are only obtained for small $\frac{T}{\rho_0}$, that is high residual resistivity alloys. In this region, $q_f < 1$, the mean free paths for longitudinal and transverse phonons are of the same order of magnitude, but in the region $q_f > 1$ they differ widely. This seems to indicate that the assumption of independent longitudinal and transverse modes may be wrong. Further discussion, and the details of the results
modes may be wrong. Further discussion, and the details of the results of Lindenfeld and Pennebaker are postponed until Chapter 5. Lindenfeld and Pennebaker made a further important contribution: they found directly from transmission electron microscopy that the dislocation densities in their annealed alloys were far too small to account for changes in $W_g T^2$ with germanium content.

This quite definite revocation of the locked in dislocation hypothesis prompted Tainsh and White, 1962, to attempt a reinterpretation of earlier measurements on both dilute copper and silver alloys. They considered that variations in the parameters of Klemens' (1954) equation for the lattice resistivity of a pure metal might explain the changes in $W_g T^2$ with alloying. Klemens' expression is, for $T \ll \Theta_D$,

$$W_g = \frac{1}{313} \left( W_1(T) \left[ \frac{\Theta_D}{T} \right]^4 N_a \right)$$

(1.22)

where $W_1(T)$ is the ideal electronic thermal resistivity and is proportional to $T^2$, $\Theta_D$ is the Debye temperature, and $N_a$ the number of conduction electrons per atom. The changes which must be explained are of the order of 100% to 1000%. $W_1(T)$ as estimated from $(\rho_{\text{ox}} - \rho_0)$ increases by something of the order of 30% between pure copper and copper 10% zinc. $N_a$ changes by very little. Rayne, 1957, observed from specific heat measurements that $\Theta_D$ decreased by about 10% between pure copper and copper 30% zinc. So quite clearly Klemens' expression cannot explain the values of $W_g T^2$ observed in annealed alloys.

1.5B Strained low residual resistivity alloys.

In most of the papers referred to in the previous section, some measurement was made on a strained alloy, and the result compared with that of the same alloy in the annealed condition. Those experiments showed the qualitative correctness of Klemens' 1958 calculation of dislocation-phonon scattering, but no attempts to test his predictions quantitatively were made. In many cases the strained alloys were in the as received, or as drawn, condition, and in no case were values of flow
stress and tensile strain given. Consequently one cannot estimate values of $W_0 T^2/N_p$ by comparison with present data relating flow stress and dislocation density for copper alloys. Lomer and Rosenberg, 1959, obtained the first experimental value for dislocation phonon scattering. They measured the thermal conductivity between 2.2°K and 4.2°K of a series of alpha brasses after various amounts of strain. Both single crystals and polycrystalline specimens were used. For a given specimen, an increase in strain resulted in a decrease of the slope of the $K/T$ against $T$ graphs, and results similar in form to those shown in fig. 7.1 of this thesis were obtained. In the interpretation of their results they assumed that dislocation phonon scattering would be the same in all their alloys regardless of composition. Dislocation densities quoted were obtained by using Klemens' 1958 formula, scaled down by a factor of six. The justification for this was an independent measurement of dislocation density in two strained copper 30% zinc polycrystalline specimens in which transmission electron microscopy was used. Although accurate values of dislocation density could not be obtained, because of the limited number of micrographs taken, it was estimated that Klemens' 1958 formula used in conjunction with values of $W_0 T^2$ gave values of dislocation density which were six times the right size. Thus Lomer and Rosenberg find for alpha brass

$$W_0 T^2 = 3.6 \times 10^{-8} \text{N}_p \text{ watt}^{-1} \text{cm}^{-2} \text{deg.}^3$$ (1.23)

They also found that for polycrystalline specimens, and for single crystals in stage II of deformation, $W_0 T^2$ was proportional to the square of the flow stress.

Kemp et al., 1959, measured the changes in lattice conductivity at liquid helium temperatures of an alpha brass specimen (30% zinc) and an arsenical copper specimen (0.35% arsenic, 0.05% phosphorus) caused by severe torsional deformation. Their specimens were from the same batch of alloys as those used by Clarebrough in the study of stored energy release from deformed metals during annealing (Clarebrough et al.,
1955 and 1960). The portion of the stored energy release due to the annealing out of dislocations can be identified, and assuming the value for the energy of a dislocation in copper given by Cottrell, 1953, the dislocation density can be calculated. In this way Kemp et al. found from their experimental results that Klemens' 1958 formula overestimated dislocation densities by a factor of eight for the arsenical copper, and by a factor of six-and-a-half for the alpha brass. Thus they found
\[ W \rho T^2 = 3.9 - 4.8 \times 10^{-8} \text{N} \rho \text{watt}^{-1} \text{cm.deg.}^{-3} \]  
which is very similar to the value of Lomer and Rosenberg (Eq.(1.23)).

Since 1959, apart from the present work at Battersea, there have been no quantitative estimates of dislocation phonon scattering from low temperature thermal conductivity measurements on alloys. Tainsh et al., 1961, reported measurements of the effect of strain on the thermal conductivity at liquid helium temperatures of two copper silicon alloys. Their specimens were deformed by drawing to a reduction of about 60% in specimen diameter. Identical deformations of a Cu 2.5A/6 Si alloy, and a Cu 4.5A/6 Si alloy gave apparent dislocation densities of 3.5\times10^4 and 7.5\times10^4 respectively. These values were obtained from the changes in \( W \rho T^2 \) between the annealed and deformed alloys using Klemens' 1958 formula, and dividing the resulting dislocation densities by 4.5. This was a correction factor assumed on the basis of the work by Lomer and Rosenberg, 1959, and Kemp et al., 1959. In Chapter 8 of this thesis, those results due to Tainsh et al., 1961, will be shown to afford a different explanation.

1.5c Superconductors and insulators.

Qualitative measurements of dislocation phonon scattering in alkali halide crystals have been made. In good crystals at liquid helium temperatures one is dealing with a pure lattice conductivity limited by specimen boundary scattering. The dislocation densities needed to cause measurable changes in the thermal conductivity are of
the order of $10^6 \text{cm}^{-2}$, which is one thousand times less than those
needed in alloys. In the alkali halides, dislocation densities are
readily obtained from etch pit methods. Although the latter methods can
underestimate dislocation densities, the values are less uncertain than
those obtained from thin film electron microscopy.

Sproull et al., 1959, obtained

$$W_nT^2 = 1.3 \times 10^{-6} N_0 \text{ watt}^{-1} \text{cm.deg.}^3$$

(1.25)

from low temperature thermal conductivity measurements on LiF crystals.
Ishiioka and Suzuki, 1963, from measurements on annealed and deformed
NaCl crystals between 4.2°K and 10°K obtained

$$W_nT^2 = 7 \times 10^{-6} N_0 \text{ watt}^{-1} \text{cm.deg.}^3$$

(1.26)

Both these values differ from those calculated from Klemens' 1958
formula by factors of between one hundred and one thousand. The latter
authors attempted a calculation of dislocation phonon scattering on the
basis of Granato's "dislocation flutter" model (Granato, 1958). This
will be mentioned in Chapter 8.

Taylor et al., 1965, have reviewed the above work, and added some
results of their own. While confirming the values given above, they
also present experimental evidence that values obtained for dislocation
phonon scattering are sensitive to the arrangement of dislocations.
Measurements on a crystal of LiF which had been deformed in such a
manner as to give a distinctly non random dislocation array gave higher
values for $W_nT^2/N_0$ than those obtained for deformed crystals of the
same material in which the dislocation array was more random.

As explained in 1.3, the situation with regard to the lattice
thermal conductivity in a superconducting specimen below $T_c$ is analogous
to that in an insulator. Rowell, 1960, measured the changes in lattice
thermal conductivity in single crystals of lead, a lead alloy, and
niobium caused by deformation. Since lead anneals at room temperature,
the deformation was carried out in the cryostat at 4.2°K by bending the
specimen around a former of radius 12cm. For the niobium specimens, the deformation was carried out at room temperature, and values of tensile strain are quoted. The equivalent tensile strain induced in the lead and lead alloy crystals was calculated from the change in form factor. The latter was obtained from the change in the room temperature resistance of the specimen caused by the deformation. Rowell compared values of Nn calculated from changes in Wg using Klemens' 1958 formula, with those calculated from the tensile strains using a theory due to Van Bueren, 1955. In the light of present knowledge, neither set of values of Nn is reasonable for the plastic strains induced. This will be discussed further in Chapter 8.

1.5D High residual resistivity alloys.

Pippard's theories of ultrasonic attenuation as applied to the lattice thermal conductivity of alloys predict a qualitative difference of behaviour between alloys of low and high residual resistivity. In particular, at low temperatures high residual resistivity alloys (\(\rho_0\) greater than about 10 microhm cm.) are expected to have a term linear in temperature in \(K_g\). Systematic measurements on high residual resistivity alloys were first undertaken in order to detect the existence or otherwise of this term. Before this time, Sladek, 1955, had observed that high residual resistivity indium thallium alloys in the normal state did not obey the Wiedemann-Franz law; Kemp et al., 1956, in their experiments on silver palladium alloys observed that for specimens of high residual resistivity the Wiedemann-Franz law appeared to break down. In both these cases, the discrepancies were such as would be explained by the existence of a linear term in \(K_g\).

Olsen, 1959, pointed out that if Pippard's theories applied, high residual resistivity alloys would be expected to have a lattice conductivity given by:

\[
K_g = CT + BT^2
\]  
(1.27)
where the coefficient $C$ would increase with increasing $\rho_0$. His measurements on dilute copper zinc alloys, however, were not able to confirm this since $\rho_0$ was too small.

The work of Zimmerman, 1959, on copper antimony alloys of residual resistivities between 12 and 40 microhm cm. confirmed the predictions of Pippard's theories. He found that assuming $K_e = \frac{L_T}{\rho_0}$, Eq.(1.27) above was obeyed. Moreover, the value of $C$ increased systematically with $\rho_0$. $C$ was zero for the alloy with $\rho_0 = 12$ microhm cm., and about four times $\frac{L}{\rho_0}$ for the alloy with $\rho_0 = 40$ microhm cm. Zimmerman calculated $K_g$ in the same manner as that used by Lindenfeld and Pennebaker described in 1.5A; however, he assumed that Pippard's attenuation coefficient for longitudinal modes applied to modes of all polarizations. Consequently his theoretical curve of $\frac{K_g}{T\rho_0}$ against $\frac{T}{\rho_0}$ lay well below that from the experimental results. Nevertheless, the qualitative predictions of Pippard's theories were confirmed.

Dreyfus et al., 1962, measured the thermal conductivity of a series of gold cobalt alloys, and found a linear term in $K_g$ when $\rho_0$ was greater than about 10 microhm cm. They also observed a large linear term for an alloy of $\rho_0 = 2$ microhm cm. However, their measurements were between 3°C and 30°C, using gas thermometers, and this latter result may be spurious.

Jericho, 1965, measured the thermal conductivity of a series of silver antimony and silver tin alloys between 0.3°C and 4°C. A helium three cryostat was used. For temperature measurement carbon resistance thermometers were calibrated against a magnetic salt, which was in turn calibrated against the 1958 helium four vapour pressure scale. Allen-Bradley resistors were used down to 0.5°C, and carbon film thermometers below this temperature. The alloys had residual resistivities of between 5 and 40 microhm cm. Assuming $K_e = \frac{L_T}{\rho_0}$, he found that above 1°C $K_g$ was given by Eq.(1.27) above, and that $C$ had significant values for $\rho_0$ greater than 10 microhm cm. The values of $C$ increased with
increasing ρ₀, agreeing with the results of Zimmerman. However, below 1⁰K Jericho found that for some of his alloys graphs of \( \frac{K_b}{T} \) against \( T \) showed a sharp increase in slope. It was thought that this might be due to real deviations from the Wiedemann-Franz law due to the onset of some inelastic scattering mechanism for electrons; the possibility of some phonon scattering mechanism which became dominant below 1⁰K was also considered, but as yet no satisfactory explanation of the effect has been put forward.

Jericho also measured the effect of a few percent strain on the lattice thermal conductivity of an alloy of residual resistivity 18 microhm cm. He found no decrease in \( B \) of Eq.(1.27), but observed a decrease in the value of \( C \).

Following Lindenfeld and Pennebaker, Jericho carried out calculations of \( K_g \) using Pippard's expressions for the mean free paths for electron phonon scattering. In addition to this, he did calculations using a combined mean free path for dislocation phonon scattering + electron phonon scattering and also for a combined mean free path for electron phonon + boundary scattering. These calculations, and his results, will be further discussed in Chapters 5 and 8.
Chapter 2

2.1 Specimen preparation and analysis.

The alloys were supplied by the International Research and Development Co. Ltd., who also carried out the chemical analyses. O.F.H.C. copper and spectroscopically pure aluminium were melted and stirred together in a graphite crucible in an atmosphere of high purity argon. The alloys were cast into ingots in graphite moulds. After the outer layers had been machined away to reduce contamination, the ingots were swaged and drawn down to wire 3mm. in diameter.

The thermal conductivity specimens consisted of 12cm. lengths cut from the 3mm. diameter rods. For the polycrystalline specimens these lengths were annealed at 750°C for at least fourteen hours, and furnace cooled. The single crystal specimens were grown in a graphite mould sealed in an airtight stainless steel container using the Bridgman technique. The rate of lowering was between 1.5 and 2 cm. per hour. The single crystals were also annealed at 750°C for fourteen hours. Copper tags of 0.4mm. thickness for the attachment of thermometers or potential leads were brazed onto the specimens about 6cm. apart.

The chemical analyses were in most cases made on 3cm. lengths of alloy cut adjacent to the thermal conductivity specimens. Where this was done the results are shown in table 2.1.

2.2 The cryostat.

Initially an all metal cryostat incorporating a liquid air radiation shield was built. This was abandoned in favour of a simpler system using a pair of glass Dewars. Fig.2.1 shows the cryostat used in all the measurements. Fig.2.2 shows the lower part of the cryostat drawn on a larger scale to show the mounting of a thermal conductivity specimen. Fig.2.3 is a schematic diagram of the pumping system. In what follows all letters refer to fig.2.1 and all numbers to fig.2.2. The pumping tubes inside the inner glass Dewar were of thin walled stainless steel
tubing. At the top, all pumping lines to the cryostat contained Speedivac screwed vacuum unions (S). This meant that the cryostat was completely demountable, a factor which proved advantageous when mending leaks or replacing electrical leads. When changing specimens, only the Wood's metal join (W) at the outer radiation shield had to be broken and remade. The inner radiation shield (R, 8) was a push fit, with thermal contact ensured by smearing the walls of the small can with vacuum grease. Because of the uncertain effects known to be due to adsorption or desorption of helium (Hoare et al., 1961), this was not used as exchange gas in the vacuum space at any stage. Using air as exchange gas, the cryostat was cooled down to 90°K, which took about two hours from starting to fill the outer Dewar with liquid air. The air exchange gas was then pumped away, and the inner Dewar filled with liquid helium to within about 20cm. of the top. The cooling of the small can (C) from 90°K was accelerated by using helium gas inside it, and introducing a removable copper rod (4) down the centre of the pressure measuring tube (3). This rod was about 15cm. long, fixed to the end of a 3mm. stainless steel tube, and served the purpose of destroying the temperature gradient between the liquid helium and the small can. The small can cooled to 4.2°K in an hour, boiling off about half a litre of helium from the glass Dewar. Once the small can had cooled, the boil off rate from the glass Dewar was less than 50c.c. of liquid helium per hour. The copper rod was withdrawn and the small can filled via the needle valve (N, 1). The pressure in the small can was always less than atmospheric when the needle valve was opened, and it was found that temperature differences of the order of 1°K existed in the liquid helium in the small can just after it had been filled, owing presumably to the Joule-Kelvin effect. In the absence of any disturbance, this temperature gradient persisted for some time, and to enable thermal equilibrium at 4.2°K to be quickly established, a ten ohm resistor was fixed to the base of the small can, and connecting this directly across a two volt accumulator achieved the desired result. The small can when full held
about 40c.c. of liquid helium which lasted at least six hours. It was found that over a period of time pumping the small can below the lambda point became increasingly difficult. The first time this happened, the cause was traced to the development of a lambda leak in the small can (Hoare et al., 1961). The can was replaced, and initially the fault disappeared, but then returned after a period of time. On this occasion an increase in the superfluid helium flow was suspected, due either to deposits of solid air in the pumping line, or to dirt. No leak could be detected below the lambda point, so it was decided to put a constriction \( Q \) in the pumping tube at the entrance to the small can (this is not shown in fig.2.2). Once this was done, no further difficulty was experienced.

The vapour pressure of the helium in the small can was controlled by pumping through a cartesian diver manostat (White, 1959). This was the stainless steel type with the diver floating on mercury, as supplied by Edwards High Vacuum Co. Ltd. It was found to give temperature control to better than a millidegree over the range 2.2°- 4.2°K, as judged from the drift of the thermometer resistances for the period during which a measurement was taken. Previous to the inclusion of a constriction in the pumping line, temperature control below the lambda point was not always possible using the manostat alone. In these cases the manostat bypass valve (fig.2.3) was opened sufficiently to cope with the excess gas flow, and the manostat would then control the difference. However, once the constriction had been included the manostat gave good control over the whole range from 1.5° to 4.2°K. The vapour pressure was measured using a mercury or oil manometer in which Apiezon oil A was used. The manometer tubes were of lcm. bore glass tubing, and a pressure release valve set to 5cm. of mercury above atmospheric pressure was incorporated in the mercury manometer (fig.2.3). Pressure differences were measured with a cathetometer to \( \pm 0.005 \)cm.
2.3 Measurement of thermal conductivity.

The thermal conductivity of a specimen was measured by passing a heat current along it, and measuring the resulting temperature gradient. The mounting of a specimen is shown in fig.2.2, and the numbers given in the text refer to this figure. One end was soldered into a copper lug on the base of the small can, and a heater (7) was soldered to the free end; Wood's metal was used in both cases. Thermometers (5) were attached to the copper tags previously brazed onto the specimen, using Wood's metal. The heater (7), which had a resistance of approximately 1100 ohms at liquid helium temperatures, consisted of 47 S.W.G. nichrome wire wound onto a piece of copper foil to which a layer of cigarette paper had been stuck. A layer of varnish was then put over the wire to ensure thermal contact. The thermometers (5) were 50 ohm, 0.1 watt Allen-Bradley resistors. These were glued into tightly fitting copper sleeves which had been previously soldered onto pieces of copper foil ½x1 cm. There was one junction (2) for the electrical leads on the base of the small can and from there to the external circuit they were of 30 S.W.G. enameled constantan wire, and were taken up the high vacuum pumping line and out through a black wax seal. They were thermally anchored at 4.2⁰K by varnishing them to the inside of the pumping line, and also taking them through a copper lug (2) as shown in fig.2.2. After passing out of the cryostat, they were soldered to a ten way plug, and the leads from the other side of the plug to the measuring circuits were of copper. To reduce thermal emfs, the ten way plug was immersed in a bath of oil. The leads from the thermometers to the junction on the base of the small can were of 47 S.W.G. tinned constantan wire, which was superconducting at liquid helium temperatures. The arrangement of the heater leads is shown in fig.2.4. By this method, if for any reason the wires cease to be superconducting, the effect is detectable, and also partially compensated for, if one may assume that half the power produced in the leads goes to the heater (Hocar et al., 1961). Calculation of heat loss down the leads shows that it is
The circuits for the measurement of heater power and thermometer resistance are shown in figures 2.4 and 2.5 respectively. The heater power was obtained by measuring the voltage across the heater and across a 100 ohm standard resistance in series with it. A Tinsley potentiometer, type 3387 B, was used, and the voltages developed were such that there was no need to use a reversing switch, the thermal emfs being negligibly small. The current supply to the heater was from a 2 volt 80 ampere hour battery of large thermal capacity supplied by Prichett and Gold, and when not actually supplying the specimen heater was switched through a dummy circuit as shown in fig.2.4.

The resistances of the two thermometers were measured by comparing them potentiometrically with a fixed wire wound resistor of nominal value 1000 ohms, which was immersed in an oil bath, and in series with the two thermometers. All values quoted for the resistances of the thermometers are relative to an assumed value of 1000 ohms for the fixed resistance. A measuring current of 1 microamp was used throughout. This was obtained by connecting the thermometer circuit plus a 2 megohm series resistance across a 2 volt accumulator similar to that used to supply the heater current. A Tinsley vernier potentiometer, type 4363 A, was used to measure thermometer resistances, and stepped down by a factor of ten, as shown in fig.2.5. As such it gave readings to 0.1 microvolt on the dials. A galvanometer amplifier (Tinsley type 5214) was used in the null detecting circuit, and both direct and reverse current readings were taken to eliminate thermal emfs. These were usually of the order of a few microvolts. The circuit was found to be very sensitive to stray electric fields; for example, any person wearing a nylon shirt moving near the circuit would cause the galvanometer to go off scale. It was necessary to screen the potentiometer, the galvanometer and the leads as thoroughly as possible.
2.4 Experimental procedure.

During a run, the sequence with which readings were taken was found to be important. An experiment was normally started at 4.2°K, and measurements taken there and at progressively lower temperatures. The temperature interval between successive measurements was about 0.2°K. Initially, the calibration and thermal conductivity measurements were made on separate runs down through the temperature range 4.2°-1.5°K. This naturally took a considerable time, and so attempts were made to take the calibration points and thermal conductivity measurements together. At first, the scatter on the calibration curves was found to be far worse than when a calibration only experiment was done. However, this difference was eliminated by the following procedure. Pumping down through each temperature interval of 0.2°K was done slowly, with the heater off, taking about ten minutes. When the desired temperature had been reached the system was left for a further five to ten minutes to allow equilibrium to be established. Calibration readings were taken then, before switching on the heater and taking the thermal conductivity readings. Calibration points were worked out while the run was in progress, and it could be judged whether or not all was well from the calibration curves. A whole set of readings, that is about fifteen experimental points plus the same number of calibration points could be taken in eight hours. The effect of errors in calibration was found to be critical, and this is discussed in Chapter 3.

2.5 Measurement of residual resistivity.

The residual resistivity of the specimens was measured at 4.2°K by immersing them in liquid helium. A current of the order of one ampere was passed through the specimen, and through a standard 5 milliohm resistor. The voltages across the two were compared using a Diesselhorst potentiometer capable of measuring to better than 0.1 microvolts. A thermoelectric free reversing switch was included in the circuit, direct and reverse current readings being taken to eliminate thermal emfs.
This measuring apparatus was built in the laboratory, and is fully described by Foxon, 1965.
Table 2.1

Composition of specimens (see notes 2 & 3, page 5). Annealed polycrystalline and single crystal specimens are referred to by a number and a number followed by an S respectively. Deformed specimens are referred to in this table by values of the tensile strain.

<table>
<thead>
<tr>
<th>Specimen no. or strain</th>
<th>Nominal comp. (%o)</th>
<th>Mean comp. of ingot (%o)</th>
<th>Actual comp. of specimen (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>1.93</td>
<td>2.09</td>
</tr>
<tr>
<td>2.9%</td>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>10.0%</td>
<td>2</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>3.96</td>
<td>4.22</td>
</tr>
<tr>
<td>10.0%</td>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>6.15</td>
<td>6.10</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>7.45</td>
<td>9.12</td>
</tr>
<tr>
<td>6.0%</td>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>83</td>
<td>8</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10.35</td>
<td>9.40</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>11.60</td>
<td>11.25</td>
</tr>
<tr>
<td>3.4%</td>
<td>12</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>6.2%</td>
<td>12</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>12.8%</td>
<td>12</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>12S</td>
<td>12</td>
<td>&quot;</td>
<td>-</td>
</tr>
</tbody>
</table>
The cryostat. The "O" ring seal through which the cooling rod was introduced and the cooling rod are not shown. The details of the lower part of the cryostat are shown in fig. 2.2. For the meaning of the letters, see section 2.2.
Fig. 2.2

The lower part of the cryostat, showing the mounting of a specimen.

1: the needle valve,
2: thermal anchor posts for the leads,
3: pressure measuring tube,
4: removable copper rod,
5: thermometers,
6: specimen,
7: heater,
8: push fit radiation shield, and
9: the outer high vacuum shield
Fig. 2.3

A schematic diagram of the pumping system.
Fig. 2.4
Circuit diagram for heater.

- $B_1$ - 2 volt accumulator.
- $B_2$ - 2 volt stabilised supply.
- $D$ - dummy heater.
- $G$ - galvanometer.
- $M$ - milliammeter.
- $R$ - rheostats.
- $S$ - 100 $\Omega$ standard resistor.
- $T$ - junction at base of small can.
- $W$ - standard cell.
Circuit diagram for thermometers. For clarity all potential leads are shown by dashed lines.

- 36 -

**Fig. 2.5**

thermometers

junction at base of small can.

- 2 megohm

fixed resistor.

potentiometer.

- B - 2 volt accumulators.
- GA - galvanometer amplifier.
- G -
- RS - reversing switch.
- R - step down rheostat for potentiometer supply.
Chapter 3

3.1 Introduction

In this chapter the derivation of the calibration curves is explained, and by looking at some of the curves obtained in practice the existence of systematic errors, and the form which they take, is demonstrated. An attempt is made to explain the sources of these errors, some of which have been eliminated. Finally the effects which they have on the thermal conductivity results is shown.

The choice of carbon resistors was dictated by their availability, and by the fact that they enable greater accuracy to be attained than is possible with gas thermometers. Other possible methods are to use encapsulated germanium thermometers or to use a thermocouple method (Berman, 1964). At the time when this project was started, neither of the latter methods was available.

3.2 Derivation of the calibration curves.

Clement and Quinnell, 1952, give the following empirical formula for the behaviour of carbon resistors in the liquid helium region:

\[
(\log_{10} R - b)^2 = \frac{a \log_{10} R}{T}
\]

where \( R \) is the resistance in ohms, \( T \) the absolute temperature, and \( a \) and \( b \) are constants. In practice this relation is not obeyed exactly. From an early set of calibration data, graphs of \( \sqrt{\frac{\log_{10} R}{T}} \) against \( \log_{10} R \) were drawn for each resistor. These were more or less the same, being almost straight lines, but slightly concave downwards. A mean value of the slope of these lines was chosen, the same for both resistors, thus fixing the value of \( a \); the actual value chosen being 2.5664. This value was used in all subsequent experiments. Using the formula quoted above, and this value of \( a \), values of \( b \) were worked out for each calibration point, and graphs of \( b \) against \( \log_{10} R \) drawn for each resistor. These graphs are referred to as calibration curves. Thus, taking values of
log_{10} R_1 and log_{10} R_2, where R_1 and R_2 are the resistances of the upper and lower thermometers respectively, values of b_1 and b_2 may be obtained from the calibration curves. Using the formula given in Eq.(3.1) and the known value of a, T_1 and T_2 may be calculated. Thus ΔT = T_1 - T_2 and T = \frac{1}{2}(T_1 + T_2) are obtained.

3.3 Observed calibration curves.

In the earlier measurements it was found that the calibration curves varied considerably from run to run. Moreover, the behaviour of an individual carbon resistor depended upon whether it was used as the top or bottom thermometer on the specimen (see fig.2.3). The type of behaviour observed is shown in fig.3.1 which gives the calibration curves for a run on the 12A6 annealed polycrystalline alloy. Comparison of the latter curves with those obtained when measuring the thermal conductivity of some annealed copper wire indicated the existence of a systematic error. The calibration curves in the copper experiment were similar for both thermometers, and showed no rapid falling off in the value of b. However, the jump at the lambda point was present in both cases, and will be discussed later. As the thermal conductance of the copper specimen was about ten times that of the alloy specimen a comparison of the behaviour in the two cases is indicative of a heat leak which gives rise to a temperature gradient down the specimen. An experiment to determine the calibration curves with the thermometers attached directly to the base of the small can was then carried out. In this case, any heat leak was assumed to have no effect, and the calibration curves obtained are hereafter referred to as "standard". As the existence of a lambda leak was suspected, and shortly after confirmed, the small can was replaced. Following this the calibration curves obtained in different runs were found to be very reproducible, and were close to the standard curves. The extent of this can be judged from fig.3.2, which shows the standard curves, and a pair of calibration curves obtained during a run after the new can was fitted. The
calibration curves for the next eight runs, over a period of three months, fell within the shaded region.

Subsequently deviations from the standard curves did occur, and were usually traced to bad thermal contact between thermometers and specimen. An exception to this was the observation that inadvertent heating of a carbon resistor during soldering at room temperature could cause a permanent change in its liquid helium resistance. The change was such as to increase the value of $b$ by about half a percent, while the form of the calibration curve remained the same. As this effect was reproduced to within $0.2\%$ of $b$ in four subsequent experiments, it was assumed to be a genuine change.

3.4 Discussion of systematic calibration errors.

During calibration it is assumed that the thermometers are at the temperature indicated by the vapour pressure of the liquid helium in the small can. The reasons why this may not be so can be divided into two kinds. Firstly, the measured vapour pressure may not correspond to the temperature of the helium at the bottom of the small can, and secondly, the thermometers may not be at the same temperature as this liquid helium.

Errors of the first kind could arise from measuring the height of the liquid columns in the manometers. Care was always taken that the cathetometer was level, and the telescope focussed on each meniscus in an identical fashion to avoid backlash. The discontinuity in the calibration curves which occurred at the lambda point corresponded roughly to the temperature at which it was convenient to change from the mercury to the oil manometer. A measurement of the density of the manometer oil at $16^\circ$ and $28^\circ$C gave the height of oil corresponding to one centimetre of mercury as 15.54 and 15.62 cm, respectively. By interpolation, an appropriate value was always used, so the jump at the lambda point could not be due to the change of manometer liquid. Since it was observed that the calibration curves down to about $2.7^\circ$K could be taken as being
continuous with the curves below the lambda point, it seemed evident that it was the points immediately above the lambda point which were in error. Accepting this, consideration of Eq. (3.1) (section 3.2) leads to the conclusion that the temperature deduced from the vapour pressure was lower than the temperature of the helium at the bottom of the small can. Two possible explanations are the hydrostatic head effect, or the existence of a temperature gradient at the surface of the liquid helium. The existence of the latter effect has been confirmed by Catalani et al., 1962. The magnitude of the effect as one goes through the surface from liquid to vapour varies from a decrease of a millidegree at 4.2°K to five millidegrees just above the lambda point, and is zero below the lambda point. This would give an error in $b$ of $-2 \times 10^{-4}$ at 4.2°K, $-7 \times 10^{-4}$ at 3°K, rising to $-25 \times 10^{-4}$ just above the lambda point. The effect should thus be noticeable between about 3°K and the lambda point, and as can be seen from fig.3.2, the magnitude predicted on this basis is similar to that observed. A calculation of the hydrostatic head correction for a height of 5cm. of liquid helium in the small can gives the same kind of deviation, and a similar magnitude. It is not possible to decide whether one or both of these effects operate, but that they disappear below the lambda point is attributed to the presence of superfluid helium. A possible objection to this explanation is that the magnitude of the jump in $b$ is not always the same for both resistors; nevertheless it is felt that the effects described give an explanation of the observed behaviour, and justify the procedure of ignoring calibration points obtained between about 2.8°K and the lambda point when drawing the calibration curves.

Errors of the second kind, due to a difference in temperature between the thermometers and the helium at the bottom of the small can, will now be considered. The obvious cause would be a heat leak into the specimen, and as a source of this the self heating of the carbon resistors is first considered. If the thermal contact between the carbon resistors and their sleeves, and these copper sleeves and the
specimen is good, it seems reasonable to assume that the effect will be reproducible at a given temperature in any single experiment. The significance of the self heating will then depend upon what temperature gradient it produces in the specimen. If this is negligible, use of the calibration curves will give the correct specimen temperature. For the 12A/o alloy at 1.5°K, which is the worst possible case, the power produced in one resistor is about $2 \times 10^{-8}$ watts. This would give rise to a temperature gradient of about $5 \times 10^{-4}$ °K per cm. down the specimen. With the heater on this temperature gradient will still be present, and the effect on $\Delta T$ should be negligible. The self heating could raise the mean temperature of the specimen by something approaching a millidegree, giving rise to an error of 0.05% in $T$, which can also be ignored. However, if the criterion of good thermal contact between the thermometer sleeve and specimen is not satisfied, deviations from the standard calibration curves are to be expected.

To explain the marked deviations from the standard calibration curves obtained in the earlier measurements, it is necessary to postulate a heat leak into the specimen which becomes accentuated as the temperature is decreased below the lambda point. This would be provided by the effects of residual exchange gas and a small lambda leak. Then, in the absence of any heater power, a temperature gradient would exist in the specimen such that the values of $T$ both used in the calculation of the calibration curves and obtained from them would be too small. The direction and magnitude of the error can be obtained by differentiating Eq. (3.1). The resulting expression is

$$\frac{\partial b}{\partial T} \frac{\partial T}{\partial R} = \frac{a \log_{10} R}{2(\log_{10} R - b)T^2} \frac{10^{\log_{10} R - b}}{T} \tag{3.2}$$

which was always positive. Thus the calibration curves obtained by using consistently low $T$ values will lie below the standard curves, which was the behaviour observed.
3.5 Calibration errors and the thermal conductivity.

Consideration of Eq. (3.2) above in conjunction with the calibration curves shown in fig. 3.1 indicates that the deviations in $b$ from the standard curves varied from about $-0.005$ at $3^\circ K$ to $-0.03$ at $1.5^\circ K$, giving rise to errors in temperature of $-0.02^\circ K$ and $-0.03^\circ K$ respectively. Thus, the fractional error in $T$ becomes larger as the temperature decreases. If it is assumed that in the first approximation the error in $\Delta T$ can be ignored, then the calculated values of $\frac{K}{T}$ will be displaced upwards from their correct values by an amount which increases as the temperature falls. This kind of behaviour was observed when the lambda leak became very bad. In general, however, it is not possible to account quantitatively or qualitatively for the differences between measurements made on specimens from the same alloy composition before and after replacing the small can. An example of this difference for the 12A/6 alloy is given in fig. 3.3, and the calibration curves used in working out the results for the earlier measurement are those shown in fig. 3.1. Similar effects were observed for other alloys. The $\frac{K}{T}$ against $T$ graphs were linear when the calibration curves obtained during a run were parallel to the standard curves within $0.1\%$ of $b$ at $4.2^\circ K$ and to within $0.4\%$ of $b$ at $1.5^\circ K$. The conclusion was drawn that unless the latter condition held, deductions made from the form of the $\frac{K}{T}$ against $T$ curves would have no validity.
Fig. 3.1
Calibration curves from an early run.

\[ b \]

\( \lambda \) point

- top resistor
- bottom II

\[ \log_{10} R \]
The standard calibration curves and those obtained immediately after fitting the new can are shown by triangles and circles respectively. Curves for the next eight runs fell within the shaded region.
An example of the effect of calibration errors in the case of the 12A/o alloy. The points represented by triangles were obtained after fitting the new can.
4.1 Introduction

The methods which can be used to separate the electronic and lattice thermal conductivities have been discussed in Chapter 1. As the results will show, for the alloys used in this work, the thermal conductivity $K$ can be represented by an expression

$$K = AT + BT^2$$

(4.1)

within the experimental error. Graphs of $K/T$ against $T$ have been plotted to show the form of the results, the values of $A$ and $B$ being obtained by a least squares analysis in each case. In no case was the value of $K/\rho_0$ used as a point at $T = 0$. Before the results are presented the experimental errors will be discussed.

4.2 Experimental errors.

The expression from which the values of the thermal conductivity were calculated was

$$K = \frac{Q}{2AT} \cdot \frac{d}{a}$$

(4.2)

where $Q$ is the heater power, $\Delta T$ the temperature difference between two points on the specimen a distance $d$ apart, and $a$ is the cross sectional area of the specimen. Measurements of the diameter of the specimen were made with a micrometer, and $d$ was measured with a travelling microscope. However, taking the finite thickness of the specimen tags and the solder fillets into account, the accuracy of the size factor $d/a$ is not better than $2\%$. Strictly speaking one should allow for the change in size factor due to thermal contraction between room temperature and liquid helium temperature. This would mean multiplying all values of $K^{-1}$ and $\rho_0$ by a factor between 0.995 and 1. Since the main interest is in the form of the results, and the relative differences caused by changes in composition and deformation, the correction has not been applied. Errors in the size factor will affect values of $K^{-1}$ and $\rho_0$ in the same
specimen in an identical fashion, and so will not affect, for example, relative differences between A and $A_0$; however, the error in the size factor must be included when comparing values of A and B obtained from different specimens. The random error in the potentiometric measurement of Q is estimated to be 0.2%. Other errors in Q could arise from heat loss by radiation from the heater, or conduction down the leads, or from heat produced in the current leads. The radiation loss would be about 0.05 microwatts if the heater temperature rose to 15°K. This seems unlikely, but in any case the loss would amount to only 0.1% of Q. Calculation of any heat loss down the heater leads showed it to be negligible. An upper limit on the error in Q can be fixed at 0.3%.

Since K is a non-linear function of T, when $\Delta T$ is finite a correction due to the curvature of the K against T graphs should be applied. This correction is the difference between the mean value of K between $T_1$ and $T_2$, and the value worked out from Eq. (4.1) with $T = \frac{T_1 + T_2}{2}$. The correction is approximately given by

$$\Delta K \approx \frac{1}{2} b (\Delta T)^2$$  \hspace{1cm} (4.3)

and for $\Delta T = 0.2°K$ the error in the $T^2$ term varies from 0.05% at 4.2°K to 0.2% at 2°K, and will therefore be neglected.

The errors in $T_1$ and $T_2$ arise from the measurement of the resistances of the thermometers, and from the values of $b$ obtained from the calibration curves. In the absence of any systematic error, values of $b$ are known to ±1 part in 15,000, assuming one reads them from the calibration graphs to ±1mm. The resistances are obtained to ±0.2 ohms for values near one thousand ohms (4°K) and to ±1 ohm for values near ten thousand ohms (1.7°K). These values are estimated from the maximum amount of drift occurring in the time necessary to take a set of readings. Consideration of Eq. (3.1) shows that values of T are obtained to ±0.03% at 4°K, and to ±0.02% at 1.5°K. It is not suggested that this accuracy applies to the actual value of the temperature, but that it can be used to estimate the error in $\Delta T = T_1 - T_2$. One finds that for
values of $\Delta T$ of $0.2^\circ K$, the error will vary from $1\%$ at $4^\circ K$ to $0.5\%$ at $1.5^\circ K$. The random error in $T$ calculated above is negligible. The method of drawing calibration curves described in 3.4 is designed to eliminate one known systematic error, but there may be others. It is unlikely that these could be more than a few millidegrees, and therefore errors in $T$ will be neglected.

The drawing of the calibration curves gives rise to a small systematic error as follows. Assuming for the sake of argument that in a set of values of $R_1$, $R_2$ and $T$ the resistance values are correct, then the pair of calibration points obtained will both be displaced up or both be displaced down from their true curves, depending upon the direction of the random error in $T$. This behaviour was observed in practice, and it was assumed that if each curve was drawn in the same way relative to the "off" points, no error would arise. However, since a discrepancy of 1mm. on the calibration graphs can be significant in view of the previous discussion, any slight differences between the drawing of the two curves should make themselves apparent. This is believed to be the explanation of the small wiggles seen in some of the $K$ against $T$ graphs.

So, neglecting errors in size factor, the maximum error in $K$ will vary from $1.3\%$ at $4.2^\circ K$ to $0.8\%$ at $1.5^\circ K$. The scatter of individual points about the best lines drawn for most of the results presented is rather less than this; it is felt better to let the results speak for themselves rather than try to justify the quotation of a smaller experimental error.

4.3 Results.

Fig.4.1 shows the graphs of $\frac{K}{T}$ and $K$ against $T$ obtained from the measurement of the thermal conductivity of some annealed commercial copper wire. This experiment was done with the aim of testing the cryostat, and it is felt that the results obtained indicate a reliable behaviour. Drawn on fig.4.1 is a horizontal line representing the value of $\frac{1}{\rho_0}$, and assuming $\rho_0$ is constant, the Wiedemann-Franz law can be seen.
to be obeyed almost within the experimental error. Although the trend of the $K_T$ against $T$ graph might be due to the type of systematic calibration error discussed in 4.2, it is very similar to that observed by Jericho, 1965, for a commercial copper specimen. Some of the discrepancy between values of $\frac{L}{\rho_0}$ and $\frac{K}{T}$ may be removed if $\rho_0$ changes between 4.2° and 1.5°K, and Jericho finds a decrease of about 0.25% in $\rho_0$ for his specimen.

Fig. 4.2 shows graphs of $K$ against $T$ obtained for the annealed polycrystalline specimens 2, 4 and 12, and shows the variation in thermal conductivity over the range of alloys studied. The thermal conductivity changes by a factor of about three between the 2% and the 12% alloy. On the scale of the diagram, the departure from linearity is not easy to see.

In figs. 4.3 to 4.5 are the results for all the annealed specimens, both single crystals and polycrystals, plotted as graphs of $\frac{K}{T}$ against $T$. These results, except for specimen 6, were obtained after the new can had been fitted, and the calibration curves obtained satisfied the criterion given at the end of section 3.5. For all cases, except perhaps specimen 6, fig. 4.4, good straight lines can be drawn through the points, though for some of the graphs there is evidence of the slight systematic departures mentioned in 4.2. For specimen 6, fig. 4.4, experimental points from two separate runs on the same specimen are included. The graph for specimen 12, fig. 4.5, shows the results of two runs on the same single crystal, marked by crosses and triangles, and one run on a different single crystal marked by squares. The results agree very well.

Leaving the single crystal results aside, it can be seen from figs. 4.3 to 4.5 that the slopes of the $\frac{K}{T}$ against $T$ curves decrease with increasing aluminium content, except perhaps for the specimens 8 and 10, which had similar values. Taking the single crystal results alone, the slopes of the $\frac{K}{T}$ against $T$ graphs again decrease with increasing aluminium
content, but in each case the slope is slightly less than the corresponding polycrystal result. This can be seen more clearly from table 4.1, which contains the values of $A$ and $B$ obtained by a least squares analysis on each set of points, and the values of $\rho_0$, $\frac{I}{\rho_0}$, and $W_g T^2$. The errors quoted for $A$ and $B$ are their standard deviations, and the error in $W_g T^2$ includes the error in the form factor. Another difference between the results for single crystals and polycrystals lies in the values of $\frac{I}{\rho_0} - A$. From table 4.1 it can be seen that these are always positive for polycrystals, but for the single crystals the value is zero, within the experimental error, for specimen 12 S, negative for specimen 8 S, and rather less than the corresponding polycrystal value for specimen 2 S.

Figures 4.6 and 4.7 show respectively how the lattice thermal resistivity varies with atomic concentration of aluminium and with residual resistivity. In both cases the single crystal results are shown as squares. It can be seen that although $W_g T^2$ for single crystals is greater than $W_g T^2$ for the corresponding polycrystal in all cases, for the 12A/6 alloy at least the increase in $W_g T^2$ is accompanied by a corresponding increase in $\rho_0$. Fig.4.7 gives a good straight line, and the intercept on the $W_g T^2$ axis can be compared with the theoretical value obtained by Klemens, 1958, for pure copper. One curious point with regard to the drawing in of errors on fig.4.7 should be noted. Since the error in the size factor is predominant, and will affect both $W_g T^2$ and $\rho_0$ in the same direction for the same specimen, the limits of error lie along a line of slope $W_g T^2/\rho_0$ drawn through the experimental point. Superimposed on this is the error in $W_g T^2$ from the standard deviation of $B$.

These results are discussed in the following chapter.
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>$\rho \times 10^6$ ohm cm.</th>
<th>$L/\rho \times 10^3$ watt cm.$^{-1}$ deg.$^{-2}$</th>
<th>$A \times 10^3$ watt cm.$^{-1}$ deg.$^{-2}$</th>
<th>$B \times 10^3$ watt cm.$^{-1}$ deg.$^{-3}$</th>
<th>$\mu_n T^2$ watt.$^{-1}$ cm.$^{-1}$ deg.$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.12</td>
<td>11.53</td>
<td>$11.21 \pm 0.02$</td>
<td>$0.764 \pm 0.004$</td>
<td>$1310 \pm 20$</td>
</tr>
<tr>
<td>2S</td>
<td>2.07</td>
<td>11.80</td>
<td>$11.64 \pm 0.03$</td>
<td>$0.700 \pm 0.009$</td>
<td>$1430 \pm 30$</td>
</tr>
<tr>
<td>4</td>
<td>3.88</td>
<td>6.30</td>
<td>$6.17 \pm 0.02$</td>
<td>$0.565 \pm 0.003$</td>
<td>$1770 \pm 35$</td>
</tr>
<tr>
<td>6</td>
<td>5.20</td>
<td>4.70</td>
<td>$4.49 \pm 0.02$</td>
<td>$0.496 \pm 0.003$</td>
<td>$2020 \pm 40$</td>
</tr>
<tr>
<td>8</td>
<td>6.63</td>
<td>3.69</td>
<td>$3.66 \pm 0.02$</td>
<td>$0.429 \pm 0.003$</td>
<td>$2330 \pm 50$</td>
</tr>
<tr>
<td>8S</td>
<td>6.50</td>
<td>3.76</td>
<td>$3.87 \pm 0.02$</td>
<td>$0.409 \pm 0.003$</td>
<td>$2445 \pm 50$</td>
</tr>
<tr>
<td>10</td>
<td>6.62</td>
<td>3.69</td>
<td>$3.58 \pm 0.02$</td>
<td>$0.438 \pm 0.003$</td>
<td>$2285 \pm 60$</td>
</tr>
<tr>
<td>12</td>
<td>7.21</td>
<td>3.39</td>
<td>$3.33 \pm 0.02$</td>
<td>$0.404 \pm 0.003$</td>
<td>$2480 \pm 60$</td>
</tr>
<tr>
<td>12S</td>
<td>7.49</td>
<td>3.26</td>
<td>$3.27 \pm 0.02$</td>
<td>$0.391 \pm 0.003$</td>
<td>$2560 \pm 60$</td>
</tr>
</tbody>
</table>
Fig. 4.1
Graphs of $K$ and $K/T$ against $T$ for annealed copper wire. The thermal conductivity points are shown as open circles.
Fig. 4.2
Graphs of $K$ against $T$ for specimens 2, 4, and 12.
Graphs of $K/T$ against $T$ for the specimens 2S, 2, and 4. Note the change of scale for specimen 4.
Fig. 4.4
Graphs of $\frac{K}{T}$ against $T$ for specimens 6, 8S, and 8.
Fig. 4.5

Graphs of $\frac{K}{T}$ against $T$ for specimens 10, 12, and 12S.
Fig. 4.6

A graph of $WgT^2$ against $\%$ aluminium. The single crystals have been assumed to have the same composition as their corresponding polycrystals.
Fig. 4.7

A graph of $W_g T^2$ against residual resistivity, $\rho_0$. Only the polycrystal results, shown by circles, were taken into account when drawing the line shown. Klemens' theoretical value for pure copper is shown.
5.1 Introduction.

In order to calculate the lattice thermal conductivity of metals at low temperatures, one needs to know the magnitude of the electron phonon interaction. Two theoretical models will be considered in relation to the results of the previous chapter. The first, due to Klemens, will be discussed briefly. The second, which is based on Pippard's theories of ultrasonic attenuation, will be discussed at length.

Finally, the results of Chapter 4 will be discussed in relation to Lindenfeld and Pennebaker's theoretical calculation of $K_g$ for copper alloys.

5.2 Klemens' model.

Klemens (1954, 1956, 1958) shows that when no other resistive mechanism is operating the value of $K_g$ in metals at low temperatures depends upon a knowledge of the interaction constants $C_j$ between electrons and the various polarization modes $j$. The evaluation of the $C_j$s is not attempted, but since they occur in the theoretical expression for the low temperature ideal electronic thermal resistivity $W_i$, Klemens expresses $K_g$ in terms of $W_i$. The magnitude of $K_g$ still depends upon how the $C_j$s are supposed to vary between the different polarization modes $j$. In the Makinson coupling scheme (Makinson, 1938) the electrons interact equally strongly with both longitudinal and transverse phonons, i.e. $C_L = C_T$. In this case Klemens obtains

$$K_g = 313 \frac{W_i^{-1}}{T^4} e^2 N_a^{-\frac{3}{2}}$$

(5.1)

where $N_a$ is the number of free electrons per atom, and $\Theta_e$ is the Debye temperature obtained from low temperature specific heat measurements.

In the Bloch coupling scheme (Bloch, 1928) the electrons interact mainly or only with the longitudinal phonons, and it is assumed that the latter are strongly coupled with the transverse phonons via normal processes: that is those phonon processes in which the total phonon wave vector and
energy are conserved. Then $C_L > C_\tau$ or $C_\tau = 0$ in particular. In this case Klemens obtains

$$K_g = 105 W_1^{-1} T^{-4} \theta_L^{-4} N_a^{-\frac{4}{3}}$$

(5.2)

where $\theta_L$ is appropriate to the longitudinal modes only. Since $W_1$ is proportional to $T^2$, both expressions (5.1) and (5.2) predict the observed temperature dependence of $K_g$. However, since $\theta_L$ is about $1.6 \theta_r$ (Blackman, 1951) the values of $W_g T^2$ predicted by Eq.(5.2) will be about 20 times that predicted by Eq.(5.1). If experimentally observed values of $W_i$ are put into the equations, and appropriate values of $\theta_v$ etc., Eq.(5.1) predicts for pure copper that

$$W_g T^2 = 7.1 \times 10^2 \text{ cm.deg.}^3 \text{ W}^{-1}.$$  

(5.3)

This is close to the extrapolated result of $8.8 \times 10^2$ shown in fig.4.7, which shows that for pure copper at any rate, Klemens' calculation is not much in error. This has been observed previously by many of the authors mentioned in 1.5A, and the correctness of the Makinson scheme seems well established.

However, Klemens' theory cannot predict the variation of $W_g T^2$ observed on alloying. Tainsh and White showed that these changes in $W_g T^2$ for copper alloys were not explained by the accompanying changes in $\theta_r$, $W_i$, and $N_a$ (see section 1.5A).

5.3 The Pippard model

Pippard derives expressions for the attenuation coefficients $\alpha_\tau$ and $\alpha_\ell$ for transverse and longitudinal ultrasonic waves in a metal. His argument is, in the case of longitudinal waves, that local changes in the electron density plus local electric fields set up by the passage of the wave distort the fermi surface. As a result of this distortion, a number of electrons find themselves with energies in excess of the local equilibrium value as electron lattice collisions are not able to restore equilibrium quickly enough. There results a continuous dissipation of energy, and the ultrasonic wave is attenuated. By calculating the rate
of energy dissipation, assuming a spherical Fermi surface, and that the phonon frequency is much less than the plasma frequency, Pippard (1955, 1960, 1962) derives the following expressions:

\[
\alpha_L = \frac{N m \nu_L}{\nu_L \nu_L} \left( \frac{1}{3} \frac{y^2 \tan^{-1} y}{y - \tan^{-1} y} - 1 \right) \quad (5.4)
\]

\[
\alpha_T = \frac{N m \nu_T}{\nu_T \nu_T} \left( 1 - \frac{3}{2y^2} [(y^2 + 1) \tan^{-1} y - y] \right) \quad (5.5)
\]

\[
\alpha_T' = \frac{N m \nu_T}{\nu_T \nu_T} \frac{2y^2}{3} [(y^2 + 1) \tan^{-1} y - y]^{-1} \quad (5.6)
\]

where Eq. (5.6) holds only for \( y \gg 1 \), and under conditions where screening of the ions by the conduction electrons is complete. In these equations \( N \) is the number of free electrons per unit volume, \( m \) is the electronic mass, \( \nu_L \) and \( \nu_T \) are the velocities of longitudinal and transverse sound waves respectively, \( t \) is the relaxation time for electrons in electron-lattice interactions, \( \rho \) is the density of the metal, and \( y \) is the product of the electron mean free path \( f \) and the phonon wave number \( q \).

The reciprocals of \( \alpha_L \), \( \alpha_T \), and \( \alpha_T' \) define mean free paths for phonons \( L_L \), \( L_T \), and \( L_T' \) respectively. The procedure followed by Lindenfeld and Pennebaker, 1962, and by Jericho, 1965, is to put \( L_L \) and \( L_T \) separately into Callaway's expression for the thermal conductivity, and calculate the separate contributions \( K_L \) and \( 2K_T \), thus

\[
K_g = K_L + 2K_T \quad (5.7)
\]

The factor 2 arises because of the two degrees of freedom for the transverse modes.

Before considering the results of these calculations, it is interesting to consider the wave number dependence of the expressions for \( \alpha_L \), \( \alpha_T \) in the limit where \( y \ll 1 \). If \( \tan^{-1} y \) is expanded in powers of \( y \), both \( \alpha_L \) and \( \alpha_T \) are found to have a quadratic wave number dependence. Hence for very high residual resistivity alloys, or very low temperatures,
one expects $K_g$ to be proportional to $T$.

In the opposite extreme, if $y > 1$, $\tan^{-1}y$ may be replaced by
\[
\frac{\pi}{2} - \tan^{-1}y - \tan^{-1}y \quad \text{and} \quad \tan^{-1}y \quad \text{may be expanded in powers of } y^{-1}.
\]
If this is done, the following expressions for $L_\perp$, $L_\parallel$, and $L'_\parallel$ are obtained:

\begin{align*}
L_\perp &= \frac{\Delta x \tau}{\text{Nm}} \cdot \frac{6}{\pi} \left( \frac{1}{y} + \frac{1}{y^2} \left( \frac{3}{\pi} - \frac{\pi}{2} \right) \right) \quad \text{(5.8)} \\
L_\parallel &= \frac{\Delta x \tau}{\text{Nm}} \left( 1 + \frac{3\pi}{4y} - \frac{3}{y^2} \right) \quad \text{(5.9)} \\
L'_\parallel &= \frac{\Delta x \tau}{\text{Nm}} \left( \frac{3\pi}{2} \left( \frac{\pi}{2y} - \frac{2}{y^2} \right) \right) \quad \text{(5.10)}
\end{align*}

correct to the second order in $y^{-1}$. It can be seen that $L_\parallel$ and $L'_\parallel$ have exactly the same terms in $y^{-1}$ and $y^{-2}$. Callaway's expression for the thermal conductivity is (Callaway, 1959)

\[
K_g = \frac{1}{6\tau^2} \sum_j \int \frac{k^4 r_\sigma^2}{\hbar^3 v_j^3} L_j \frac{x^4 \tau^2}{(e^x - 1)^2} \quad \text{(5.11)}
\]

where

\[
x = \frac{\hbar v_j q}{kT}. \quad \text{(5.12)}
\]

Remembering that $y = qf$, it can be seen from Eq.(5.12) that substitution of $L_\perp$ and $L_\parallel$ into Eq.(5.11) will give

\[
K_g = CT + BT_\parallel + DT_\parallel^2 \quad \text{(5.13)}
\]

whereas the substitution of $L_\perp$ and $L'_\parallel$ will give

\[
K_g = CT + BT_\parallel. \quad \text{(5.14)}
\]

It will now be shown that if the relative magnitudes of $B$, $C$, and $D$ are calculated, Eq.(5.14) explains the results given in Chapter 4 for the annealed polycrystalline alloys very well, and that the existence of the $T^2$ term in Eq.(5.13) does not accord with these experimental results.

Putting the expressions for $L_\perp$ and $L_\parallel$ from Eqs.(5.8) and (5.9)
into Eq. (5.11), expressions for $K_L$ and $K_T$ are obtained. These expressions are then substituted into Eq. (5.7), and the following equations obtained for the coefficients in Eqs. (5.13) and (5.14):

$$D = M \cdot 2f v_T^{-1} J(4)$$  \hfill (5.15)

$$B = M \cdot 3h k^{-1} \left( \frac{2}{N} + \frac{\pi}{2} \right) J(3)$$  \hfill (5.16)

$$C = M \cdot h^2 k^2 r_k^{-1} \left( \frac{8}{N} - \frac{\pi}{2} \right) \frac{d v_T}{v_T} J(2)$$  \hfill (5.17)

where

$$M = \frac{1}{6 \pi^2} r_k^2 a (h^3 N v_T)^{-1}$$  \hfill (5.18)

$v_T$ is the fermi velocity, assumed constant, and

$$J(n) = \int_0^\infty x^n e^x (e^x - 1)^{-2} dx$$  \hfill (5.19)

In particular

$$J(2) = 3.3$$

$$J(3) = 7.2$$  \hfill (5.19a)

$$J(4) = 26.0$$

The $\frac{2}{N}$ term in Eq. (5.16) and the $\frac{8}{N} - \frac{\pi}{2}$ term in Eq. (5.17) are the contributions from the longitudinal modes in each case. Since experimentally $BT^2$ is observed to be the dominant term, one can see that on this model the transverse modes contribute roughly twice as much to $K_T$ as do the longitudinal modes. However, as Eq. (5.16) shows, $B$ is independent of the electron mean free path $f$, and so the Pippard model, like the Klemens model, cannot explain the observed variation of $B$ with alloying. The coefficient $C$ is negative as $v_L$ is roughly twice $v_T$.

From Eqs. (5.15) to (5.17) one obtains

$$\frac{D}{B} = \frac{52}{47.5} \cdot \frac{r_k}{v_T} \approx \frac{5}{\rho_0} \text{ deg}^{-1}$$  \hfill (5.20)
where \( p_0 \) comes from using the expression \( f = 8 \times 10^{-6} p_0 \) cm. and is measured in microhm cm. (Chambers, 1952), and the values of \( v_L = 4.7 \times 10^5 \text{cm./sec.}, v_T = 2.3 \times 10^5 \text{cm./sec.} \) for pure copper have been used.

The magnitude of \( D \) predicted by Eq. (5.20) is such as would easily be observed in the 2\% alloy; no such cubic term was seen, and the experimental results of the previous chapter favour the choice of \( L_u \) and \( L_T \), leading to Eq. (5.14) for \( K_g \).*

A comparison of the observed values of \( \frac{C}{B} \) with that predicted by Eq. (5.21) can be made. It is assumed that the Wiedemann-Franz law holds, and then \( C = A - \frac{L_u}{p_0} \). The results of this comparison for the polycrystalline alloys are shown below:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(-C/B_0 ) deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A/0</td>
<td>( \cdot20 \pm \cdot02 )</td>
</tr>
<tr>
<td>4A/0</td>
<td>( \cdot06 \pm \cdot01 )</td>
</tr>
<tr>
<td>6A/0</td>
<td>( \cdot08 \pm \cdot01 )</td>
</tr>
<tr>
<td>8A/0</td>
<td>( \cdot01 \pm \cdot01 )</td>
</tr>
<tr>
<td>10A/0</td>
<td>( \cdot04 \pm \cdot01 )</td>
</tr>
<tr>
<td>12A/0</td>
<td>( \cdot02 \pm \cdot01 )</td>
</tr>
</tbody>
</table>

The agreement between the theoretical prediction and the experimental results is good. However, an alternative explanation in terms of grain boundary scattering must be considered, since, as was shown in

* The expansion of the attenuation coefficients to second order, and the following analysis using Callaway's equation, was first done by Charsley. The results of this analysis, given in a paper by Charsley and Salter, 1965, are correct except that neglect of the second order term in \( L_r \) led to the conclusion that the value of \( C \) in Eq. (5.13) would be positive.
section 1.4, this would give rise to a small negative linear term in $K_g$. Moreover, it can be seen from table 4.1 that for single crystals $C_B$ is either zero, positive, or rather less than the corresponding polycrystal result.

A mean free path, $b$, for boundary scattering can be defined, and as a first approximation it will be assumed that $b$ is much greater than $L_j^1$ or $L_j$. Combined mean free paths $L_{BL}$ and $L_{BT}$ can then be defined by

$$L_{BL}^{-1} = L_j^{-1} + b^{-1}$$ (5.22)

i.e.

$$L_{BL} = L_j - \frac{L_j^2}{b}$$ (5.23)

and similarly

$$L_{BT} = L_j - \frac{L_j^2}{b}$$ (5.24)

If in the boundary scattering terms only the terms proportional to $(qf)^2$ in $L_j^2$ and $L_j^2$ are considered, then as $b$ is independent of $q$, and $q$ is proportional to $T$, there will be a small negative linear term in $K_g$ (see Eq.(5.11)). If the coefficient of this term is $C_b$, then substitution into the Callaway expression, and using Eq. (5.7), gives

$$-C_b = \frac{M}{b} \cdot \frac{h^2 \nu_f}{k_3} \nu_f \left( \frac{36}{\gamma_3} + \frac{\nu_f}{\nu_L} \cdot \frac{\gamma_2^2}{2} \right) J(2).$$ (5.25)

If one assumes that the difference between $\frac{L}{\rho_0} - A$ for a polycrystal and $\frac{L}{\rho_0} - A$ for the corresponding single crystal is due to boundary scattering, then the experimentally observed values of $\frac{C_b}{C_B}$ are as follows:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$-\frac{C_b}{C_B}$/Bdeg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A/0</td>
<td>0.22 ± 0.07</td>
</tr>
<tr>
<td>8A/0</td>
<td>0.34 ± 0.10</td>
</tr>
<tr>
<td>12A/0</td>
<td>0.14 ± 0.09</td>
</tr>
</tbody>
</table>

The mean grain size of the polycrystalline specimens was about 0.1 mm. Using this value for $b$, and comparing Eqs.(5.25) and (5.16) one obtains
which agrees well with the experimentally observed values given above.
Since the conductivity of cubic crystals is isotropic, it does not seem possible that the intercept differences are due to an orientation effect. Neither is it likely that the differences between the single crystal and polycrystalline specimens are due to experimental error: the times at which single crystal measurements were made are dispersed among the times at which polycrystal measurements were done, and all polycrystalline specimens, whether annealed or strained, give values of $A$ which are less than $\frac{L}{\rho_o}$.

Thus the small negative linear term observed in $K_g$ has at least three possible explanations, one in terms of the Pippard theory, one in terms of boundary scattering, and one in which both effects contribute. The first possibility, the Pippard theory alone, is ruled out, and while it is not believed that the experimental results so far obtained enable one to distinguish between the last two possibilities, the existence of an observable effect due to boundary scattering seems definite.

5.4 Comparison of the results with computed curves.

The results of Chapter 4 will now be considered in relation to the curves of $\frac{K_g}{T}$ against $T$ calculated by Lindenfeld and Pennebaker as previously explained. Inspection of fig. 4.7 shows that the lattice thermal conductivities of all the polycrystalline annealed alloys are well represented by the equation

$$K_g = \frac{T^2}{880 + 210\rho_o} \text{ watt cm}^{-1} \text{ deg}^{-1}$$

(5.27)

where $\rho_o$ is in microhm cm. In view of the previous discussion, as the linear term in $K_g$ is in part due to boundary scattering, it has been neglected in Eq. (5.27). In fig. 5.1 graphs of $\frac{K_g}{T\rho_o}$ against $\frac{T}{\rho_o}$ have been
plotted between 4°K and 1°K for ρ₀ = 1, 2, 4, 6 and 8 microhm cm. Also on the graph is a dotted line representing the theoretical curve calculated by Lindenfeld and Pennebaker for copper alloys. Since they used the value of $L_T$, given by Eq. (5.9), which predicts the wrong temperature dependence giving a large cubic term, the agreement in magnitude between theory and experiment must be fortuitous. It can be seen from fig. 5.1 that for $\frac{T}{\rho_0}$ greater than about $5 \times 10^5$, the theoretical curve predicts that $\frac{K_S}{T}$ should be proportional to $T^2$, whereas it is observed to be proportional to $T$.

One further comment in respect of an observation by Jericho may be made. He found that if, instead of plotting graphs of $\frac{K_S}{T\rho_0}$ against $\frac{T}{\rho_0}$ by varying $T$ for a given alloy, one fixed $T$ and compared values of $\frac{K_S}{T\rho_0}$ for different alloys, much better agreement with the theoretical curve was obtained. He could not say why this was. It should be clear that what he observed was the dependence of $\frac{K_S}{T\rho_0}$ upon $\rho_0^{-1}$. This dependence is shown in fig. 5.1 by the dashed curve for values of $T$ of 4°K and 1°K. It can be seen that the dependence of $\frac{K_S}{T\rho_0}$ upon $\rho_0^{-1}$ is nearer quadratic than linear for fixed $T$; this can also be inferred from Eq. (5.27). Moreover, with a suitable choice of $T$, the fit with the calculated curve can be made very close.

5.5 Unexplained results.

It was mentioned in Chapter 4 that in all cases values of $W_gT^2$ for polycrystals are less than the corresponding single crystal results. In the case of the 12A6 single crystal, the increase in $W_gT^2$ is accompanied by an increase in $\rho_0$, and the point for this specimen in fig. 4.7 lies on the line drawn through the polycrystalline alloy results. However, this is not the case for the 2A6 and 8A6 alloys. Both these alloys give points lying above the line drawn in fig. 4.7. The reasons for this are not known.
Comparison of theoretical and experimental curves of $K_g/T\rho_o$ against $T/\rho_o$. The numbers give the value of $\rho_o$ appropriate to each full line. For further details see section 5.4.
Chapter 6

6.1 Diffraction contrast and the visibility of dislocations.

Electron microscopy has greatly facilitated the study of defects in crystalline solids, and has led to a better understanding of the ways in which they can affect physical properties. The recent book by Hirsch et al., 1965, covers both the theoretical and the practical aspects of transmission electron microscopy very thoroughly; nevertheless a qualitative explanation of the mechanism of diffraction contrast will be given.

Metal specimens suitable for viewing in the electron microscope are of the order of one thousand angstroms thick, and the ones looked at are usually single crystal and typically a few microns square. Electrons are scattered out of the incident beam by Bragg reflection from suitably oriented crystallographic planes. The de Broglie wavelength of electrons accelerated from 100kV is about 0.04 angstroms, and the lattice spacing in metals is typically 3 angstroms. The Bragg equation

\[ n\lambda = 2d\sin\theta \tag{6.1} \]

then shows that the reflecting planes make only a small angle, of the order of minutes of arc, with the incident beam. For most purposes the reflecting planes can be considered parallel to the incident beam. That different Bragg reflections can occur from the same selected area is due to the foil being bent in some way. If one views a bent specimen in bright field, the contrast is in the form of dark lines, referred to as bend contours, which correspond to the regions in the crystal at which strong Bragg "scattering" of the incident electrons occurs. Plate 6.1 shows a crystal of molybdenum trioxide with its diffraction pattern superimposed. If the pattern is rotated by 26° clockwise, the correlation of the bend contours with the diffraction spots can be seen. Each bend contour corresponds to one spot on the diffraction pattern. In a specimen of non uniform thickness, one may also see thickness
fringes, and an example of these near a wedge-shaped crack is shown on plate 6.2. The presence of a dislocation line will alter the reflecting condition of crystallographic planes near it. If the corresponding planes in regions of good crystal are near the Bragg reflecting condition this can give rise to strong contrast effects easily distinguishable from thickness fringes or bend contours. Fig. 6.1 shows crudely how this occurs in the case of an edge dislocation. However, if the displacements caused by a dislocation lie in the Bragg reflecting planes, no contrast can occur. This would be the case in fig. 6.1 if the reflecting planes were in the plane of the diagram, and is expressed by the invisibility criterion, namely

\[ \mathbf{g} \cdot \mathbf{b} = 0 \]  

(6.2)

where \( \mathbf{g} \) is the reciprocal lattice vector of the reflecting planes, and \( \mathbf{b} \) is the burgers vector of the dislocation. In general a specimen placed in the microscope will not have a set of crystallographic planes in the optimum orientation for rendering dislocations visible, and it is more or less imperative that the specimen can be tilted relative to the electron beam in a controlled manner. In the Siemens Elmiskop I which was used in these experiments, this facility is provided by the Valaré specimen holder which gives controlled tilts of ±22° in two perpendicular directions. It is, however, important that the specimen should not be tilted more than about ±5° from the horizontal, because of the problem of determining specimen thickness. For an arrangement of dislocations seen in the electron microscope, the operating Bragg reflection(s) can be obtained by taking a selected area diffraction pattern. Then if the distribution of dislocations is assumed to be random among the six \( \langle 110 \rangle \) type burgers vectors, a factor can be introduced to allow for the fraction of invisible dislocations. When one or more reflection is operating the invisibility factor is found by inspection of the \( \mathbf{g} \cdot \mathbf{b} \) relation between all possible \( \langle 110 \rangle \) vectors and each \( \mathbf{g} \).
6.2 Preparation of specimens for electro-polishing.

When conductivity measurements had been completed on a specimen, it was cut into 2cm. lengths using the spark slicing attachment of the Servo-Met spark machine (Type SMC) supplied by Metals Research, Cambridge. Lengths were not cut closer than 2mm. from the solder fillets where the specimen tags were attached, nor closer than 1.5cm. from the ends of a specimen. The lengths were chemically polished until they were 2.3mm. in diameter, this being the size of specimen suitable for the Valdré specimen holder. The solution used was that quoted by Tegart, 1959, and was as follows:

30% Nitric acid  
10% Hydrochloric acid  
10% Orthophosphoric acid  
50% Glacial acetic acid.

During the chemical polishing the temperature was kept below 30°C. Then using the spark slicer, and a simple jig, parallel sided circular discs of approximately 0.5mm. thickness were cut from the lengths. Each 2cm. length gave about twenty discs, as material is wasted by spark erosion. To reduce damage, all cuts were made on range six, each slice taking about ten minutes. It was found that burrs were left on each side of the discs at the end of a cut, which damaged the P.T.F.E. holder (to be described). These were partly removed by rubbing each side of a disc gently on fine emery cloth. Only two opposite edges of a disc were affected by this process, the central portions remaining untouched. The discs were then given a further light chemical polish.

6.3 Final thinning of specimens.

The final thinning was done by electro-polishing in a P.T.F.E. holder supplied by Aeon Laboratories Ltd. This holder is fully described in an article by Dewey and Lewis, 1963. The holder, and the experimental set-up in which it was used, are shown in fig.6.2. The
"screw down" platinum probe provides electrical contact with the specimen which is the anode, and the cathode used in all cases was a piece of platinum strip. The disc in the holder was illuminated from one side and viewed from the other with a lens. It was found that the largest areas of thin foil were obtained if the electropolishing was continued for a few seconds after a hole appeared in the disc.

The P.T.F.E. holder is designed to protect the edges of a disc specimen and produce a flat profile in the central portion. This profile is only obtained under suitable electro-polishing conditions, which depend upon both the electrolyte used and the current density. If leakage occurs at the edges of a specimen, particularly near the platinum probe contact, rapid attack occurs and the disc does not perforate in the centre. This problem can be eliminated by protecting the edges of the specimen near the probe, and the probe itself, with Lacomit varnish.

The choice of electro-polishing solution varied from alloy to alloy and from time to time, but in all cases a two stage process was used. An initial rapid polish at about 12 volts with a current of 0.25 amp for about 2 minutes produced the correct profile. The voltage was then reduced to 4 to 6 volts with a current of 0.1 amp, and polishing continued until perforation occurred. For polishing the 12A/° alloy a solution of 33% nitric acid in methanol was used at room temperature. Washing was done in absolute alcohol at -20°C. For the other compositions, the same solution was tried at both room temperature and -20°C to -30°C. A 10% solution of orthophosphoric acid in distilled water was also tried at room temperature. Eventually a solution recommended by Aeon Laboratories Ltd. for the polishing of aluminium was found most satisfactory, and was used for polishing both the 2A/° and the 8A/° alloys. This solution, which gave the best results when used at 0°C, was as follows:
4.0% Methyl alcohol
30% Orthophosphoric acid
20% Nitric acid
10% Water.

Washing was done first in distilled water and then in methanol, both at room temperature. After removal from the washing solution the discs were allowed to dry and were immediately viewed in the electron microscope.

6.4 Determination of foil thickness.

In two of the methods of obtaining dislocation density to be described below a knowledge of the foil thickness is required. If in a foil the ends of a dislocation line confined to a (111) plane move, the direction of motion will define the lines of intersection of the (111) plane with the foil surfaces (fig. 6.3). It is an experimental observation (e.g. Howie and Whelan, 1962) that when a dislocation moves in the microscope, these intersections and/or the region between them may show contrast. An example of this is shown in plate 6.3. If the orientation of the foil normal is known (as this is assumed to be parallel to the incident beam) the slip plane can be identified as a particular {111} plane, and the angle $\theta$ between its normal and the foil normal found. As fig. 6.3 shows, the foil thickness $t$ can be calculated from the relation

$$ t = w \tan \theta $$

(6.3)

where $w$ is the slip trace width. The orientation of the foil is obtained from the selected area diffraction pattern, and in the general case where only one slip trace is observed, the identification of the {111} plane requires use of the stereographic projection. However, in many cases this is not necessary since for foil normals in the $[100]$, $[110]$, $[111]$ directions no ambiguity arises. Moreover, in many cases two or more slip traces of different widths and/or directions may be obtained. In this case, as is shown in plate 6.4, the tables prepared
by Crocker and Bevis, 1964, enable the foil thickness and orientation to be obtained directly from the ratio of slip trace widths, and the angle between them. The tables may give one, two or four solutions in any given case. Choice of the correct solution was facilitated by correlating the orientation from the tables with that from the diffraction pattern, and also by rejection of values for t which seemed too large or too small. Where three different slip traces were seen the ambiguity is almost removed, and additional information could be obtained about the orientation from the tables prepared by Drazin and Otte, 1964. The accuracy with which foil thickness can be obtained by these methods will be discussed in the last section of this chapter.

6.5 Determination of dislocation density from micrographs.

Three methods were used, the choice depending upon the observed dislocation arrangement, and in the case of method II upon the failure to produce slip traces in the microscope. Where methods I and II could be applied to the same plate, the values of dislocation density obtained usually agreed to within 10%. Before these three methods are described, the definition of dislocation density will be discussed.

Dislocation density may be found defined as either total line length per unit volume (L/V) or as the number of dislocations intersecting unit area of a given surface (N/A). As is pointed out by Schoek, 1962, application of each of these definitions to a specific dislocation array will not in general give the same numerical answers. Moreover, it does not necessarily follow that one of the definitions is right and the other wrong, but rather that the definition to be used depends upon context. For example, in the measurement of stored energy, or density changes due to dislocations, L/V is clearly the relevant parameter. Where direction is involved, as in the measurement of transport properties, N/A measured on a plane parallel to the direction of current flow might be a more suitable definition. Theoretical calculations of dislocation phonon scattering are made on single straight
dislocations oriented in a specific way, but most authors quote their final answers for a random array of dislocations. In this case L/V is the relevant parameter, and all values of dislocation density quoted in this thesis are measures of the line length per unit volume. In the first two methods described below, what is measured from the plates is N/A, and for a random array of dislocations, it can be shown that the relation between this and L/V is given by

\[
\frac{L}{V} = N_p = 2 \times \frac{N}{A}
\]  
(Schoeck, 1962).

**Method I**

A semicircular grid of ten radial lines each 3cm. long was placed over the plate, and the total number of intersections of dislocation lines with the grid lines counted. The grid was rotated by 180° and the process repeated. In some cases it was found easier to project the plate \(x2\) onto a grid of 6cm. lines drawn on white paper. This is illustrated in plate 6.5. From this count, the number of intersections per unit length of grid line, \(n\), was obtained. Knowing the thickness of the foil, \(t\), one has effectively found the mean number of dislocations intersecting a plane of area \(t \times 1\) which is perpendicular to the plane of the foil. Introducing the factor of 2 previously discussed, the dislocation density calculated from the plate is given by

\[
N_p = 2 \times \frac{n \times M^2}{t}
\]  
(6.5)

where \(M\) is the linear magnification in the microscope, and \(t\) is in centimetres as calculated from measurement of the slip trace width. This value of \(N_p\) must then be multiplied by the invisibility factor. The above method in essence was first described by Ham, 1961.

**Method II**

In this method, due to Ham and Sharpe, 1961, the total number of
intersections which dislocations make with the foil surfaces is counted. That is, the foil surfaces are used as the intersected planes. This has the great advantage that one does not need to know the foil thickness. If the number of ends counted is \( N \), and the area of the plate \( A \text{ cm}^2 \), then the dislocation density is given by

\[
N_d = 2 \times \frac{N \cdot M^2}{2 \cdot A}
\]  

(6.6)

where the factor of a half is introduced as the intersections with the top and bottom surfaces of the foil are counted. This value must then be multiplied by an invisibility factor depending upon the operating reflections. Plates 6.6 and 6.7 show two micrographs to which this method may be applied. In 6.6 the counting is easy, but in 6.7 it is more difficult in places to distinguish between what might be either three ends or a dislocation node.

**Method III**

In the 12\% alloy, dislocations are frequently observed mainly on one slip system. From the foil orientation, and the slip plane width \( w \), the foil thickness \( t \) is found as previously described. Thus, by Pythagoras' theorem, a dislocation lying in the slip plane with a projected length \( \bar{p} \) has a true length \( \bar{d} \) given by

\[
\bar{d} = \sqrt{\bar{p}^2 + \bar{w}^2}.
\]  

(6.7)

If the mean projected length of dislocations seen on the slip system is \( \bar{p} \), and \( N \) are counted on a plate of area \( A \), \( L/V \) can be calculated directly from

\[
\frac{L}{V} = N_d = \frac{N \cdot \sqrt{w^2 + \bar{w}^2}}{A \cdot t} \times M^2.
\]  

(6.8)

The invisibility factor is again applied. Plates 6.8 and 6.9 show two micrographs to which this method was applied.
6.6 The reliability and accuracy of dislocation density measurements.

In determining values of dislocation density from micrographs, the foil thickness \( t \), the area \( A \) of the plate, and the magnification of the microscope \( M \) are required. Apart from the error in \( t \) arising from the measurement of slip trace width from the plate, say 5\%, an additional unknown factor arises because the foil is not normal to the electron beam. Thus the orientation obtained from selected area diffraction or slip trace analysis is not the true foil normal. If the angle and axis of tilt are known, it is possible to calculate the correction exactly, and for angles less than 5° the error in the thickness is typically 5-10\% (Hirsch et al., 1965). \( M \) is known to \( \pm 2\% \), \( A \) to about \( \pm 2\% \), so that the overall accuracy neglecting any errors in counting dislocations is about 15\%. However, in dislocation density measurement, the main sources of error are believed to be systematic, and arise because the dislocations seen in thin foils may not be typical of the bulk material. For example, dislocations may be introduced owing to careless handling of a thin foil, or there may be loss and rearrangement of dislocations during the thinning process. These will be discussed in turn.

Dislocations introduced by damage

In this investigation, the use of a disc method makes the likelihood of damaging the foil small. The thin areas are in the central region of the disc, and all handling is by the thick outer rim. In any case in polycrystalline material, the type of dislocation array caused by bending the foil is easily distinguished from that normally present in undamaged foils. In damaged regions strong bend contours are seen, and also groups of long parallel dislocations which sometimes interact with one another producing widely spaced networks (Wilsdorf and Schmitt 1962).

Dislocation rearrangement

Valdré and Hirsch, 1963, showed that in stainless steel, which has a low stacking fault energy, up to 20\% of the dislocations moved during
the thinning process. These movements were in the main local, of the order of the foil thickness, and equivalent to rotation of the dislocation lines towards the foil normal. They concluded that the dislocation arrangements seen were not very different from the bulk material, and that dislocation densities obtained from the foils would be underestimates by at the most 30%.

Ham and Sharpe, 1961, have presented evidence for the rearrangement of dislocations during thinning in aluminium, which has a high stacking fault energy. They observed that values of \( N_p \) obtained using method II of 6.5 were about 20% higher than the values obtained using method I on the same micrograph. Their explanation was that the dislocations in the bulk material were randomly distributed, but that on thinning, dislocations threading the foil rotated towards the foil normal. The value obtained from method II would be typical of the bulk, since although the ends of dislocations have moved, the number of ends has not changed; but the value obtained by method I would be smaller than that in the bulk material. However, since the distribution of dislocations in the bulk material may not have been random, and the error typical of a dislocation density measurement is 15%, their conclusions are doubtful.

**Dislocation loss**

An experiment carried out by Mader et al., 1963, on a wedge shaped foil of aluminium in which they plotted the number of dislocations visible against distance from the edge of the foil indicated a definite loss near the edge of the foil. Work on carefully oriented single crystal slices by for example Mader, 1963, Hirsch and Steeds, 1964, has shown that screw dislocations must frequently escape from a foil by cross-slip. In some cases dislocation arrays were observed in which no screw dislocations remained. The only quantitative work to date on dislocation loss is that by Ham, 1962. He compared the dislocation densities seen in pure aluminium and in aluminium 0.5% silver after the same plastic strain. In the latter case the specimens were aged at
100°C prior to thinning. For the foils prepared from pure aluminium, the dislocation densities were about 60% less than those from the heat treated foils, and this was assumed to be due to segregation of silver to the dislocation lines in the latter case, making it more difficult for them to slip out of the foil.

**Copper aluminium alloys**

No experimental work has been done on the loss and rearrangement of dislocations in copper aluminium alloys. For alloys containing more than about 8% aluminium the stacking fault energy is very similar to that of stainless steel, and has a value of about 5 ergs/cm.$^2$ (Howie, 1961). The 2% alloy has a stacking fault energy much nearer that of pure copper, for which the value is believed to be 40 ergs/cm.$^2$ (Friedel, 1964). However, any dislocation loss from the alloy is expected to be less than that from pure copper because of the effect of solute hardening. That is, as impurity atoms are added to the parent metal, the shear stress for any given strain increases, which means in effect that the dislocations find it more difficult to move in the alloy. It might be thought that the dislocations are pinned in the alloy by segregation of solute atoms to them, as was suggested by Ham, 1962, for his aluminium 0.5% silver alloy. However, although a yield drop is observed in copper aluminium alloys, Koppenaal and Fine, 1961, attribute it to the destruction of short range order rather than to Cottrell or Suzuki locking. Solute hardening in copper aluminium alloys has been studied for single crystals by Koppenaal and Fine, 1962, and by Panin et al., 1965, and is well established.

Following Valdré and Hirsch, values of the dislocation density obtained from the 8% and 12% alloys will be assumed to be underestimates by not more than 30%. In the absence of any evidence to the contrary, and on the basis of the existence of solute hardening, the same loss factor will be assumed for the 2% alloy.
Fig. 6.1
Illustrating diffraction contrast at an edge dislocation. The crystal planes shown are meant to be just off the reflecting condition.
Fig. 6.2
The P.T.F.E. holder.
Fig. 6.3

Illustrating the geometry of a slip trace.
Plate 6.1 x 80,000

Bend contours in a molybdenum trioxide crystal with its diffraction pattern superimposed.
Thickness fringes near a wedge shaped crack in the Cu 4A/6 Al alloy.
Plate 6.3 $\times$ 80,000

A slip trace in the Cu 2A/o Al alloy.
Plate 6.4 x 80,000

Slip traces in the Cu 2A/6 Al alloy.
Dislocations in the Cu 2A/o Al alloy after 10% strain; illustrating method I of 6.5.
Dislocations in the Cu 2A/o Al annealed alloy; illustrating method II of 6.5.
Dislocations in the Cu 84/o Al alloy after 6% strain; illustrating method II of 6.5.
Dislocations in the Cu 12\% Al alloy after 0\% strain; illustrating method III of 6.5.
Dislocations in the Cu 12Al alloy after 6% strain; illustrating method III of 6.5.
Chapter 7

7.1 Deformation of specimens.

All the measurements described in this chapter were made on polycrystalline specimens deformed in tension in a tensile machine manufactured by T.C. Howden & Co., at a strain rate of 10 cm. per minute. The strain was measured by comparing the positions of fiducial marks before and after pulling using a travelling microscope. Values quoted for the flow stress are the maximum force per unit area during a test. The results are given later in table 7.3.

7.2 Thermal conductivity results.

As discussed in Chapter 1, dislocation phonon scattering and electron phonon scattering give relaxation times which have the same frequency dependence. The effect of plastic deformation on a given alloy is to leave the form of the $\frac{K}{T}$ against $T$ curves unchanged, but to reduce the slope $B$. This is clearly shown in fig. 7.1 for the 2A/0 alloy. The results for the annealed alloy are repeated for the sake of comparison. It can be seen that a strain of 2.9% produces a measurable change of slope. The remaining thermal conductivity results for the strained alloys are shown in fig. 7.2, and in this case the graphs for the annealed alloys are omitted. The lines shown, and the values of $A$ and $B$ in each case, were obtained in the same manner as for the annealed alloys. The values of $A$, $B$, $\rho_0$, etc. for the strained alloys are given in table 7.1. The annealed alloy results are reproduced in this table for comparison, but the strained specimens were not always originally the annealed specimens for which thermal conductivity data are given. Where this was not the case, the value of $\rho_0$ prior to deformation is given immediately above the data for the relevant strained specimen. One anomaly is that the value of $\rho_0$ for the 6% strained 12A/0 alloy is lower than that of the annealed alloy. Although errors in the size factor could account for this, it was thought that it might be due to a short range ordering effect, but attempts to reproduce it were not
successful (Brooker and Charsley, 1965, unpublished). Nevertheless, similar effects in alpha brass have been reported by Lomer and Rosenberg (see Clarebrough et al., 1960), and the existence of short range ordering effects in copper aluminium alloys is well known (see for example Koppenaal and Fine, 1961, and Fadin et al., 1962); for these reasons no attempt is made to correlate changes in $\rho_0$ due to strain with values of dislocation density.

7.3 Dislocation densities.

For the 2% and the 12% alloys, a few foils were prepared from annealed specimens. The values of $N_p$ found were less than $2 \times 10^8/\text{cm.}^2$ on average. No quantitative measurements of dislocation density were made on the 4% strained alloy, and the reasons for this will be discussed later. Table 7.2 shows the results of the dislocation density measurements for the remaining alloys. In table 7.2 $m$ is the total number of micrographs analysed in each case, and $g$ is the number of separate grains for which dislocation densities were obtained. For the 12% alloy results, the values of $N_p$ are the means of the $m$ values weighted according to the actual size of the area looked at. For the remaining alloys, the 2% and the 8%, the values of $N_p$ are the means of the values obtained for the $g$ separate grains, since comparable areas were analysed in each grain. The errors quoted in table 7.2 are the standard deviations of the $g$ values about the mean for the 2% and 8% alloys, and of the $m$ values in the case of the 12% alloy.

For the 8% and the 12% alloys, the dislocation density within a grain was fairly uniform, and the distribution of values of $N_p$ for individual grains about the mean was approximately Gaussian. This was not the case for the 2% alloy. In this case for both 2.9% and 10% plastic strain, histograms of the values of $N_p$ obtained for separate grains had two peaks about equally spaced on either side of the mean value of $N_p$. The ratios of the dislocation densities at these two peaks was about three. It might be thought that this variation could be
attributed to the dislocation cell structure seen in this alloy, in which tangles of dislocations form cell walls and the interiors of the cells are relatively dislocation free. Some indication of this can be seen in plates 7.1 and 7.2. However, since each value of \( N_0 \) is an average dislocation density over the whole of a grain, which includes both the cell walls and the cell interiors, this cannot be the explanation. It is possible that the two peaks reflect a genuine distribution of dislocation density from grain to grain in the strained 2A/o alloy. However, one cannot say this with any certainty since with disc polishing techniques large thin areas covering several adjacent grains are not obtained.

7.4 Dislocation arrangements.

Plates 7.1 to 7.6 show one micrograph from each of the deformed alloys on which dislocation density measurements were made. These plates show qualitatively both the changes in dislocation density with strain for a given alloy, and the differences between the dislocation arrangements seen in alloys of different compositions.

The first point is illustrated by plates 7.1 and 7.2 in the case of the 2A/o alloy, and by plates 7.4, 7.5 and 7.6 for the 12A/o alloy; this is more clearly seen if it is realized that the magnification changes by a factor of two between plates 7.1 and 7.2, between plates 7.4 and 7.5, and between plates 7.5 and 7.6. The values of the tensile strain are given with the plates.

The second point, the changes in dislocation arrangement with aluminium content, is illustrated by plates 7.1, 7.3 and 7.5, which are for the 2A/o, 8A/o and 12A/o alloys respectively. These changes are well known, and have been studied by, among others, Howie and Swann, 1961, and Swann and Nutting, 1961. In the 2A/o alloy (plate 7.1) the dislocations are found in irregular tangles, whereas in the 8A/o alloy (plate 7.3) the dislocation structure is much more ordered. The change in going to the 12A/o alloy (plate 7.5) is very striking; the
dislocations are arranged mainly on one set of slip planes, and often occur as groups of parallel dislocations of like sign on the same slip plane (see for example plates 6.8 and 6.9 which are both micrographs of dislocations in the 12A/6 alloy). The other important feature is that very many of the dislocations seen in the 12A/6 alloy are extended. That is, the single dislocation splits into two partial dislocations separated by a region of stacking fault. The latter gives rise to a characteristic fringe contrast which can be seen in plate 7.5.

The reasons for these changes in dislocation structure are the decrease in stacking fault energy as more aluminium is added, which lowers the probability of cross slip occurring, and the effects of alloy hardening. These will be discussed in the next chapter.

7.5 Combined results.

Table 7.3 shows the values of stress $\tau$, strain $\epsilon$, dislocation density $N_d$, dislocation resistivity $W_{d}T^2$, and the values of the thermal resistivity per unit dislocation density $W_{d}T^2/N_d$ for all the strained alloys. In the values of $N_d$, no correction for dislocation loss has been made. Values of $W_{d}T^2$ were obtained as explained in section 1.3. Work hardening theories predict that $\tau^2$ should be proportional to $N_d$ (Wiedersich, 1964); hence if $W_{d}T^2$ is proportional to $N_d$, a graph of $\sqrt{W_{d}T^2}$ against $\tau$ will give a straight line. This graph is plotted in fig.7.3. Although there are only two points in each case for the 2A/6 alloys, these lie close to straight lines drawn through the origin. The points for the 4A/6 and 8A/6 alloys are also shown on fig.7.3. In fig.7.4, $\sqrt{N_d}$ is plotted against $\tau$, and while a reasonable straight line can be drawn through the points for the 12A/6 alloy, the same is not true for the 2A/6 alloy.

These results are discussed in the next chapter.
Table 7.1
Thermal conductivity results for strained alloys.

<table>
<thead>
<tr>
<th>Nominal comp. A/o</th>
<th>Strain %</th>
<th>$\rho \times 10^6$ ohm cm.</th>
<th>$L/\rho \times 10^3$ watt cm$^{-1}$ deg.$^{-2}$</th>
<th>$A \times 10^3$ watt cm$^{-1}$ deg.$^{-2}$</th>
<th>$B \times 10^3$ watt cm$^{-1}$ deg.$^{-3}$</th>
<th>$W_g$ cm$^2$ deg.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Annealed</td>
<td>2.12</td>
<td>11.53</td>
<td>11.21 ± 0.02</td>
<td>764 ± 0.04</td>
<td>1310 ± 20</td>
</tr>
<tr>
<td>2</td>
<td>2.9</td>
<td>2.12</td>
<td>11.53</td>
<td>11.17 ± 0.04</td>
<td>556 ± 0.15</td>
<td>1800 ± 90</td>
</tr>
<tr>
<td>2</td>
<td>Annealed</td>
<td>2.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2.16</td>
<td>11.34</td>
<td>11.29 ± 0.03</td>
<td>239 ± 0.01</td>
<td>4190 ± 260</td>
</tr>
<tr>
<td>4</td>
<td>Annealed</td>
<td>3.88</td>
<td>6.30</td>
<td>6.17 ± 0.02</td>
<td>566 ± 0.03</td>
<td>1770 ± 35</td>
</tr>
<tr>
<td>4</td>
<td>10.9</td>
<td>3.92</td>
<td>6.25</td>
<td>6.20 ± 0.02</td>
<td>185 ± 0.07</td>
<td>3720 ± 220</td>
</tr>
<tr>
<td>8</td>
<td>Annealed</td>
<td>6.63</td>
<td>3.69</td>
<td>3.66 ± 0.02</td>
<td>429 ± 0.03</td>
<td>2330 ± 50</td>
</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>6.70</td>
<td>3.65</td>
<td>3.55 ± 0.02</td>
<td>269 ± 0.07</td>
<td>3720 ± 190</td>
</tr>
<tr>
<td>12</td>
<td>Annealed</td>
<td>7.21</td>
<td>3.39</td>
<td>3.33 ± 0.02</td>
<td>404 ± 0.03</td>
<td>2480 ± 60</td>
</tr>
<tr>
<td>12</td>
<td>7.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>6.2</td>
<td>7.21</td>
<td>3.39</td>
<td>3.21 ± 0.02</td>
<td>290 ± 0.06</td>
<td>3450 ± 150</td>
</tr>
<tr>
<td>12</td>
<td>Annealed</td>
<td>7.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>12.8</td>
<td>7.42</td>
<td>3.29</td>
<td>3.07 ± 0.04</td>
<td>22 ± 0.01</td>
<td>4550 ± 320</td>
</tr>
</tbody>
</table>
Table 7.2

Dislocation densities of strained alloys.

<table>
<thead>
<tr>
<th>Nominal comp. A/o</th>
<th>$\varepsilon$</th>
<th>m</th>
<th>g</th>
<th>$N_s \times 10^9$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.9</td>
<td>43</td>
<td>23</td>
<td>4.7 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
<td>31</td>
<td>17</td>
<td>11.3 ± 1.0</td>
</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>43</td>
<td>24</td>
<td>8.4 ± 1.0</td>
</tr>
<tr>
<td>12</td>
<td>3.4</td>
<td>16</td>
<td>-</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>12</td>
<td>6.2</td>
<td>17</td>
<td>-</td>
<td>4.6 ± 0.4</td>
</tr>
<tr>
<td>12</td>
<td>12.8</td>
<td>7</td>
<td>-</td>
<td>8.6 ± 1.0</td>
</tr>
</tbody>
</table>
Table 7.3

Combined thermal conductivity and dislocation density results for strained alloys.

<table>
<thead>
<tr>
<th>Nominal comp.</th>
<th>$\epsilon$</th>
<th>$\gamma$</th>
<th>$W_p T^2$</th>
<th>$N_p \times 10^9$</th>
<th>$\frac{W_p T^2}{N_p} (\times 10^7)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/o</td>
<td>%</td>
<td>K/cm$^2$</td>
<td>watt-cm-deg$^2$</td>
<td>cm$^{-2}$</td>
<td>watt-cm$^3$deg$^3$</td>
</tr>
<tr>
<td>2</td>
<td>2.9</td>
<td>431</td>
<td>4.90 ± 1.10</td>
<td>4.7 ± 0.4</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
<td>1015</td>
<td>2880 ± 280</td>
<td>11.3 ± 1.0</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td>4</td>
<td>10.9</td>
<td>1347</td>
<td>3660 ± 260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>1230</td>
<td>1390 ± 240</td>
<td>8.4 ± 1.0</td>
<td>1.7 ± 0.5</td>
</tr>
<tr>
<td>12</td>
<td>3.4</td>
<td>430</td>
<td>-</td>
<td>1.0 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>6.2</td>
<td>1078</td>
<td>970 ± 210</td>
<td>4.6 ± 0.4</td>
<td>2.1 ± 0.7</td>
</tr>
<tr>
<td>12</td>
<td>12.8</td>
<td>1618</td>
<td>2070 ± 380</td>
<td>8.6 ± 1.0</td>
<td>2.3 ± 0.7</td>
</tr>
</tbody>
</table>
Fig. 7.1
Graphs of K/T against T for the 2A/6 alloy in the annealed condition, and after different amounts of strain.
Fig. 7.2
Graphs of $K/T$ against $T$ for all strained alloys except the 2A/o alloy. Note the change of scale for the 4A/o alloy.
Fig. 7.3
Graphs of \((w_0 T^2)\frac{1}{2}\) against flow stress for the 2A/6 and 12A/6 alloys. Points for the 4A/6 and 8A/6 alloys are also shown.
Fig. 7.4

Graph of \( \tau \) against \( \sqrt{N} \). No attempt has been made to draw a line through the points for the 2A6 alloy.
Plate 7.1 $x$ 40,000

Dislocations in the Cu 2A6 Al alloy after 2.9\% strain.
Dislocations in the Cu 2A/6 Al alloy after 10% strain.
Plate 7.3 x 80,000

Dislocations in the Cu 8A/o Al alloy after 6% strain.
Dislocations in the Cu 12A/o Al alloy after 3.4% strain.
Dislocations in the Cu 12A/6 Al alloy after 6.2% strain.
Dislocations in the Cu 12A6 Al alloy after 12.8% strain.

Plate 7.6 x 80,000
8.1 Introduction

In this chapter, the values obtained theoretically for dislocation phonon scattering will first be given. Then the significance of the experimental results of the previous chapter will be discussed. Finally these results will be discussed in relation to the work of others.

Throughout this chapter the expression \( \frac{W_0 T^2}{N_d} \) will be written as \( S \).

8.2 Calculations of dislocation phonon scattering.

Associated with a dislocation line is a core region and a long range stress field, the latter falling off as \( r^{-1} \), where \( r \) is the distance from the dislocation core (Cottrell, 1953). Dislocation phonon scattering at low temperatures is expected to be mainly due to the effect of the strain field. The disordered core region has a width of at the most two or three lattice spacings, and is not "seen" by the phonons at low temperature because of their long wavelength. The strain field gives rise to phonon scattering via the anharmonicity of the interatomic forces. This introduces terms cubic and higher in the atomic displacements into the Hamiltonian representing the vibrational energy of the lattice. Thus interactions between phonons in different modes become possible, and scattering occurs. The difficulty associated with calculations of dislocation phonon scattering is that a knowledge of the anharmonic forces is required. This problem has been approached in two ways. Both Klemens, 1958, and Carruthers, 1961, make the approximation that the anharmonic forces can be described by a suitable introduction of the Grüneisen constant \( g \), and both obtain an expression

\[
S = \frac{m v k^2}{(gb)^2}
\]

(8.1)

where \( m \) is a numerical constant, \( v \) is the velocity of sound, and \( b \) is the burgers vector of the dislocations. For a random array of edge and screw dislocations, the following value is obtained for pure copper:
\[ S = 5 \times 10^{-9} \text{ watt}^{-1} \text{ cm}^{3} \text{ deg}^{3} \] (8.2)

Bross and Seeger, 1963, have refined the calculation by using values of the anharmonic force constants which were derived from measured values of the third order elastic constants. The calculation was done for an elastic continuum, and at low temperatures where long wavelength phonons predominate this is a good approximation. Bross and Seeger obtain for pure copper after an average over edge and screw dislocations randomly distributed
\[ S = 6 \times 10^{-9} \text{ watt}^{-1} \text{ cm}^{3} \text{ deg}^{3} \] (8.3)
which is not significantly different from the value of Klemens.

Granato, 1953, derived an expression for dislocation phonon scattering based on the idea that a phonon can cause a dislocation segment to vibrate in the Peierls-Nabarro potential well. While obtaining answers of the same order of magnitude as those given above, his expression predicts that the lattice thermal conductivity limited by dislocation phonon scattering should have a \( T^{3.5} \) dependence. This is not observed experimentally. Nevertheless, the very large discrepancies between the values of \( S \) obtained from theory and experiment in the alkali halides has led some workers to attempt calculations based on the dislocation flutter model (Ishioika and Suzuki, 1963). To the present author's best knowledge, the results of such calculations have not yet been published.

8.3 Dislocation phonon scattering in copper aluminium alloys.

In the discussion which follows, it will be considered that the second value of \( S \) given in table 7.3 is spurious, because the value of the dislocation density obtained for 10\% strain in the 2A/\% alloy is too small. The reasons for believing this are

(a) Graphs of \( \frac{\sqrt{\tau}}{kT^2} \) against \( \tau \) give good straight lines passing through the origin for both the 2A/\% and the 12A/\% alloys (fig.7.3);
however, while a reasonable straight line can be drawn through the points for the 12\% alloy on a graph of $\sqrt{N}$ against $\tau$ (fig. 7.4), the same is not true for the 2\% alloy.

(b) If the value of $S$ obtained from the 2.9\% strained alloy is assumed to be correct, then a systematic change in the value of $S$ with aluminium content is observed (table 7.3).

c) The estimation of dislocation densities in the cell walls of a dislocation substructure is difficult because the images of the dislocations overlap. For the 2\% alloy after 2.9\% strain the cell structure is already forming but the individual dislocations can still be distinguished (plate 7.1). This is no longer generally true after 10\% strain, and values of dislocation density may be underestimates (plate 7.2).

d) Evidence that dislocation densities obtained from electron microscopy for copper and aluminium are too small by a factor which increases as the dislocation density increases has been presented by Foxon and Rider, 1965. They consider that the magnitude of the discrepancy can be correlated with stages in the formation of the dislocation substructure. They suggest that the error is due to a combination of dislocation overlap, dislocation loss, and dislocation rearrangement.

It can be seen from table 7.3 that if the second value is neglected $S$ increases with the aluminium content of the alloys. This change is believed to be genuine, although if the experimental errors are taken into account, the different values almost overlap. The size of this experimental error was one reason for not making dislocation density measurements on the 4\% strained alloy. Another related reason is that if the changes in $S$ with composition are correlated with changes in stacking fault energy, the value expected for the 4\% alloy would not be significantly different from that obtained for the 2\% alloy. Approximate values for the stacking fault energy of copper aluminium alloys can be obtained from the work of Howie and Swann, 1961, and are
32, 23, 7, and 3.5 ergs/cm$^2$ for the 2A/o, 4A/o, 8A/o, and 12A/o alloys respectively. The values for the 2A/o and 4A/o alloys are obtained by extrapolation. Comparison of these values of stacking fault energy $\gamma$ with the values of $S$ given in table 7.3 indicates the following empirical relationship:

$$S = 2\left(\frac{4}{3}\right)^{\frac{1}{3}} \times 10^{-7} \text{ watt}^{-1} \text{ cm}^3 \text{ deg}^3$$

(8.4)

where the expression has been normalised to fit the value of $S$ obtained for the 2A/o alloy, and $\gamma$ is in ergs/cm$^2$. Eq. (8.4) predicts values of $S$ for the 2A/o, 4A/o, 8A/o, and 12A/o alloys of 1, 1.1, 1.7, and 2.1 x $10^{-7}$ watt$^{-1}$ cm$^3$ deg$^3$ respectively. On the latter basis the values of $S$ for the 2A/o and 4A/o alloys are not significantly different.

Possible reasons for the changes in $S$ with aluminium content in copper aluminium alloys will now be considered. Firstly, the scattering power of an isolated dislocation may increase with the aluminium content. This could arise from changes in the elastic constants, which would change the velocity of sound, and the Grüneisen constant; however, observed changes in the elastic moduli with alloying cannot account for changes in dislocation phonon scattering of the order of 100% (Rayne, 1959). The segregation of aluminium atoms to dislocation lines or stacking faults will not produce an increased scattering on the strain field model. The segregation of solute atoms to the strain field of a dislocation will only occur if it results in a reduction of the strain field, and hence cannot be responsible for an increase in dislocation phonon scattering power. The splitting of dislocations into partials cannot increase the scattering power, since this will not occur unless the square of the burgers vector of the whole dislocation is greater than the sum of the squares of the burgers vectors of the partials. Hence the increased likelihood of splitting into partials with decreasing stacking fault energy will not explain the observed changes in dislocation phonon scattering power, as from the theoretical
calculations the latter is proportional to the square of the burgers vector.

Secondly, the change in $S$ may be due to the marked changes in dislocation arrangement with added aluminium. As aluminium is added, the stacking fault energy decreases, and the equilibrium width of stacking fault between the partials of a split dislocation increases. This reduces the probability of cross slip, and dislocations tend to be more and more confined to their slip planes. This results in an increasing regularity of the dislocation structure, which is illustrated by plates 7.2, 7.3, and 7.5. There are two ways in which this can give rise to the increase in $S$ observed between the $2\%$ and $12\%$ alloys. One possibility is that in the $2\%$ alloy, the dislocations are very tangled, and this will result in some mutual cancellation of long range stress fields; but as more aluminium is added the dislocations become less tangled, and each will contribute fully to the scattering. This amounts to saying that the value of $S$ for the $12\%$ alloy is more representative of a dislocation phonon scattering power in copper than is the value for the $2\%$ alloy, and also that for large deformations in any alloy, the value of $S$ would be smaller than that obtained for small deformations in the same alloy; there is as yet no definite evidence for the latter. The other possibility is that pile-ups may occur. Klemens, 1956, suggested that the existence of dislocation pile-ups would explain the observed discrepancies between experimental and theoretical values for $S$. If all the dislocations are arranged in pile-ups of $P$ dislocations of the same burgers vector on the same slip plane, then if each pile-up scatters as a dislocation of burgers vector $Pb$, the scattering is increased by a factor of $P$: that is $\frac{N}{P}$ pile-ups, each scattering as $(Pb)^2$. Rows of dislocations of the same burgers vector are often seen in the $12\%$ alloy, but the spacing of the dislocations is seldom less than two or three hundred angstroms. Nevertheless, the rows of dislocations may sometimes be from pile-ups which have relaxed during the electropolishing process. Since the dominant phonon wavelength varies
from about 50 ångstroms at 4·2°K to about 150 ångstroms at 1·5°K, it is quite likely that the higher value for S in the 12A/6 alloy arises in part from coherent scattering. Evidence for this in the alkali halides, LiF in particular, has been given by Taylor et al., 1965. If the ratio of S between the 2A/0 and any other alloy is denoted by F, and if the increased value of S is assumed to be due only to the creation of Y pile-ups each of P dislocations, then assuming there are no pile-ups in the 2A/0 alloy,

$$FN_p b^2 = (N_p - YP)b^2 + YP^2b^2$$  \hspace{1cm} (8.5)

and the fraction of dislocations arranged in pile-ups is

$$\frac{YP}{N_p} = \frac{F - 1}{P - 1}.$$  \hspace{1cm} (3.6)

F for the 12A/6 alloy is about 2, and on the basis of the above equation one needs a fraction \((P - 1)^{-1}\) of the dislocations arranged in pile-ups of P dislocations each to account for the observed value of F. In practice there will be pile-ups containing varying numbers of dislocations, but if for the sake of argument a value of P = 6 is assumed for the 12A/6 alloy, then 1/5th of the dislocations would have to be in pile-ups. From the evidence of transmission electron microscopy this does not seem unreasonable.

From the work which has so far been done at Battersea, it is not possible to distinguish between the above possibilities, and it may be that they all contribute in part to the observed changes in S with increasing aluminium content in copper aluminium alloys. But it seems definite that S does change, so that any interpretation of thermal conductivity measurements on strained copper alloys of differing composition assuming a fixed value for S throughout is liable to be wrong.

8.4 Comparison with other work.

If the values of S obtained for the 2A/6, 8A/6, and 12A/6 copper aluminium alloys are taken at their face values, then Klemens' or Bross...
and Seeger's theoretical values are too small by a factor of between 20 and 50. If the maximum dislocation loss of 30%, discussed in Chapter 6, is assumed, then the factor is reduced to between 14 and 35. The theoretical calculations were done for pure copper, which has a stacking fault energy usually accepted as about 40 ergs/cm². On the basis of Eq.(8.4) for zero aluminium content a value of S still 12 times as large as the theoretical value is obtained. Even if the value of about 170 ergs/cm² for the stacking fault energy of copper given by Seeger et al., 1959, is considered correct, the value of S from Eq.(8.4) is still 8 times as large as the theoretical value. In the present author's opinion, contrary to that of Seeger, it seems unlikely that refinement of the strain field scattering model for dislocation phonon scattering will ever produce the experimentally observed values.

Since values of the stacking fault energy of alpha-brasses may be obtained from the data of Howie and Swann, 1961, one may estimate on the basis of the present results values of S for the alpha-brasses used by Lomer and Rosenberg, 1959, and Kemp et al., 1959. Lomer and Rosenberg made their dislocation density measurements on Cu 30% Zn, which has a stacking fault energy of about 6 ergs/cm². Thus from Eq.(8.4), their value of S should be about $1.8 \times 10^{-7}$ watt⁻¹ cm⁻³ deg⁻³, which is about four times as great as their stated value. The present author believes that this discrepancy is due to errors in dislocation density measurements, and that Lomer and Rosenberg's interpretation of their results for alpha-brasses containing from 7% to 30% zinc on the basis of a constant value for S is suspect.

The stacking fault energy of the Cu 15% Zn alloy used by Kemp et al. is about 20 ergs/cm² from Howie and Swann's data, and from the present work a value for S of about $1.2 \times 10^{-7}$ watt⁻¹ cm⁻³ deg⁻³ is expected. This exceeds by a factor of three the result they obtained. Since the dislocation densities were estimated indirectly from stored energy measurements, and since the deformation was by severe torsional
strain leading to a non-uniform dislocation distribution normal to the heat current, the measurement of Kemp et al. may well be in error. However, one cannot be categorical until more careful experiments on alpha-brass have been carried out.

Tainsh et al., 1961, in the measurements described in section 1.5∥, found that for identical deformations of a Cu 2·25A/₆ Si alloy and a Cu 4·5A/₆ Si alloy \( \bar{W}_s T^2 \) was 8\( \times 10^3 \) and 17\( \times 10^3 \) watt\(^{-1}\) cm. deg.\(^3\) respectively. Imura et al., 1963, have measured the stacking fault energies of copper silicon alloys by the same method as Howie and Swann, and from their results one obtains values of about 15 and 5 ergs/cm.\(^2\) for the Cu 2·25A/₆ Si alloy and the Cu 4·5A/₆ Si alloy respectively. On the basis of Eq.(8.4) the dislocation densities would be 6·5\( \times 10^{10} \)/cm.\(^2\) and 9\( \times 10^{10} \)/cm.\(^2\) for the Cu 2·25A/₆ Si alloy and the Cu 4·5 Si alloy respectively. There is considerable evidence, admittedly for much lower deformations, that the dislocation density for a given strain in copper alloys decreases with the stacking fault energy (Swann, 1963), so that the values for \( N_p \) given above seem more likely than those calculated by Tainsh et al. assuming a constant value for \( S \).

The results of Rowell, 1960, on deformed lead and lead alloy single crystals will be reconsidered. The relevant data are given below:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( \bar{W}_s ) (at 1°K)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>lead</td>
<td>6·19</td>
<td>0·19</td>
</tr>
<tr>
<td>lead alloy</td>
<td>4·74</td>
<td>0·16</td>
</tr>
</tbody>
</table>

The values of the equivalent tensile strain are given, but in fact the specimens were deformed by bending. From the formula (Cottrell, 1953)

\[
N_p = \frac{1}{Rb},
\]

(8.7)

where \( R \) is the radius of bending, and \( b \) the burgers vector, one may estimate the minimum dislocation density introduced. From Eq.(8.7) this
is $2.5 \times 10^6$ lines/cm. There is no information available on dislocation densities in deformed lead single crystals. Bolling et al., 1962, deformed 20 lead single crystals in tension at low temperatures and for all except one the easy glide region extended past 4% tensile strain. For copper single crystals deformed 2% in the easy glide region, $N_p$ would not be greater than about $10^8$ lines/cm. Assuming the same value of $N_p$ for lead, $S$ would lie between $2 \times 10^{-6}$ and $6 \times 10^{-8}$ watt$^{-1}$ cm.$^3$ deg.$^2$. The latter value is 40 times as great as that worked out from Klemens' 1958 formula by Rowell.

The points emerging from the discussion of this chapter, and of Chapter 5, are summarized in the conclusion which follows immediately.
Conclusions

1. The lattice thermal conductivity of copper aluminium alloys at liquid helium temperatures is well represented by the equation

$$K_g = CT + BT^2$$

where the major contribution comes from the quadratic term. There is no detectable term cubic or higher in $T$.

2. For annealed alloys $B$ is limited by electron phonon scattering, and shows a systematic variation with residual resistivity. Variations of this kind have been known for over ten years, and still remain unexplained theoretically.

3. For polycrystalline specimens the observed values of $C$ are consistent with a model in which only electron-phonon scattering is taken into account. However, comparison of values of $C$ for polycrystals and single crystals of similar composition indicates that $C$ in polycrystals arises in part from boundary scattering.

4. Values of $W_s T^2/N_s$ obtained in this work differ from those obtained theoretically for pure copper by others by a factor of between 14 and 50, and from those obtained experimentally by others for alpha brass by a factor of between 3 and 4.

5. For copper aluminium alloys, the values of $W_s T^2/N_s$ change systematically with aluminium content. This is probably due to the coherent scattering of phonons by dislocation pile-ups whose frequency of occurrence can be correlated with aluminium content.
Suggestions for further work

1. Measurement of the thermal conductivity of polycrystalline specimens of the same composition but with different mean grain sizes will test the boundary scattering hypothesis.

2. Although others have not found significant changes in residual resistivity over the range 1·5° to 4·2°K in their alloys, it would be desirable to measure \( \rho_0 \) over this range for the alloys used in this work.

3. Having gained experience in the temperature range 1·5° to 4·2°K it would be desirable to extend the range in both directions.

4. The experiments done by others on deformed alpha-brass should be repeated paying particular attention to the dislocation density determination.

5. Measurement of the thermal conductivity of a deformed specimen of the 12A/6 alloy both free and under stress is expected to confirm the dislocation pile-up hypothesis.

6. Measurement of the thermal resistivity introduced by specific arrangements of dislocations in alloys would be desirable. This may be possible if measurements are made on single crystals of particular orientations which have been deformed in tension. Moreover, it may be possible to use etch pit methods to obtain dislocation densities which can then be compared with those obtained from electron microscopy.

7. Experiments involving all the above suggestions have been planned at Battersea, but it is clear that there is also much scope for theoretical work. In the annealed alloys, the changes of \( B \) with impurity content need to be explained. From the strained alloy results, it seems that calculations of \( W_0 T^2/N_0 \) need to be reconsidered. This is particularly so in the case of the alkali halides.
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