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

by

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The thermal conductivity of a specimen of alpha-brass has been measured and the dislocation-phonon scattering power, $\sigma$, deduced. The dislocation density was determined by transmission electron microscopy. By comparison with similar measurements made on copper-aluminium alloys (Salter, 1965), it has been shown that $\sigma$ depends on the type and concentration of solute element and not upon the dislocation arrangement. A theory to account for the variation in $\sigma$ (Klemens, 1968), has been critically considered.

For annealed specimens at liquid helium temperatures the lattice thermal conductivity, limited by electron-phonon scattering, has a quadratic temperature dependence. However, for deformed specimens deviations from a pure $T^2$ dependence were found and have been attributed to the scattering of phonons by dipole dislocations.

Measurements have been made of the thermal conductivity of specimens of Cu+2at.%Al, Cu+12at.%Al, and Cu+10at.%Au after successive amounts of tensile
deformation. The value of $\sigma$ for the latter alloy has been deduced. The results are used to provide information on the mechanism of work hardening in these materials. It is shown that the important parameter is the relative atomic size of solute and solvent and not the electron concentration. Measurements of the residual electrical resistivity of the specimens yield information on the variation in stacking fault widths with deformation.
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NOTES

1. Tables, diagrams (figures) and plates are to be found, in that order, at the end of the relevant chapters.

2. The abbreviation at.% is used for atomic per cent.

3. The copper base alloys studied in this work are referred to by the nominal concentration, expressed in at.%, and type of solute followed, where applicable, by the degree of tensile strain, e.g. 12Al(21%) indicates that the specimen is copper + 12at.% aluminium, strained 21%.

The actual compositions of the specimens appear in Table 2.1.
1.1 Introduction.

At low temperatures, the lattice thermal conductivity of a crystalline specimen depends not only on the concentration but also on the type of defects present. Measurements of the thermal conductivity are thus a useful method of studying defects in bulk specimens. When the research described here was initiated, the dependence of dislocation-phonon scattering upon the solute content in dilute copper-aluminium alloys had been established experimentally by means of measurement of the lattice thermal conductivity. This result and the theories advanced to explain it on the basis of a variation in dislocation arrangement from one specimen to another did not agree with the results obtained by other workers on different copper alloys. Accordingly, the primary aim of this work was to undertake a very careful investigation of dislocation-phonon scattering in an alpha-brass specimen using more refined techniques to measure the lattice thermal conductivity and to study the dislocation density using transmission electron microscopy. The results indicate that the dislocation-phonon scattering is dependent upon solute type and concentration and not on dislocation arrangement. This was confirmed by the experiments of Salter who compared the lattice thermal conductivity of a specimen under
tension and also in a relaxed condition (Charsley et al., 1967). Measurements of the lattice thermal conductivity were then used to study the plastic deformation of certain copper alloys and to deduce the dislocation-phonon scattering power for a copper-gold alloy. The value of using thermal conductivity measurements to deduce dislocation densities becomes evident as the densities are greater than those which can be determined by electron microscopy. The refinements in measuring techniques enabled the values of the conductivity to be obtained more accurately and its sensitivity to the relative spacings between individual dislocations is shown to be detectable experimentally. A simple theoretical model is shown to give good qualitative agreement with the experimental results.

1.2 The Lattice Thermal Conductivity.

The theoretical derivation of the lattice thermal conductivity is here outlined in a simplified form. A very full discussion is given in two comprehensive reviews by Klemens, 1958, and Carruthers, 1961.

The heat current $Q$ can be expressed as the sum of the heat current carried by all normal modes

$$Q = \sum_{q, j} N_j(q) \hbar \omega_j(q) \frac{\partial \omega_j(q)}{\partial q},$$

(1.1)

where $N_j(q)$ is the distribution function for phonons of wave number $q$ and angular frequency $\omega$ for polarization branch $j$. $2\pi\hbar$ is Planck's constant.

At equilibrium, the value of $N_j(q)$ is given by

$$N_j(q) = \left( \exp \frac{\hbar \omega_j(q)}{kT} - 1 \right)^{-1},$$

(1.2)
where $k$ is Boltzmann's constant and $T$ is the absolute temperature. If $N_j(q) = N'_j(q)$, then $Q = 0$. For infinite perfect crystals any departure of $N_j(q)$ from its equilibrium value persists indefinitely and gives rise to an infinite thermal conductivity in the absence of U-processes i.e. three-phonon processes in which momentum is not conserved (Peierls, 1929). However, in real crystals any deviation of $N_j(q)$ from $N'_j(q)$ disappears in the absence of a temperature gradient due to the various scattering processes which limit the thermal conductivity. The usual approach in calculating the thermal conductivity is to use a relaxation time approximation in the Boltzmann equation. The validity of this has been discussed by Ziman, 1960, and Carruthers, 1961, and the additivity of reciprocal relaxation times for different scattering processes is discussed in section 1.4. If the return to equilibrium proceeds exponentially, a relaxation time $T_j$ can be defined such that

$$\frac{d N_j(q)}{d t} = N'_j(q) - N_j(q) = -\frac{n_j(q)}{T_j(q)} , \quad (1.3)$$

where $n_j(q)$ is the deviation from equilibrium and the term $\frac{d N_j(q)}{d t}$ denotes the rate of change due to interactions.

In the steady state in the presence of a temperature gradient the Boltzmann equation can be set up to equate the effect of the temperature gradient tending to increase $n_j(q)$ and interaction processes tending to decrease it. Then

$$\frac{d N_j(q)}{d t} = -v \cdot (\text{grad } T) \frac{d N_j(q)}{d T} . \quad (1.4)$$

The term on the right denotes the rate of change of $N_j(q)$ arising from the drift motion of phonons in the
temperature gradient. Here $v_j(q)$ is the group velocity of the phonons given by

$$v_j(q) = \frac{\hbar \omega_j(q)}{\delta q} \quad .$$

(1.5)

It is usual to make the approximation that $N_j(q)$ can be replaced by $N_j(q)$ in the right-hand term of (1.4) in which case with equations (1.2) and (1.3)

$$n_j(q) = -\left[ v_j(q) \cdot (\text{grad} \ T) \tau_j(q) S_j(q) \right] (\hbar \omega_j(q))^{-1} \quad ,$$

(1.6)

where

$$S_j(q) = \frac{(\hbar \omega_j(q))^2}{kT} \frac{\exp \hbar \omega_j(q)/kT}{(\exp \hbar \omega_j(q)/kT - 1)^2} \quad ,$$

(1.7)

is the specific heat associated with the mode $(q,j)$. Combined with (1.1) this gives for $Q$:

$$Q = \sum_{q,j} (v_j(q) \cdot \text{grad} \ T)v_j(q) \tau_j(q) S_j(q) \quad .$$

(1.8)

The thermal conductivity tensor is defined as

$$Q_{\ell m} = -K_{\ell m} (\text{grad} \ T)_{m} \quad ,$$

(1.9)

where $\ell$ and $m$ denote components of vectors. In the isotropic case this gives, for the conductivity, $K$,

$$K = \frac{1}{\tau} \sum_j S_j(q)v_j^2(q) \tau_j(q) \quad d_\gamma \quad ,$$

(1.10)

where the summation over $q$ has been replaced by an integral. This expression is similar to that obtained from the kinetic theory of gases if a mean free path $L_j(q)$ is defined as

$$L_j(q) = v_j(q) \tau_j(q) \quad .$$

(1.11)

The quantitative calculation of values of $K$ from (1.10) involves many further assumptions as discussed in the
review by Carruthers, 1961. However, qualitative predictions of the temperature dependence of $K$ can be made as $S_J(q)$ has a $T^3$ dependence and $v_J(q)$ is a constant in the range of very low temperatures. Then if $L_J(q)$ varies as $q^{-n}$

$$K \propto T^{3-n}.$$  (1.12)

Klemens, 1958, lists values of $n$ for the various scattering mechanisms on the basis of his theory; e.g. $n$ has a value of unity for both dislocation-phonon and electron-phonon scattering and a value of 3 for boundary scattering. These different values of $n$ make it possible to separate the various contributions to the thermal resistivity; this is discussed in detail in the next section.

1.3 Separation of the Thermal Conductivity into its Electronic and Lattice Components.

In metals and alloys the thermal conductivity $K$ is the sum of an electronic component $K_e$ and a lattice component $K_g$, i.e.

$$K = K_e + K_g.$$ (1.13)

The electronic component of the thermal resistivity $\rho_e(=1/K_e)$ is the sum of two terms $\rho_i$ and $\rho_o$ where $\rho_i$ is the 'ideal' and $\rho_o$ is the residual thermal resistivity. $\rho_i$ is due to the scattering of electrons by the thermal vibrations of the crystal lattice; $\rho_o$ arises from the scattering of these electrons by impurities such as vacancies, interstitials or dislocations.

In order to measure $K_g$, the total conductivity $K$
must first be determined. The value of $K_e$ is then calculated from values of the electrical resistivity, and $K_g$ is deduced by subtraction. However, in pure metals which are non-superconducting, $K_e$ is much greater than $K_g$ and hence the latter cannot be detected using present experimental techniques. It is thus necessary to reduce $K_e$ so that it becomes comparable in magnitude to $K_g$. There are three methods of achieving this in practice:

(i) Reduction of $K_e$ by applying a magnetic field to the specimen. This method has not been widely used as the theory of the variation of $K_e$ with magnetic field is somewhat obscure and experimentally there are problems in producing magnetic fields large enough to give sufficient reduction in $K_e$.

(ii) Reduction of $K_e$ in specimens which are superconducting. At temperatures close to $T_c$, the superconducting transition temperature, the electrons and phonons both contribute to the thermal conductivity. However, if the temperature is sufficiently low, of the order of $T_c/5$, the conduction electrons carry no thermal current, neither do they scatter the lattice waves (Montgomery, 1958). The thermal conductivity then consists purely of the lattice contribution and the specimen behaves in this respect like a dielectric crystal. The range of specimens that can be investigated in this manner is rather limited and measurements have to be made at $1.5^\circ K$ and below in most cases.

(iii) Reduction of $K_e$ through alloying. This has the effect of reducing the electron mean free path without appreciably affecting $K_g$ and is the method employed in
For copper alloys having a residual electrical resistivity \( \rho_o \) greater than one microhm cm it is assumed that below about 100 K, \( K_e \) is limited by impurity scattering and that \( K_e \) and \( \rho_o \) are related by the Wiedemann-Franz law

\[
K_e = LT/\rho_o = L \omega_0^{-1} \quad (1.14)
\]

Here \( L \) is the Lorenz number which is equal to 2.445 x 10^{-8} watt ohm deg^{-2}. If \( \rho_o \) is measured for the same specimen, the lattice contribution to the thermal conductivity is then

\[
K_g = K - LT/\rho_o \quad (1.15)
\]

The Wiedemann-Franz law should be valid when the scattering of electrons is elastic. The reason for this, somewhat simplified, is that at low temperatures the electron-phonon interaction results in electrons being scattered through only small angles. This has little effect on the flow of electric current as the electronic charge is unaltered but the electron energy is changed by a factor \( kT \), where \( k \) is Boltzmann's constant, and the thermal current is reduced much more. The Wiedemann-Franz law then no longer holds. This point is discussed in detail by Ziman, 1964. When the electrons are scattered elastically the electrical resistivity is independent of temperature at liquid helium temperatures and indeed \( \rho_o \) has been observed to be constant (Lindenfeld and Pennebaker, 1962).

In high residual resistivity alloys (\( \rho_o \) greater than 10 microhm cm) the analysis of the thermal conductivity in terms of the Wiedemann-Franz relationship is complicated by the fact that there is a term linear in \( T \) in the lattice
thermal conductivity. This situation is briefly reviewed later in this chapter.

For low residual resistivity alloys (\( \rho_c \) less than 10 microhm cm) the lattice thermal conductivity is limited by electron-phonon scattering and is expected to be proportional to the square of the absolute temperature (Klemens, 1954). However, the Pippard theory (Pippard, 1955, 1960) predicts the possibility of a \( T^3 \) term and higher power terms in the expression for \( K_g \) (see e.g. Jericho, 1965; Salter 1965). The expression for the total thermal conductivity may then be written as

\[
K = AT + BT^2 + \text{higher powers of } T. \quad (1.16)
\]

A graph of \( K/T \) plotted against \( T \) will then be a straight line of slope \( B \) having an intercept \( A \) on the \( K/T \) axis. Any significant curvature of the graph could indicate the presence of powers of \( T \) higher than \( T^2 \) in equation (1.16) and a finite value of \( (L/\rho_c - A) \) demonstrates either the existence of a term linear in temperature in the lattice thermal conductivity or a deviation from the Wiedemann-Franz law. For this reason it is undesirable to adopt the practice, followed by some authors (e.g. Kemp et al., 1957; Lomer and Rosenberg, 1959), of giving weight to the value of \( L/\rho_c \) as a point at \( T = 0^\circ K \) when drawing graphs of \( K/T \) against \( T \).
1.4 The Components of the Lattice Thermal Resistivity

The lattice thermal resistivity may be expressed as a sum of separate resistivities arising from different phonon scattering mechanisms. Thus

$$K_g^{-1} = W_g = W_e + W_p + W_\delta + W_p + W_u$$  \hspace{1cm} (1.17)

where $W_e, W_p, W_\delta, W_p$ and $W_u$ are respectively the resistivities due to electrons, dislocations, grain boundaries, point defects and Umklapp processes (Mendelssohn and Rosenberg, 1961). It is, in general, a poor approximation to add resistivities as the frequency dependence of the different scattering mechanisms is not the same. The sum of the resistivities due to the various processes is

$$\sum_i W_i = \sum_i \frac{1}{\tau_i} \propto \sum_i \left[ \int \tau_i(q) v^2(q) S(q) dq \right]^{-1},$$  \hspace{1cm} (1.18)

but the thermal resistivity is correctly given by

$$W = \frac{1}{K} \propto \left[ \int \left(\sum_i \frac{1}{\tau_i} \right)^{-1} v^2(q) S(q) dq \right]^{-1}.$$  \hspace{1cm} (1.19)

It is only valid to define a combined relaxation time if the various scattering mechanisms are independent (Carruthers, 1961). In dilute alloys at liquid helium temperatures $W_p$ can be ignored as the phonon wavelength is large compared with the size of a point defect. $W_u$ is also negligible as the dominant phonon wavenumber is small compared with the smallest reciprocal lattice vector. $W_e$ and $W_p$ are both expected to have the same temperature dependence and under these conditions, provided electron-phonon and dislocation-phonon scattering dominate any other scattering mechanisms, equation (1.17) is a good
approximation. Considering the phonons to be scattered only by electrons, dislocations and grain boundaries and inserting the temperature dependence for each mechanism (Klemens, 1958) gives

\[ W_g = E T^{-2} + D T^{-2} + G T^{-3} \]  \hspace{1cm} (1.20)

where E, D and G are the temperature independent coefficients describing the magnitude of the phonon scattering by electrons, dislocations and grain boundaries. If \( G \ll E + D \) the lattice conductivity may be written as

\[ K_g = (W_g)^{-1} = \frac{T^2}{E+D} - \frac{GT}{(E+D)^2} \]  \hspace{1cm} (1.21)

Under the conditions described above for dilute alloys at liquid helium temperatures when the Wiedemann-Franz law is valid and the graphs of \( K/T \) versus \( T \) are linear, it is common practice to write \( (E+D) \) as \( W_g T^2 \) in referring to that part of the conductivity which has a quadratic temperature dependence. Then the total conductivity is given by

\[ K = AT + BT^2 \]  \hspace{1cm} (1.22)

and the reciprocal of the slope B of the \( K/T \) versus \( T \) graph is equal to \( W_g T^2 \). For the alloys in the annealed condition \( W_g T^2 \) is limited by electron-phonon scattering (Salter, 1965). Differences between \( W_g T^2 \) for annealed and strained specimens then give values for \( W_p T^2 \) corresponding to the dislocation densities introduced.
1.5 Review of Experimental Work.

Dislocation-phonon and electron-phonon scattering have been extensively studied in recent years in a variety of materials which can be divided roughly into three groups according to the behaviour of their thermal conductivity at low temperatures. They are:

(a) Alloys with high residual electrical resistivities.
(b) Superconductors and insulators.
(c) Alloys with low and medium residual electrical resistivities.

The last of these groups has attracted much attention in recent years and the alloys studied in this research fall into this category. Accordingly, in this review, only a brief outline of the work on materials of groups (a) and (b) is given and this is followed by a more detailed examination of the results obtained for low residual resistivity alloys.

(a) Alloys with high residual electrical resistivities.

Pippard, 1955 and 1960, derived expressions for the attenuation coefficients for transverse and longitudinal waves in a metal. The reciprocals of these attenuation coefficients are then used to define mean free paths for electron-phonon scattering. When Pippard's theories of ultrasonic attenuation are used to calculate the lattice thermal conductivity of alloys it is found that the behaviour of the latter depends upon the residual electrical resistivity of the material. For alloys with a high value of $\rho_e$, (i.e. greater than 10 microhm cm) $K_g$ is predicted to contain a term linear in temperature (Pippard, 1957).
This provided an explanation of the breakdown of the Wiedemann-Franz law previously observed by Sladek (1955) for indium-thallium alloys and Kemp et al., 1956, on silver-palladium alloys of high residual electrical resistivity. Zimmerman, 1959, showed that for copper-antimony alloys having values of $\rho_o$ between 12 and 40 microhm cm, the lattice thermal conductivity was given by

$$K_G = CT + BT^2 \quad (1.23)$$

where the value of $C$ increased systematically with $\rho_o$.

More recently, Jericho, 1965, measured the thermal conductivity of a series of silver-antimony and silver-tin alloys. His results agreed well with those of Zimmerman and in this case the coefficient, $C$, was significant for values of $\rho_o$ greater than 10 microhm cm.

(b) **Superconductors and Insulators.**

Measurements of dislocation-phonon scattering have been made on alkali halide crystals. In the case of near-perfect crystals at liquid helium temperatures the lattice thermal conductivity is limited by boundary scattering. For these materials the density, $N_p$, of intentionally introduced dislocations can be determined using etch pit methods. For LiF crystals, Sproull et al., 1959, found from low temperature thermal conductivity measurements that $W_p T^2 = 1.3 \times 10^{-6} N_p$ watt cm deg$^{-1}$. This indicated that the scattering of phonons by dislocations was 1,000 times more effective than was predicted by the theory at that time (Klemens, 1951, 1955). Similar discrepancies between theory and experiment were found by
Ishioka and Suzuki, 1963, for NaCl and Taylor et al., 1965, for LiF. Various ideas have been put forward to explain these differences and indeed in 1958, Klemens revised his theory and increased the theoretical estimate of the dislocation-phonon scattering power by a factor of 15. However, a discrepancy still remains and it has been attributed by some authors (Moss, 1965) to the scattering power of dislocations being enhanced through a co-operative effect arising from certain geometrical arrangements of dislocations.

It has already been pointed out in this chapter that at temperatures below $T_c/5$ the lattice thermal conductivity of a superconductor behaves similarly to that of an insulator. The change in conductivity due to the introduction of dislocations has been measured by Rowell, 1960, for single crystals of lead, niobium and a lead-bismuth alloy. Using the Klemens, 1958, formula, values of $N_p$ were calculated from the change in $W_g$ with deformation and were compared with those calculated from a theory of tensile strain. It has been suggested (Salter, 1965) that the calculated values of the dislocation density were impossibly large. Using a formula due to Cottrell, 1953, Salter calculated the probable dislocation density for a copper specimen deformed in an identical fashion to Rowell's lead specimen. Comparison of the known deformation characteristics of the two metals indicated that Rowell had over-estimated the dislocation density of his specimen. On the basis of Salter's calculation, Klemens theory under-estimates the scattering of phonons by dislocations by a factor of 40.
(c) **Alloys having low residual electrical resistivity.**

This group of materials is by far the most extensively studied using measurements of the lattice thermal conductivity and the various experiments are best reviewed in a roughly chronological order. Early work was carried out on annealed alloys and was, in effect, a study of the electron-phonon interaction. Kemp et al., 1956, measured the lattice thermal conductivity of some silver-palladium and silver-cadmium alloys and found that $W_g T^2$ was a function of solute concentration. When the results were extrapolated to zero concentration the value obtained for the pure metal agreed well with the theoretical result (Klemens, 1954) assuming the Makinson coupling scheme in which electrons interact equally with phonons of all polarizations. Some of the alloys were deliberately strained and it was observed that the conductivity was proportional to $T^2$ but with a smaller coefficient than in the annealed case. The additional resistance was attributed to dislocation-phonon scattering and the density of dislocations, $N_p$, was calculated using Klemens' 1955 formula. However, this yielded improbably large values for $N_p$ and it was tentatively suggested that groups of piled-up dislocations giving an effectively larger Burgers vector were the cause of the enhanced scattering. The increase in $W_g T^2$ with increasing solute content was thought possibly to result from a variation in electron-phonon scattering with electron concentration. This supposition was tested by adding another monovalent metal, gold, to copper (Kemp et al., 1957) but $W_g T^2$ was still found to increase with increasing
solute concentration. In order to account for this it was suggested that the increase in $W_g T^2$ was due to dislocations locked into the alloy by impurity atoms. At the time, this was not an unreasonable explanation since electron-phonon and dislocation-phonon scattering both have the same temperature dependence and also in view of the fact that when a copper-zinc specimen was re-annealed close to the melting point a decrease in $W_g T^2$ was observed. However, in order to satisfy this theory the values of $N_p$ would have had to be impossibly large, e.g. Cu+0.5at.%Fe gave an increase in $W_g T^2$ corresponding to $N_p = 5 \times 10^{11}$ lines/cm$^2$ (White and Woods, 1954). However, in 1962, Lindenfeld and Pennebaker measured $K_g$ for a series of annealed copper-germanium alloys and using transmission electron microscopy showed that $N_p$ for their specimens was far too small to account for the changes in $W_g T^2$ with alloying. Instead, the changes in $K_g$ resulting from increasing germanium content were correlated with changes in $\rho_0$. Their experimental results lay close to a universal curve of $K_g/T \rho_0$ versus $T/\rho_0$ and were compared with a theoretical curve calculated from the kinetic formula combining equations (1.10) and (1.11) in section 1.2 of this chapter. Values of $L_j(q)$ were computed from Pippard's 1955 theory of ultrasonic attenuation, treating the longitudinal and transverse modes independently. It has been pointed out (Salter, 1965) that agreement between theory and experiment is only good for small $T/\rho_0$, i.e. higher residual resistivity alloys, and that the assumption of independent longitudinal and transverse modes may be incorrect. Tainsh and White, 1962, re-examined earlier results and
considered the various terms in the Klemens 1954 expression for $W_g$. However they concluded that even allowing for the greatest uncertainty in any of these terms, the Klemens' formula could not explain the variation of $W_g T^2$ with alloying.

The experimental results described above were chiefly concerned with annealed alloys. However, in 1959, Lomer and Rosenberg attempted to measure dislocation-phonon scattering in a series of alpha-phase copper-zinc alloys. The thermal conductivity was determined between 4.2 and 2.20K for each specimen strained by various amounts in a manner very similar to that used in this research. The dislocation densities were calculated using Klemens' 1958 formula assuming that dislocation-phonon scattering was independent of alloy composition. In addition, $N_p$ was roughly determined directly for two strained specimens containing 30% Zn but no attempt was made at a serious study and only a small number of electron micrographs were examined. In the light of these values for $N_p$ it was shown that the theory underestimated the dislocation-phonon scattering by a factor of 6. Thus, the final values of $N_p$ quoted by Lomer and Rosenberg were those calculated from the Klemens' theory but scaled down by the factor of 6. The value of dislocation-phonon scattering for alpha-brass was given by $W_p T^2 = 3.6 \times 10^{-8} N_p \text{watt cm deg}^2$. The results of this work and the reported variation of $N_p$ with deformation are fully discussed in chapters 4 and 6 of this thesis.

At the same time as the above work was being carried out, Kemp et al., 1959, were studying dislocation-phonon
scattering in alpha-brass and arsenical copper specimens which had been severely deformed in torsion. Their deformation and annealing conditions were selected so that comparison could be made with studies of the release of stored energy made by Clarebrough et al., 1955 and 1960, since their specimens came from the same material. Taking Cottrell's, 1953, estimate of the energy of a dislocation in copper a value of $N_p$ for the specimens was deduced. Considerable difficulty was experienced in interpreting the results especially in the case of alpha-brass where a large energy release in stage I corresponded to only a small change in the lattice thermal conductivity. The analysis was further complicated by recrystallisation occurring during the measurements. However, Kemp et al. found that Klemens' 1958 formula under-estimated the dislocation-phonon scattering by a factor of 6.5 for alpha-brass and 8 for arsenical copper. Their result of

$$\nu T^2 = 3.9 \rightarrow 4.8 \times 10^{-5} N_p \text{ watt cm deg}^3$$

is almost identical within experimental error to Lomer and Rosenberg's value.

The first really detailed experimental work on dislocation-phonon scattering was carried out by Salter, 1965. He measured the lattice thermal conductivity of a series of alpha-phase copper-aluminium alloys in the temperature range 4.2° to 1.5°K for both annealed and deformed specimens. In the case of annealed alloys the lattice thermal conductivity was limited by electron-phonon scattering, there being good correlation between the lattice conductivity and the electron mean free path as calculated from Pippard's (1955, 1960) theory of ultrasonic attenuation.
The results indicated the presence of a small linear term in the lattice thermal conductivity which could not be entirely accounted for on the basis of the Pippard theory. The difference in this linear term between single and polycrystals showed that grain-boundary scattering was also present. This was later confirmed (Salter and Charsley, 1967) and is discussed in more detail in chapter 5. The measurements on the strained alloys produced an important result. Using transmission electron microscopy to undertake a detailed study of the arrangement and density of dislocations in these alloys, it was discovered that the dislocation-phonon scattering, defined as \( \sigma = W_\rho T^2/N_\rho \), increased with increasing solute content. Taking results from each end of the range of concentrations studied it was found that \( \sigma = 1.0 \times 10^{-7} \text{ watt cm}^{-3} \text{ deg}^{-3} \) for Cu+2 at.% Al and \( \sigma = 2.1 \times 10^{-7} \text{ watt cm}^{-3} \text{ deg}^{-3} \) for Cu+12 at.% Al. During the electron microscope investigation it was noticed that the arrangement of dislocations changed with increasing solute content from a tangled structure for very dilute alloys to a far more ordered array with dislocations confined to their slip planes in the case of the Cu+12 at.% Al. This change in dislocation arrangement was correlated with the decrease in stacking fault energy as more solute was added and it was suggested that for the more regular arrays, pile-ups of dislocations enhanced the phonon scattering and hence gave larger values of \( \sigma \). However, this theory did not agree with the comparatively small value of \( \sigma \) obtained by Lomer and Rosenberg for Cu+30 at.% Zn. This was surprising as the latter specimen and Cu+12 at.% Al have very similar stacking fault energies and the dislocation
structure in both materials was known to be identical. It was thus suggested that Lomer and Rosenberg's result was in error.

As described in chapter 4 of this thesis a detailed investigation of dislocation-phonon scattering in Cu+30at.%Zn was carried out which yielded a value similar to that of Lomer and Rosenberg. This result indicated that dislocation-phonon scattering is not dependent upon the dislocation arrangement. Further evidence of this was supplied by Salter who measured the lattice thermal conductivity of a Cu+12at.%Al single crystal under stress and also in a relaxed condition. The effect of stress is to decrease the average spacing of dislocations in a pile-up and hence the conductivity was expected to differ between the stressed and relaxed states if dislocation-phonon scattering depended on dislocation arrangement. However, no significant difference was found (Charsley et al., 1967). In the same series of experiments, Salter also tried to detect any anisotropy in the scattering of phonons by edge and screw dislocations. A flat single crystal of Cu+12at.%Al was deformed in tension and two cross-shaped specimens were machined out of it. The thermal conductivity was measured in two directions at right-angles to each other for each cross. Knowing the relative orientations between edge and screw dislocations and the direction of the thermal current it was discovered that there was an anisotropy in the scattering of phonons by screw dislocations but no such effect was observed for edge dislocations.
The result of the experiments on alpha-brass (Charsley et al., 1968) inspired Klemens (Klemens, private communication) to attempt an explanation for the variation in $\sigma$ with solute concentration in a semi-quantitative manner (Klemens, 1968). His theory is based on the idea that phonons are scattered by the modulation of the impurity concentration by the formation of "Cottrell atmospheres" around dislocations. The phonon rain field is shown to be proportional to $[\gamma + \gamma']$ where $\gamma$ is the Grüneisen constant and $\gamma' = -\alpha \beta v_o K C_o / k T_o$. Here, $C_o$ is the average impurity concentration at an equilibrium temperature $T_o$, $\alpha v_o$ is the excess atomic volume of the impurity atom, $K$ is the bulk modulus of the material and $k$ is Boltzmann's constant. $\beta \propto \frac{1}{2} (m - m') / m$ where $m$ and $m'$ are the masses of the parent and impurity atoms respectively. Obviously, if $\alpha \beta$ is negative the atmosphere enhances the scattering and if it is positive the scattering is reduced. On this model Klemens calculated the relative values of $\sigma$ for the copper-aluminium alloys studied by Salter and the Cu+30at.%Zn studied in this thesis. The agreement between theory and experiment is reasonable in view of the approximations involved and is fully discussed in chapter 4.

Apart from the work described in this thesis, to the best of the author's knowledge, the most recent measurement of dislocation-phonon scattering has been carried out by Zeyfang (1967) who measured the lattice thermal conductivity, after strain, of a Cu+4.6at.%Ga alloy. Using a mean theoretical value for $\sigma$ of $10.5 \times 10^7$ watt cm$^{-1}$ deg$^{-2}$ (Bross et al., 1963) he calculated values for $N_\sigma$. 
Comparison of these values with those obtained for copper strained by the same amount using electron microscopy (Essman, 1966) indicated that $N_p$ deduced from thermal measurements was six times too large. An investigation into the relative values of $N_p$ for pure copper and copper-gallium using X-ray data indicated that $N_p$ for the latter was 20% higher for a given deformation. Zeyfang thus deduced that thermal measurements yielded values of $N_p$ which were approximately five times too great and suggested that the discrepancy was possibly due to the fact that the elastic constants used in obtaining a theoretical value for $N_p$ are greater at liquid helium temperatures than at ambient temperatures (Salama and Alers, 1967). Zeyfang thus arrived at a value for $\sigma$ of $0.5 \times 10^7$ watt cm$^{-3}$ deg$^{-1}$ which was almost identical with measurements on alpha-brass and was in good agreement with the Klemens' model outlined above. Zeyfang also observed that at low temperatures the lattice thermal conductivity for heavily deformed specimens had a temperature dependence stronger than quadratic which was attributed to enhanced phonon scattering from closely spaced dislocations in pile-ups.
2.1 Preparation of Specimens.

All the alloys used in this research were supplied by International Research and Development Co. Ltd. The copper aluminium alloys were prepared by melting together "oxygen-free high conductivity" copper and spectroscopically pure aluminium in a graphite crucible. The melt was stirred in an atmosphere of high purity argon and the alloy drop cast into a graphite mould. The outer layers were removed to avoid any contamination and the ingots swaged and drawn down to rods 3 mm diameter in the case of the 2A1 alloy and 7 mm for the 12A1 alloy. A similar procedure was adopted in the manufacture of the alpha-brass and copper gold alloys, spectroscopically pure zinc and gold being used respectively as the solute. In the case of the brass a calculated extra amount of zinc was added to allow for the evaporation of this element from the melt. Approximately 10 cm lengths were cut from the rods to make the thermal conductivity specimens. The quoted compositions of the alloys are mean values taken from analyses at each end of the "as received" material and appear in table 2.1. The 12A1 specimen was made with a larger diameter than the other alloys as some of it was also required by other workers in the department. In order to be used for thermal conductivity work it was turned down on the lathe to 3 mm diameter but two discs of material were left about 6 cm apart for the attachment of thermometers.
The specimens were all annealed at 750°C for 14 hours and furnace cooled. In the case of copper-aluminium and copper-gold alloys this was done in vacuo, the specimens being contained in graphite tubes. In order to avoid loss of zinc, the brass specimens were wrapped in foil of similar composition and annealed in sealed evacuated silica tubes. Two copper tags, 0.5 mm thick, spaced about 5 cm apart, were brazed on to each of the 2A1 and 30Zn specimens while for the 12A1 polycrystal the tags were attached with Wood's metal on to the discs already turned out of the specimen. In this last case, great care was taken to fix the tags so that they only made contact with the discs themselves without getting any Wood's metal on to the gauge length. This is important as this solder is superconducting at 4.2°C and hence the size factors for electrical and thermal measurements would be dissimilar. The 12A1 single crystal also had tags attached with Wood's metal but for this specimen the size factor for electrical conductivity was not needed.

The single crystals of 12A1 were grown in graphite moulds sealed in an airtight stainless steel container using the Bridgman technique with a rate of lowering of 2 cm per hour. As crystals of approximately 4 mm diameter were desired and the available material was of 7 mm diameter, a two stage process was used. The first involved using a casting mould to produce some rods of alloy roughly 4 mm in diameter. These were then placed in a second mould in which they were grown into a single crystal. The inside surface of this mould had been carefully reamed to facilitate the removal of the crystal without introducing any damage.
Most of the specimens deformed in tension were strained on a tensile testing machine manufactured by Tensometer Ltd. (type "E"). The exceptions were the 12Al(21%) polycrystal and the 12Al single crystal strained in tension; these were deformed on a tensometer (type W) made by Hounsfield Ltd. All the specimens were deformed at a constant strain rate of 2 mm/min, the amount of strain being measured by comparing fiducial marks before and after pulling using a travelling microscope.

2.2 The Cryostat.

Previous work in the department on thermal conductivity was carried out using a cryostat described in some detail by Salter, 1965. The apparatus used in this research was designed to overcome some of the limitations of its predecessor, thus permitting measurements to be made with greater accuracy. Two cryostats were, in fact, built during the course of this research, the first of which was discarded for reasons which are described later. The second, shown in Figs. 2.1 and 2.2, which was of similar design to the first but smaller, worked satisfactorily and all but two of the thermal conductivity measurements were made with this. The exceptions were the two initial experiments on alpha-brass which were made on the previous apparatus of Salter, 1965. Fig. 2.3 is a schematic diagram of the versatile pumping system which was employed.

In the description of the apparatus letters refer to Fig.2.1.

The temperature in the cryostat was reduced from 4.2°K by pumping liquid helium in the small copper can (A) which had a volume of about 40 cc, the helium liquid being admitted from the inner glass dewar via the needle valve (Na).
The temperature was measured by means of a helium vapour pressure bulb (B) machined out of the large copper block (D) to which the specimen was attached. This method was considered superior to reading the pressure over the boiling helium in the small can (A) as it would then be doubtful if the measured temperature corresponded to that of the block (D) which was soldered to the base of the can via a thick copper post. Such uncertainty could have arisen because of the hydrostatic head effect or the presence of a temperature gradient at the surface of the liquid helium (Cataland et al, 1962). The magnitude of these effects has been discussed by Salter, 1965. Bolted to the underside of the copper block (D) and enclosing the specimen was a vacuum-tight copper radiation shield (H). The second (outer) radiation shield (J) was made of brass. Both shields were sealed using indium wire seals. These proved to be much better than Wood's metal seals, being less prone to leaks and obviating the need to apply heat to the cryostat which could damage other solder connections. The use of two independently evacuated radiation shields enabled helium exchange gas to be admitted to the space between them. This facilitated the cooling down of the apparatus without having the gas coming into contact with the specimen or thermometers which would be undesirable (Hoare et al, 1961). The pumping tubes below the top plate (Fig. 2.2) were made of thin walled German silver tubing with the exception of the tube connecting the copper anchor box (C) to the block (D); this was made of stainless steel. Differential contraction of these two materials caused the inner radiation shield to move laterally by a small amount during the cooling down process and the
shields, which were separated by approximately 3 mm at room temperature, were liable to touch unless accurately aligned at the start of each experiment. In order to indicate when the shields were touching, a simple circuit was constructed with an insulated electrode fixed to the side of the inner shield, an external lamp being illuminated if this made contact with the outer shield.

As mentioned at the beginning of this chapter, a cryostat was initially constructed on the design described above but considerable trouble was experienced with helium oscillations set up in the tube (Q) which had a diameter of 1/8". These resulted in a large amount of heat being transmitted to the vapour pressure bulb (B). In an attempt to break up the oscillations lengths of 1" diameter tubing were inserted into the tube (Q); this proved to be partly successful. However, it was still difficult to get the vapour pressure bulb to follow changes in temperature of the helium can so that particular cryostat was abandoned. With the experience thus gained a second apparatus was designed with slight modifications to the original and of smaller overall dimensions which made it more economical to operate.

The copper block (D) contained two vapour pressure bulbs. One of these could be filled with liquid helium from the dewar through the needle valve (Nb). The other, which for convenience is not shown on the diagram, had a tube connecting it with the top plate of the cryostat where it was closed with a tap through which it could be evacuated. This second bulb was incorporated so that 3He vapour pressure thermometry could be employed if necessary but it was not in fact used. The copper can (A) was machined from a
solid block so as to reduce the chance of "lambda leaks" occurring when the liquid helium became superfluid. A constriction \( (F) \) of 1.5 mm diameter was placed in the pumping line above the helium can to reduce the film flow below the lambda point. At the top of the cryostat all tubes were connected to the various parts of the pumping system with "Speedivac" screwed unions so that it was easily demountable.

The cryostat was cooled down to 90°K using liquid air in the outer glass dewar and a few centimetres of air exchange gas in the vacuum jacket of the inner dewar. A similar pressure of helium exchange gas, obtained from a storage bladder, was used in the space between the radiation shields. About 4 hours were needed for the apparatus to cool down to liquid air temperature and during this time the specimen chamber, helium can and vapour pressure bulb were evacuated to avoid the possibility of ice forming. At the end of this period the air exchange gas was pumped from the vacuum space of the inner dewar and this vessel was then filled with liquid helium, some helium exchange gas being admitted to the small can to aid the cooling process. An efficient transfer required approximately three litres of liquid helium to fill the inner dewar to about 30 cm above the top of the outer radiation shield. Directly the transfer was completed, the exchange gas was pumped out of the can \((A)\) which was then almost filled with liquid helium through the needle valve. It was known from experience how long this valve had to be open to pass sufficient liquid into the can to last about 8 hours. The needle valve \((Nb)\) to the evacuated vapour pressure bulb was then opened and closed again as quickly as possible so as to
allow only a very small amount of liquid to enter the bulb which had a volume of 1 cc and was easily overfilled. If the liquid level rose above the top of the bulb and into the tube it was impossible to get reliable temperature readings. Gas from the helium can could always be condensed into the bulb if further liquid was needed. A carbon resistor (R) attached to the copper block was, with a battery, used as a heater to establish thermal equilibrium between the bulb and helium can and to destroy any temperature gradients in the liquid.

The pressure over the helium in the can (A) while being pumped was controlled by a stainless steel cartesian diver manostat (White, 1959) in parallel with a needle valve and butterfly valve. By adjustment of the manostat at temperatures above the lambda point and in addition the needle valve below the lambda point, the temperature could be kept constant to a millidegree or better, judging from the drift in resistance of the thermometers over the period of time in taking a reading. A mercury manometer was used to measure the vapour pressure of the helium above the lambda point while below this an oil manometer was employed filled with "Apiezon A" oil having a density approximately 1/15th that of mercury. The density of the oil was previously measured over the temperature range 15 - 30°C so that its value relative to mercury was known for the temperature of the oil at the time of the experiment. The change in density of the mercury with variation in room temperature was negligible. The oil and mercury levels were measured with a carefully levelled cathetometer reading to .001 cm and the vapour pressures of helium thus obtained were converted to temperature readings using the
2.3 Method of Measurement.

The specimen was mounted vertically, its upper end being soldered with Wood's metal into a copper holder which was in good thermal contact, via an indium seal, to the base of the copper block (D). A heater was similarly soldered to the other end of the specimen. Two copper tags were brazed on to most of the specimens, although in certain cases Wood's metal was used; the thermometers were attached to these tags. The heater consisted of 47 S.W.G. nichrome wire wound on to a copper former which had been sprayed with P.T.F.E. giving good electrical insulation without impairing thermal conduction, the ends of the resistance wire being connected to two platinum wire terminals in insulated sleeves which passed through holes drilled in the top of the former. The heater resistance was 10,000 ohms at liquid helium temperatures and 44 S.W.G. nichrome wire was used to connect it to the thermal anchor post (P). By using the arrangement of the heater leads shown in Fig. 2.5 any error introduced by heat produced in the current leads is partially compensated for if it is assumed that half this power goes to the heater.

The thermometers were 47 ohm, 1/10th watt Allen-Bradley resistors mounted so as to fit reasonably tightly in a hole drilled through a small copper block into which they were glued with a varnish manufactured by The Oxford Instrument Co. Ltd. especially suitable for use in these circumstances as it did not crack at low temperatures. These copper blocks had a second hole drilled through them
at a right angle to the axis of the thermometer, through which passed a 6 B.A. screw so that they could each be clamped to a copper tag on the specimen. Good thermal contact was ensured by crushing a small length of indium wire between the two copper surfaces. This method of fixing the thermometers was preferred to soldering with Wood's metal as it saved the resistors from being heated above room temperature which could have altered the electrical characteristics (Salter, 1965). Current and potential leads of 47 S.W.G. nichrome wire connected the thermometers to the anchor post (P) and, when soldering on these leads, great care was taken to avoid heating the thermometers by holding the mounts in cold wet cotton wool. The heat conducted down the leads was calculated to be negligible.

From the junction (P) the leads were of 30 S.W.G. enamelled constantan wire; these were individually thermally anchored at the post (P) by passing each through a fine hole drilled in the copper and varnishing it in place. The 16 leads were taken up the tube (E) which was used for pumping the inner radiation shield and emerged at the top of the cryostat through a black wax seal from which they were taken to two 8-way plugs immersed in an oil bath. Screened copper cable was used between these plugs and the electrical measuring apparatus. The leads were anchored at 4.2\(^0\)K at the copper anchor block (C) which was 5 cm above the top of the outer radiation shield. The side of this block, which was removable for access to the leads, was bolted into position with four 8 B.A. bolts and sealed with an indium ring seal. The pumping tubes entering and leaving the anchor block were offset from one another to avoid heat being radiated down into the specimen chamber. An
annealed copper post (G) joined the block to the top of the outer radiation shield so as to ensure that the anchor was kept at approximately 4.2°K after the liquid helium level in the dewar had fallen below it.

The resistance of the thermometers was measured on a Tinsley potentiometer, type 4363D-Auto, calibrated to read to 0.1 microvolts by comparing them in turn with a "standard" resistor which was a fixed wire wound resistance of approximately 2,000 ohms immersed in an oil bath. The measuring circuits for the thermometers and heater are shown in Figs. 2.4 and 2.5 respectively. A measuring current of about 1 microamp was obtained by connecting in series a 2 megohm resistance and a 2 volt battery of capacity 200 ampère hours. The null detecting circuit incorporated a galvanometer amplifier and galvanometer. Both forward and reverse current readings were taken to eliminate thermal emfs which were of the order of a few microvolts and thus easily detected with the instruments used. These instruments were carefully screened and screened connecting cable was used in most cases.

The heater power was measured using a second potentiometer (Tinsley type 3387B), the voltage across the heater being compared with that developed across at 10,000 ohm standard resistance in series with it. In this circuit the thermal emfs were negligible and no reversing switch was necessary. The current to the heater was supplied from a large capacity accumulator and passed through a dummy circuit when the heater was switched off.
2.4 Experimental Procedure

Experimental runs commenced at $4.2^\circ K$ and the temperature was reduced by intervals of approximately $0.2^\circ K$; a calibration and thermal conductivity measurement was taken at each stage. The pumping down through $0.2^\circ K$ lasted about 5 minutes, after which the temperature was set with the manostat at the value required and another 5 minutes elapsed to allow ample time for equilibrium to be established before a calibration reading was taken. It was found that the best procedure was to align the cathetometer cross-wires accurately on the mercury meniscus in the manometer and then to take the readings on the potentiometer for the resistance of the thermometers. Directly after this, the actual height of the mercury column was measured and any change in the position of the meniscus while the electrical readings were being taken was immediately obvious. The heater was then switched on and again 5 minutes were allowed for equilibrium during which time the calibration point was worked out; if the point appeared to be in error, the readings could then be repeated at a similar temperature before the run proceeded further. The measurements for heater power and thermometer resistance were then taken; the heater was switched off and the system pumped down further.

2.5 Measurement of Electrical Resistivity

The residual electrical resistivity of each specimen was measured at $4.2^\circ K$ by immersing it in liquid helium boiling under atmospheric pressure and comparing it potentiometrically with a standard resistance of 0.005 ohms.
A current of approximately 1 ampere was used and the voltages developed were read with a Diesselhorst potentiometer (Tinsley type 3589-R) measuring to better than 0.1 microvolts. Using a thermo-electric free reversing switch, thermal emfs were eliminated by taking forward and reverse current readings. This laboratory apparatus is described by Foxon, 1965. A later modification substituted a special constant current supply unit instead of a large capacity accumulator used previously (Foxon et al., 1967).

One experiment was also carried out to measure the residual resistivity of a specimen at approximately 0.2 degree intervals between 4.2° and 2°K. The apparatus was very similar to that used for all the measurements made at 4.2°K except that a vacuum-tight top plate had to be fitted to the helium dewar. The pressure over the helium in the dewar was reduced and the temperature controlled using a vacuum system of similar design to that used for the helium pumping system in the thermal conductivity cryostat.
Table 2.1

Composition of specimens (see notes 2 & 3, page 7).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mean comp. of ingot (at.% of solute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Al.</td>
<td>1.93</td>
</tr>
<tr>
<td>12Al.</td>
<td>12.18</td>
</tr>
<tr>
<td>30Zn.</td>
<td>27.20</td>
</tr>
<tr>
<td>10Au.</td>
<td>9.90</td>
</tr>
</tbody>
</table>
The lower part of the cryostat showing a mounted specimen.

Key to Diagram

A: Small copper helium can.
B: Helium vapour pressure bulb.
C: Thermal anchor block.
D: Disc-shaped copper block.
E: Pumping line containing leads.
F: Constriction.
G: Copper post.
H: Inner radiation shield.
J: Outer radiation shield.
Na, Nb: Needle valves.
P: Thermal anchor post.
Q: Tube connecting bulb (B) to manometer.
R: Heater resistor.
S: Specimen.
T: Thermometers in copper mounts.
W: Specimen heater.
Fig. 2.2
The top part of the cryostat.

(N.B. The lower part is shown in Fig. 2.1)
Fig. 2.3

Schematic Diagram of the Pumping System.
Fig. 2.4

The circuit diagram for the thermometers.

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Galvanometer amplifier</td>
</tr>
<tr>
<td>B</td>
<td>2 volt accumulator</td>
</tr>
<tr>
<td>G</td>
<td>Galvanometer</td>
</tr>
<tr>
<td>P</td>
<td>Anchor junction at base of small helium can</td>
</tr>
<tr>
<td>R</td>
<td>Rheostat</td>
</tr>
<tr>
<td>R₁, R₂</td>
<td>Thermometers</td>
</tr>
<tr>
<td>R₃</td>
<td>Fixed resistor</td>
</tr>
<tr>
<td>S</td>
<td>Reversing switch</td>
</tr>
</tbody>
</table>
Fig. 2.5
The circuit diagram for the heater.

Key:
A: 2 volt stabilised supply
B: 2 volt accumulator
D: Dummy heater
G: Galvanometer
M: Micro-ammeter
P: Anchor junction at base of small helium can
R: Rheostats
S: Standard cell
Y: 10,000 ohm standard resistor
3.1 Introduction

In this chapter the method of calibration of the carbon resistance thermometers is described and the associated errors are assessed. The resulting values for the thermal conductivity are compared with those obtained using a different calibration procedure which involved the use of a computer. Finally, all the sources of error in the thermal conductivity measurements are discussed and the overall accuracy of the results is estimated.

3.2 Method of Calibration

Clement et al, 1952, proposed an empirical relationship between the resistance and temperature of carbon resistors at liquid helium temperatures:

\[ T = \frac{a \log_{10} R}{(\log_{10} R - b)^2} \quad (3.1) \]

\( T \) is the temperature in degrees Kelvin, \( R \) the resistance in ohms and \( a \) and \( b \) are constants. This relation was used to calibrate the thermometers but as it was not exactly obeyed, the practice was to fix 'a' and determine the variation of 'b' with temperature for each experiment. The value of 1.6100 was taken for 'a' for both resistors. This was a good approximation to the values of the slopes of graphs of \( \sqrt{\frac{\log_{10} R}{T}} \) versus \( \log_{10} R \) for both thermometers. The calibration graphs for each
experiment were obtained by taking the fixed value of 'a' and plotting values of 'b' against corresponding values of \( \log_{10} R \) for each thermometer. Knowing \( R_1 \) and \( R_2 \), the resistances of the upper and lower thermometers respectively for the thermal conductivity readings, values of \( b_1 \) and \( b_2 \) could be found from the calibration graphs. The corresponding temperatures \( T_1 \) and \( T_2 \) were calculated using equation (3.1) and hence \( \Delta T = T_2 - T_1 \), and \( T = \frac{T_1 + T_2}{2} \).

3.3 The Form of the Calibration Curves

The first set of calibration curves from which the value of 'a' was calculated was obtained by attaching the thermometers to a short annealed copper post which was fixed directly to the copper block D (Fig. 2.1). This procedure was adopted to give the best possible thermal contact between the thermometers and the helium in the vapour pressure bulb. The calibration curves thus obtained were henceforth regarded as a "standard" with which to compare curves obtained in subsequent experiments. All the thermal conductivity results reported in this thesis were obtained during experiments for which the values of 'b' from the calibration graph differed from those of the "standard" curves by less than 0.1%. The importance of this is discussed in section 3.5.

A typical calibration curve is shown in Fig. 3.1 with an indication of the temperature range included. Note that on this diagram the ordinates for the two thermometers are shifted relative to one another.
Errors Associated with the Calibration Procedure

Errors would occur in the calibration if the temperature as measured from the difference in liquid levels in the manometers did not correspond to the actual temperature of the thermometers. Such a state would arise if the thermometers were not at the same temperature as the vapour pressure bulb or if the vapour pressure was not a true indication of the temperature in the bulb. In the former case, self heating of the thermometers would have been an obvious source of error. Berman, 1952, suggested that for reliable thermometry the heat produced in the resistor should raise its temperature by less than 0.1 millidegrees above that of the surroundings. For resistors similar to those used in this work, this places an upper limit on the power dissipation of .004 microwatt at 1°K and 0.04 microwatt at 4.2°K. The maximum power dissipated in practice was 0.002 microwatt. However, this assumed good thermal contact between the thermometer resistor and the specimen. Self heating could give rise to a temperature gradient along the specimen and could raise the mean temperature of the specimen, but it has been calculated (Salter, 1965) that even for the highly strained 12Al which had the greatest thermal resistance of all the specimens measured in this research and hence was the worst possible case, the error introduced in T and ΔT was negligible. On one occasion the calibration curve differed seriously from the "standard", the discrepancy being traced to a loose fitting thermometer in its mount. The thermal conductivity results obtained from this run were rejected.

The second kind of error mentioned above was that the temperature as measured from the helium vapour pressure
was not a true indication of the temperature of the vapour pressure bulb. At the beginning of every experimental run the cathetometer was carefully levelled and for each measurement of the position of a meniscus the telescope was adjusted and focussed in an identical fashion to avoid any errors due to backlash. The density of the manometer oil had been carefully measured at 2 Centigrade degree intervals between $16^\circ$ and $30^\circ$C so that, by interpolation, the correct value could be used for the ratio between the density of oil and mercury corresponding to the temperature of the oil at the time of the experiment. On two occasions, the calibration curves exhibited a slight discontinuity which coincided with the changeover from the mercury to the oil manometer; the cause of this was found to be a leak on one of the glass taps which resulted in air being condensed into the vapour pressure bulb.

It has been pointed out (Montgomery et al, 1963) that, below the lambda point, the vapour pressure of helium in a bulb may give a falsely high value for the temperature. This is because the superfluid helium film climbs up the inside of the bulb and pressure sensing tube to a point where it evaporates, the vapour produced recondensing on to the liquid surface. This constitutes a heat input to the bulb in which the liquid will be at a slightly higher temperature than the surroundings due to the Kapitza boundary resistance at the solid liquid interface. One method of overcoming this would be to measure the vapour pressure of the helium using a "static" sensing tube in a small cavity which is also pumped. In order to assess the extent of this effect on the apparatus, a pressure sensing tube was placed in the main helium pumping line so that the pressure
of the helium was measured just above the constriction. Experiments were also carried out below the lambda point with the vapour pressure bulb connected into the pumping line. However, there was never any measurable difference in vapour pressure between any of these methods and the pressure as read from the unpumped helium bulb was taken as a correct indication of the temperature of the copper block D.

3.5 The Effect of Calibration Errors on the Thermal Conductivity.

It has been shown (Charsley et al, 1965) that when the calibration graphs differed from the "standard" curves the fractional error in T became greater as the temperature decreased. This effect gave rise to curvature of the K/T versus T graphs. The empirical criterion for valid results was that values of 'b' should deviate from the standard values by less than ± 0.1% at 4.2°K and ± 0.4% at 1.5°K. For some of the specimens investigated in this work the K/T versus T graphs are curved or "kinked". The physical meaning of these results is fully discussed later but it must here be stated that the calibration curves for these experiments were in no way different from those yielding straight K/T versus T graphs and that in all experiments the 'b' values differed from the "standard" values by less than 0.1% at 4°K and 0.2% at 1.8°K. In one experiment the relative position of the two thermometers on the specimen was reversed but there was no difference in the curves for the individual resistors.

If, for a given calibration point, the temperature as
measured from the helium vapour pressure did not exactly correspond to the temperature of the thermometers, then the values of 'b' for the point in question would be either too great or too small. However, the error would be in the same sense for both resistors. The associated error in calculating the thermal conductivity values was reduced by drawing each smooth calibration curve in a similar position relative to each point of the erroneous pair.

3.6 Comparison of Results using a Different Calibration Method

In the method described above the calibration curves were drawn manually. It was of interest to compare the thermal conductivity values thus obtained with those resulting from computed calibration data.

Sousa, 1968, quoted the following relationship between temperature and resistance for carbon resistors:

\[ \frac{1}{T^*} = \frac{a_n}{(\log R)^n} + \ldots + a_2 + a_1 (\log R) + \ldots + a_0 (\log R)^n \]

in which \( n \) was taken equal to 3

\[(3.2)\]

where \( a_n \) are constants (n integer). This reduces to an expression similar to equation (3.1) when \( n = 1 \).

The results from 15 experiments were investigated by fitting the calibration data to equation (3.2) with either 7 or 5 arbitrary constants, \( (n = 3 \) or \( n = 2 \) respectively). The constants \( a_n \) were determined for each thermometer by a least squares fit and equation (3.2) was used to calculate empirical temperatures \( T_1^* \) and \( T_2^* \).

The deviations \( \epsilon_i = T_1^* - T_i \) and \( \epsilon_i = T_2^* - T_i \) of the points from the computed relation were printed out. From each
pair of resistance values corresponding to a thermal conductivity measurement, values of $T'$ were determined and hence a value for the conductivity was obtained. Small corrections to this value were made using the known differences between $T'$ and $T$.

The $K/T$ versus $T$ graphs obtained using this method do not in general agree very well with those obtained originally using the manual method described in section 3.2. For the 2A1 annealed polycrystal both calibrations yield straight line $K/T$ versus $T$ graphs which agree well (Fig. 3.2). An example of a kinked $K/T$ versus $T$ graph calculated using both methods of calibration is shown in Fig. 3.3. In many cases, however, use of the computer method gave $K/T$ versus $T$ graphs which had a large amount of scatter — as much as 3%. These graphs were extremely sensitive to the omission of even one calibration point whenever that calibration point appeared to be in error. Taking $n = 2$ and $n = 3$ in equation (3.2) had little effect on these curves.

The computer method of calibration was used to supply additional evidence that the kink in the $K/T$ versus $T$ graphs was not in fact due to some calibration error and in this respect the venture was a success. The computed results never produced straight lines where there was originally a kink and in cases where both methods produced a graph of the same shape the manual method always gave similar or less scatter on the points than the computed. One reason for the scatter on the latter curves was probably that the computer treated all calibration points as being of equal significance but when the points were plotted manually those which may have been slightly in
error were obvious and it was justifiable to draw a smooth curve ignoring such points.

Before the computer method can be used with confidence further analysis needs to be carried out possibly taking a value of \( n = 1 \) in equation (3.2). This should give a smoother calibration curve analogous to the manual plot and could well give less scatter on the final thermal conductivity results.

3.7 Discussion of Experimental Errors

The qualitative errors associated with the calibration procedure have been discussed above; the quantitative accuracy of the thermal conductivity measurements will now be assessed.

Values of thermal conductivity \( K \) were calculated from the expression

\[
K = \frac{Q \cdot d}{\Delta T \cdot a}
\]

where \( Q \) is the heater power and \( \Delta T \) is the temperature difference between the two thermometers spaced a distance \( d \) apart along a specimen of cross sectional area \( a \).

The accuracy of \( T_1 \) and \( T_2 \) and hence \( \Delta T \) was dependent upon the error in values of \( b \) read from the calibration graph. Systematic errors apart, assuming that the calibration graphs could be drawn and read to \( \pm 1 \) mm above and \( \pm 2 \) mm below the lambda point the \( b \) values were known to \( \pm 1 \) part in 40,000 and \( \pm 1 \) part in 20,000 respectively. Considering the extent of the drift of resistance in the course of taking a set of readings at a given temperature it is reasonable to state that values of \( R \) were known to
then shows that the values of $T$ were obtained to $0.02\%$ at $4^0\text{K}$ and $0.015\%$ at $1.8^0\text{K}$ and although these do not apply to absolute values of $T$ they can be used to estimate the errors in $\Delta T = T_2 - T_1$; this error is found to be $0.8\%$ at $4^0\text{K}$ and $0.3\%$ at $1.8^0\text{K}$.

Drawing the calibration graphs as described in section 3.5, the random error in $T$ is calculated to be negligible. It was assumed that any systematic errors in $T$ were unlikely to be more than a few millidegrees and hence errors in $T$ itself will be neglected.

The non-linearity of the relation between $K$ and $T$ implies that there will be a difference between the true value of $K$ at the temperature $\frac{T_1 + T_2}{2}$ and the mean value of $K$ between $T_1$ and $T_2$. This difference is given by $\Delta K = \frac{1}{2}B(\Delta T)^2$ and taking $\Delta T = 0.2^0\text{K}$ the percentage errors in the quadratic term in the thermal conductivity are $0.05\%$ and $0.2\%$ at $4^0\text{K}$ and $2^0\text{K}$ respectively.

Errors in the measurement of the heater power, apart from the random error in potentiometric measurement estimated at $0.1\%$, arise from heat conduction along the leads, including the leads to the thermometers, heat produced in the current leads and heat loss by radiation from the heater. If the helium can was at $1.5^0\text{K}$ and the heater temperature rose to $10^0\text{K}$, which is very unlikely, then the heat loss by radiation would give rise to a maximum error of less than $0.05\%$ of $Q$; the other sources of error are calculated to be negligible using the heater leads arrangement described in Chapter 2. Thus the maximum error in the measurement of heater power is $0.15\%$. 
There remains the error associated with the measurement of the size factor $d/a$. The separation, $d$, of the thermometer tags was measured with a travelling microscope and the diameter of the specimen with a micrometer screw gauge. Having regard to the thickness of the specimen tags and the solder connections to the specimen, the size factor is only accurate to between $\pm 2.0\%$ and $\pm 2.5\%$ depending on the size of specimen used. As the size factor affects values of $K$ and $L/\rho_0$ in the same manner, the errors will not affect $(L/\rho_0 - A)$ for a given specimen but must be included when comparing different specimens or the same specimen after different amounts of strain. The change in size factor due to thermal contraction between room and liquid helium temperatures affects all readings in the same sense and has not been taken into account in these calculations.

Thus apart from errors in the size factor, the errors in the values of $K$ will vary from $\pm 1.0\%$ at $4^\circ K$ to $\pm 0.7\%$ at $1.8^\circ K$. These are maximum estimates and as seen from the graphs the actual scatter of points is less than these.

Finally, the errors in the determination of the residual electrical resistivity of the specimens needs to be considered. In this case the estimated maximum error of $0.03\%$ in the potentiometric measurement of the resistance is negligible compared with the error inherent in the values for the size factors of the specimens as discussed above.
Fig. 3.1
Typical Calibration Curves.
Fig. 3.2
Graph of $K/T$ vs. $T$ for specimen 2A1, annealed, showing effect of method of calibration.

- $\bigcirc$ Computed method
- $\times$ "Manual" method
Fig. 3.3 Graph of K/T vs. T for 12Al single crystal strained to stage III showing effect of method of calibration.
**Dislocation-Phonon Scattering in Copper Alloys.**

4.1 **Introduction**

In Chapter 1, recent work by Salter, 1965, on the dislocation phonon scattering per unit dislocation density in some alpha-phase copper aluminium alloys was described. This scattering, defined by the relation \( \sigma = \frac{W_L T}{N_d} \), was found to vary with the aluminium content of the alloys. The theory was advanced that this might be due to the change in dislocation arrangement with increasing solute concentration. The fact that \( \sigma \) for the Cu+12at%Al was twice as large as that for the Cu+2at%Al was explained on the basis of coherent scattering of phonons from pile-ups of dislocations in the former case. Accordingly, it appeared reasonable to assume that an alloy such as Cu+30at%Zn would have a value of \( \sigma \) similar to that of the Cu+12at%Al since their stacking fault energies are not very different (Howie and Swann, 1961) and their dislocation arrangements are similar. However, Lomer and Rosenberg, 1959, had made a direct comparison between dislocation densities as determined by transmission electron microscopy and by lattice thermal conductivity measurements on a deformed Cu+30at%Zn alloy. In this work only a rough comparison was made and there was no attempt to make a detailed study. They found that the values of dislocation density estimated using Klemens' theory (Klemens, 1958) were too large by a factor of six. Although their final quoted dislocation densities were all calculated using the theoretical predictions, the numerical
values were all reduced by this factor of six. For Cu+30at.%Zn they found \( \sigma = 0.36 \times 10^{-7} \text{ watt}^{-1} \text{ cm}^{3} \text{ deg}^{-1} \). This was six times smaller than Salter's corresponding value for Cu+12at.%Al and hence was considered to be probably in error.

The work on alpha-brass here described was carried out to obtain a more reliable correlation between lattice thermal conductivity and dislocation density in this alloy. The results of the thermal conductivity experiments and electron microscopy determinations are presented in sections 4.3 and 4.7 respectively.

4.2 Experiments on Specimens deformed in Torsion.

Charsley et al., 1968, suggested that the variation of \( \sigma \) could arise from the segregation of solute atoms to the neighbourhood of dislocations. This idea was put on a more quantitative basis by Klemens, 1968, who considered the enhanced scattering of phonons by Cottrell atmospheres surrounding dislocations. The modulation of the impurity concentration about the dislocations was shown to increase the phonon scattering by dislocations if heavy impurities are associated with positive impurity dilatation, or light impurities with negative dilatation, and to decrease the phonon scattering for the opposite combinations.

As a preliminary investigation into this theory, thermal conductivity experiments were performed on two specimens which were deformed and cooled rapidly in an attempt to prevent any solute atmospheres forming around the dislocations. They were later remeasured in an aged
condition and any change in the thermal conductivity graphs might be attributable to solute atoms diffusing to dislocations. In order to accomplish this in practice it was decided to mount the annealed specimen in the cryostat with the thermometers and heater attached and then to deform it rapidly, fit the radiation shields and cool down to liquid nitrogen temperature as soon as possible. It was most convenient to deform the specimen in torsion and it was twisted about its long (vertical) axis so that one thermometer tag was turned through $360^\circ$ relative to the other giving a shear strain at the surface of 0.18. The time that elapsed between deformation and cooling down to liquid nitrogen temperature was 10 minutes, after which it remained at this temperature for 12 hours before being cooled to $4.2^\circ$K and below with liquid helium. On completion of the thermal conductivity measurements the specimen was kept at room temperature for 5 days before it was remeasured in the aged condition. The whole experiment was performed twice, once on a single crystal of Cu+12at%Al and a second time on a specimen of polycrystalline Cu+10at%Au.

For convenience, these results are combined with the thermal conductivity results for alpha-brass in section 4.3. All the results are discussed in section 4.8.
4.3 Results of Thermal Conductivity Measurements.

As discussed in Chapter 1, the temperature dependence of the lattice thermal conductivity is the same for both dislocation-phonon scattering and electron-phonon scattering. When a specimen is plastically deformed the form of the K/T against T graphs remains unchanged, but the slope B is reduced. This is evident in Fig. 4.1 which shows the K/T versus T graphs for the polycrystalline alpha-brass in the annealed condition and also after 4.4% tensile strain. As indicated in section 2.2 these two experiments were carried out in the cryostat described by Salter, 1965. Values of A, B, etc. are given in table 4.1 assuming a linear relationship between K/T and T.

Figs. 4.2 and 4.3 show the thermal conductivity graphs, before and after ageing, of the 12Al single crystal and 10Au polycrystal respectively. In both cases the curve for the aged specimen lies above that for the sample in the unaged condition. The slope of this curve for the single crystal differed very little from that of a similar specimen measured in an annealed condition. It was possible that as the specimen was single, few defects were introduced by the deformation and thus any effect due to atmosphere formation, such as a change in the slope of the K/T versus T graph after ageing, might have been too small to be easily observed. Thus the experiments were repeated with the polycrystal 10Au and in this case the slope of the curve was 50% less than that for a similar annealed sample. For specimens deformed in tension, the relationship between the lattice thermal conductivity and dislocation density was known (Chapter 6). However, this
relation would not apply for specimens deformed in torsion as in this case the distribution of dislocations is inhomogeneous and hence no estimates were made of the dislocation density for these samples.

Table 4.2 shows values of $A$, $B$, $\delta$, etc. for the torsionally deformed specimens combined with the annealed values from other similar samples. The $K/T$ versus $T$ graphs for the 12A1 single crystal show a slight kink as mentioned in section 3.5 but the results for the twisted specimen 10Au do not exhibit this effect. A full discussion of this phenomena is postponed until Chapter 5.

4.4 Preparation of Alpha Brass Specimens for Electron Microscopy.

After the thermal conductivity and residual electrical resistivity measurements had been made on the brass specimen, it was cut in two places between the thermometer tags, each cut being about 3mm from the tag. This centre part of the specimen was then electro-polished in a 20% solution of orthophosphoric acid in water until the specimen diameter was 2.3mm which corresponded to the size of the Valdré holder in the electron-microscope. The polishing solution was surrounded by an ice bath to ensure that the temperature of the specimen was kept below about 10°C. The specimen was then cut into discs approximately 0.5mm thick. All the cutting was done with a Servomet spark machine cutter manufactured by Metals Research Ltd. Initially, a moving wire cutter was used but this proved
unsatisfactory for accurate work as kinks occurred in the wire which gave an uneven profile to the disc. Furthermore, the wire (tinned soft copper, 28 S.W.G.) was comparatively thick and hence a large amount of material had to be removed to cut each disc. To overcome these problems a jig was made to hold a fixed 2 inch length of 33 S.W.G. tungsten wire which cut three discs before it needed replacing. Cutting on range 6, a fine range, took about 5 minutes per disc. By supporting the specimen along its entire length, including that part of the specimen which was being cut into a disc at the time, burring of the edges of the disc at the end of each cut was avoided. The importance of this will be seen later.

A standard technique for preparing thin films from disc specimens is to use a P.T.F.E. holder made by Aeon Laboratories Ltd. which is designed to give a dished specimen profile and large thin areas suitable for electron microscopy. However, some difficulty had been experienced in the past in obtaining the correct profile because gases were produced by the anodic dissolution of the metal. These gases form bubbles which retard the polishing action unless quickly removed. To avoid this problem the preparation of the discs for electron microscopy was divided into two stages, the first of which gave the correct specimen profile (see Fig. 4.5a) and the second, in the P.T.F.E. holder, produced thin areas.

The preliminary polish was carried out using a jet technique. The stainless steel jet forming the cathode was mounted vertically above the disc placed on a stainless steel gauze (the anode). The stream of electrolyte
was supplied from a constant pressure head reservoir and was continuously circulated from the collection tank beneath the specimen using a peristaltic pump. This system had a large number of variable parameters associated with it but it was found experimentally that the most critical was the jet diameter. Accordingly, the applied voltage was fixed at 80 volts and a pressure head of 30 cm of electrolyte was used, the solution itself being 15% orthophosphoric acid in water. A range of jet sizes from 1 mm to 2.3 mm diameter was tried with the jet held 0.5 cm above the specimen. Polishing the disc for 60 seconds with the 1 mm jet produced a hemispherical type of pit of similar diameter to the jet, in the centre of the specimen. At the other extreme, a 2.3 mm jet polished the whole area of the disc without forming a dished profile. Eventually, a 1.75 mm diameter jet was found to give the best result except that a small "hill" remained in the centre of the flat bottomed dimple. This was very simply eliminated by mounting the peristaltic pump and polishing assembly on the same base board so that small vibrations from the pump motor were transmitted to the jet. A diagram of the jet assembly is shown in Fig. 4.5b.

When both sides of the disc had been polished using the jet method, it was transferred to a P.T.F.E. holder for final thinning. This holder has been fully described by Dewey and Lewis, 1963, and the experimental set up by Salter, 1965. Initially, an electrolyte of 30% fuming nitric acid and 70% methanol at a temperature of about -20°C was tried; this had proved to be successful in polishing a Cu+12at%Al alloy. However, in the case of
alpha-brass, it was found that when perforation occurred, no thin areas of foil were produced. Various concentra-
tions of orthophosphoric acid in water were then used and eventually the best results were obtained with a 50\% solution at 0°C with a current of 0.2 amps at 10 volts. Using a light source behind the holder and a simple lens system for viewing the disc, polishing was stopped as soon as a hole appeared in the specimen. It was then washed in distilled water followed by absolute ethyl alcohol, carefully removed from the P.T.F.E. inserts and transferred to a Valdré holder for observation in the electron microscope. This washing procedure was found to be very important to avoid oxide film being formed on the surface of the speci-
men.

For some time no thin foils were obtained using this method, as the specimen in the P.T.F.E. holder was polished preferentially at the edges instead of the centre. The fault was traced to worn P.T.F.E. inserts which had been damaged by using burred disc specimens. Once the speci-
men was fully supported during the cutting process, as described earlier, and new inserts had been fitted, thin areas were obtained successfully.
4.5 The Use of Transmission Electron Microscopy for Measuring Dislocation Density.

The theory and technique of electron microscopy of thin foils is covered in a comprehensive review by Hirsch et al, 1965. Accordingly, no attempt is made here to reproduce the standard general theories but only some specific aspects which are pertinent to determining the dislocation density in alpha-brass.

There are two ways of defining dislocation density: either as the line length per unit volume, or as the number of dislocations intersecting a unit area of plane surface. The choice of definition depends on the physical context and the relation between the densities calculated from the two methods is a function of the particular dislocation arrangement. Theoretical calculations of dislocation phonon scattering assume individual straight dislocations but the results are often quoted for a random array of defects. The appropriate parameter is then the line length per unit volume and this definition of dislocation density is employed throughout this work. For a random array of dislocations it can be shown that this value is twice the value obtained by the use of the other definition, (Schoeck, 1962).

When counting dislocations on micrographs it is necessary to remember that unless several strong Bragg reflections are operating, some dislocations are invisible. Selected area diffraction patterns were taken in each case to determine the operating Bragg reflections. On any given micrograph dislocations were usually observed on more than one slip system and assuming a random distribu-
tion of dislocations among the 6 $\langle110\rangle$ type Burgers Vectors
the proportion of invisible dislocations could be found
using the invisibility criterion $g \cdot b = 0$, where $b$ is the
Burgers Vector and $g$ is the reciprocal lattice vector of
the reflecting planes.

Three methods were used to obtain dislocation densi­
ties from the electron micrographs:

(i) The counting of dislocation intersections with
planes perpendicular to the foil surface. This method
was first described by Ham, 1961, and was discussed in more

(ii) The counting of dislocation intersections with foil
surfaces as described by Ham and Sharpe, 1961.

(iii) The direct measurement of the projected line length
of the dislocations.

Methods (i) and (iii) require a knowledge of the foil
thickness. This was calculated either from one slip trace
and the orientation of the foil normal as determined by
electron diffraction, or from two or more slip traces of
different widths and/or directions. In the latter case
the tables prepared by Crocker and Bevis, 1964, were used
which enabled the foil thickness and orientation to be
obtained directly from the ratio of the slip trace widths
and the angle between them.

The choice of method used to determine the dislocation
density depended upon the type of dislocation structure ob­
served in any given micrograph. For example, method (iii)
could only be used where there were regular arrays of dis­
locations while method (ii) was only suitable for areas of
foil having a comparatively low density of untangled dis­
When two different methods could be used, values of dislocation density agreed to better than $\pm 10\%$. In all cases allowance was made for the invisibility factor (Hirsch et al, 1965).

4.6 The Reliability of the Dislocation Density Determination.

Although electron microscopy provides a direct method of measuring dislocation densities in thin foils, it must be remembered that these measurements sample only a minute fraction of the bulk specimen and that the defect structure in the material of the foil may itself change during the thinning process.

Inaccuracies associated with the determination of the dislocation density thus arise from two sources: there is the finite error inherent in taking actual physical measurements from electron micrographs and there is also the uncertainty as to whether a defect structure observed on an electron micrograph is characteristic of the bulk specimen.

Errors of the first kind are more easily estimated. In order to determine the dislocation density the area of the plate $A$, the magnification of the image $M$ and in most cases the foil thickness $t$ are needed. Both $A$ and $M$ are known to about $\pm 2\%$ and the slip trace width, used for determining $t$, to about $\pm 5\%$. The main error in $t$, however, arises from the fact that the foil surface is often not normal to the electron beam and the orientation obtained from selected area diffraction is not the true foil normal.
If the angle of tilt and its axis are known a correction can be applied and it has been shown (Hirsch et al, 1965) that for angles of less than 5° the error in t is between ±5° and ±10%. Thus, the error involved in measuring dislocation densities from the plates amounts to approximately ±15%.

Errors of the second kind are more difficult to discuss quantitatively. Dislocations may be introduced accidentally during the process of thinning and transferring the thinned specimen to the electron microscope but such damage is unlikely to have occurred in the present experiments as all the handling was done by the thick outer rim of the disc. In any case, this damage should be easily recognisable in polycrystalline materials as it would consist of long nearly straight dislocations lying parallel to the foil surface (Wilsdorf and Schmitz, 1962). Such dislocation arrangements were not observed in the present experiments.

Rather than dislocations being introduced during thinning, it is more likely that some will be lost. Various authors (e.g. Mader, 1963; Hirsch and Steeds, 1964), have found that screw dislocations escape from foils by cross slip. Ham, 1962, showed that for an aluminium-silver solid solution which had been cold rolled, more dislocations were lost during thinning for an unaged rather than an aged sample and it was assumed that the ageing process made it more difficult for the dislocations to escape from the foil. It was inferred that at least 60% of the dislocations were lost in the course of thinning the unaged specimen. Foxon and Rider, 1968, found that for polycrystalline copper
deformed in tension, dislocation loss took place during thinning, the loss increasing rapidly with dislocation density above a critical density. This loss was thought, at least in part, to be due to overlapping images of dislocations. However, these authors found that the dislocation loss was very small in aluminium with a small amount of impurity present, (Foxon and Rider, 1966).

In addition to dislocation loss, re-arrangement of the defects also takes place. This has been shown for stainless steel by Valdre and Hirsch, 1963, who found that up to 20% of the dislocations moved, the proportion decreasing with increasing deformation. The movements were mainly local and it was considered that the general character of the dislocation structure remained unaltered. However, local rotations of dislocations towards the foil normal can affect the actual value of the measured dislocation density. The number of dislocation ends remains unchanged but the line length per unit volume is decreased and hence using the former to estimate the dislocation density gives a more accurate indication of conditions in the bulk specimen (Ham and Sharpe, 1961).

For alloys of 2at%, 8at% and 12at% aluminium in copper, Salter, 1965, followed the estimate of Valdre and Hirsch, 1963, and placed an upper limit on the underestimation of the dislocation density at 30%. The 30Zn specimen investigated in this work had a stacking fault energy of about 6 ergs/cm² which was similar to Cu+12at%Al. As a result of solid solution hardening, dislocations are less likely to be lost during thinning in this material than they are in, for example, pure copper. Hence, it will be
assumed that the values quoted for the dislocation density of 30Zn are under-estimates by not more than 30%. In the present work, an error of this magnitude was not really important, provided that it did not vary markedly from one alloy to another.

4.7 Results of Electron Microscopy of Alpha-Brass.

In order to determine the dislocation density in the alpha-brass strained 4.4% in tension, a total of 14 separate grains were studied, 31 micrographs being analysed. Of the three methods of measuring the dislocation density outlined in section 4.5, the first was used in the majority of cases. For many of these, method (iii) could have been employed equally as well but it was far more tedious to execute and hence was only used for a few micrographs, principally as a check. Many of the plates showed dislocations in pile-ups although occasionally some grains with higher dislocation density than average having tangled dislocations were observed. On the whole, the arrangement of dislocations was similar to that observed by other workers for Cu+12at%Al (e.g. Salter, 1965, Mitchell et al, 1967, Steeds and Hazzledine, 1964).

The dislocation density was fairly uniform throughout any given grain and the final value for $N_p$ was the mean over all grains. There was an approximately Gaussian distribution of values of $N_p$ about the mean which is in agreement with Salter's (1965) observations for Cu+8at%Al and Cu+12at%Al. Plates 4.1 and 4.2 show some typical
dislocation arrangements.

The final value of \( N_p \) for the 4.4% strained alpha-brass was \( 6.6 \pm 1.1 \times 10^4 \text{ cm}^{-2} \). This, combined with the thermal conductivity values given in Table 4.1, gives a value for \( \sigma \) of \( 0.42 \pm 0.18 \times 10^{-7} \text{ W cm}^{-1} \text{ deg}^{-3} \). This agrees well with the estimate of \( 0.36 \times 10^{-7} \text{ W cm}^{-1} \text{ deg}^{-3} \) for \( \sigma \) found by Lomer and Rosenberg, 1959.

4.8 Discussion of Dislocation-Phonon Scattering.

Fig. 4.4 shows the values of \( \sigma = \frac{W_p T^3}{N_p} \) obtained by Salter (1965) and the corresponding value for Zn determined in this work plotted as a function of solute concentration. These results suggest that one of two extreme possibilities may exist:

(i) Drawing the best straight line through the values of \( \sigma \) for the copper-aluminium alloys indicates a value of \( 8 \times 10^{-8} \text{ W cm}^{-1} \text{ deg}^{-3} \) for pure copper and implies that the value of \( \sigma \) for copper-zinc alloys decreases with increasing solute concentration. This is indicated by the dashed lines on Fig. 4.4.

(ii) Taking the greatest variation in \( \sigma \) for copper-aluminium alloys as indicated by the maximum estimated errors for individual determinations gives a minimum value of \( 3 \times 10^{-8} \text{ W cm}^{-1} \text{ deg}^{-3} \) for pure copper. In this case \( \sigma \) for copper-zinc alloys is virtually independent of solute concentration. This is shown by the solid lines in Fig. 4.4.

The values of \( \sigma \) which have been deduced by extrapola-
tion for pure copper are an order of magnitude greater than the theoretical estimates for a random arrangement of dislocations (Klemens, 1958; Carruthers, 1961). Bross et al., 1963, have shown that for screw dislocations in copper

\[ \sigma = 5.3 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1} \text{ deg}^{-3} \]

and for edge dislocations

\[ \sigma = 7.0 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1} \text{ deg}^{-3} \]

These values are very similar to those obtained by Klemens and Carruthers. Bross also considers the components of the thermal resistivity for the case of an edge dislocation. If the dislocation line is in the z-direction with the Burgers vector in the x-direction then

\[ \sigma_{xx} = 6.0 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1} \text{ deg}^{-3} \]

and

\[ \sigma_{yy} = 15.2 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1} \text{ deg}^{-3} \]

In the specimens examined in this work it was commonly found that dislocations were in the form of dipoles of predominantly edge character. Considering the errors involved in the experimental determination of \( \sigma \) the discrepancy between this value and that predicted by the theory is less than an order of magnitude.

Lomer and Rosenberg, 1959, found that the dislocation densities, deduced from thermal conductivity results on the basis of a fixed \( \sigma \), of 7, 15 and 30 at.\% Zn in copper all fell on a universal curve when plotted against strain for strains up to 20%. In view of this the second of the two alternatives for the variation of \( \sigma \) with solute concentration outlined above would seem to be more plausible. It is certain that \( \sigma \) changes far less with solute content for copper-zinc alloys than for alpha-phase copper-aluminium
alloys. For both alloy systems the stacking fault energy decreases as the solute concentration increases and for 12A1 and 30Zn the arrangement of dislocations has been established in section 4.7 to be similar. It thus seems highly probable that $\sigma$ is independent of the arrangement of dislocations in the material. In this connection an experiment designed to investigate the scattering of phonons from dislocation pile-ups (Charsley et al., 1967) is important. A specimen of Cu+12at.%Al was deformed and its thermal conductivity measured under stress and also in the relaxed condition for both a single and a polycrystal. The effect of stress is to decrease the spacing of the dislocations in the pile-up and it was expected that this would result in a change in the conductivity. However, no significant difference was found between the conductivities of the stressed and relaxed specimens and in the light of all the experiments described here it is concluded that the value of $\sigma$ depends very little on the dislocation arrangement.

One difference between the two alloy systems investigated is that the mass difference between copper and aluminium is large while that between copper and zinc is very small. In this respect the latter alloy is similar to the Cu+4.6at.%Ga specimens studied by Zeyfang, 1967. The value he obtained for $\sigma$ was $0.5 \times 10^{-7}$ W cm$^{-1}$ deg$^{-1}$ which is almost identical with the value here obtained for 30Zn. However, mass difference scattering should be unimportant at liquid helium temperatures (Klemens et al., 1962) and it has been found that for annealed alloys the lattice thermal conductivity appears not to be correlated with
the mass difference between solute and solvent atoms. Instead, good correlation exists for these alloys between lattice thermal conductivity and electron mean free path (Lindenfeld and Pennebaker, 1962; Charsley and Salter, 1965). As both electron-phonon and dislocation-phonon scattering yield the same temperature dependence for the thermal conductivity it is unlikely that mass difference scattering is important in the latter case. Thus, if mass difference does affect the dislocation-phonon scattering it must be due to some interaction between solute atoms and dislocations. Such an effect could arise from the segregation of solute atoms to dislocations (Charsley et al., 1968) to form "Cottrell atmospheres" (Cottrell, 1953): these regions of different density from the matrix could cause enhanced scattering of the phonons. This suggestion prompted Klemens, 1968, to calculate the magnitude of this effect for the copper aluminium alloys which had been studied (see Chapter 1). He found that there would be an enhancement of the dislocation-phonon scattering over that of the pure metal (or copper-zinc) for the 2at.%, 8at.% and 12at.% aluminium in copper in the ratio 1:1.5:3:5. This was not unreasonable agreement with the empirical ratio of 1:2:4:5. However, the calculation assumed that, in the regions of interest which were 10 to 100 atomic spacings from the dislocation core, the concentration of solute atoms was greater than the average value. In order to obtain enhanced scattering for aluminium in copper on this theory the size of the solute atom needed to be less than that of the solvent. It was thus necessary to take the ionic radius of alumin-
ium (0.51\AA) to calculate the fractional volumetric distor-
tion rather than a value of 1.43\AA obtained from considera-
tion of the change in lattice spacing with aluminium con-
centration. However, the calculations of Bullough and
Newman, 1962, on the distribution of solute atoms during
atmosphere formation indicate that when equilibrium is
attained there is a reduction of solute concentration be-
low the average value at distances of the order of 100\AA
from the dislocation core. Fig. 4.6 is a sketch of the
two types of solute distribution around a dislocation
according to the models of Klemens and also Bullough and
Newman. For the latter of these models, if the atomic,
as opposed to the ionic, radius is taken for aluminium,
enhanced scattering of phonons from the Cottrell atmos-
pheres will still result although the ratio of the in-
creased scattering over that of a pure metal is not in
such good agreement with experiment as Klemens' original
calculation. Again, taking the value for the pure metal
as unity, the ratios of the phonon scattering from dislo-
cations for the 2at.%, 8at.% and 12at.% copper aluminium
would be 1:1.2:2.1:2.9. Although this modification to
Klemens' theory gives reasonable results for copper-
aluminium it does not predict the observed behaviour of
dislocation-phonon scattering for copper-gold which con-
sists of a more massive solute with a larger atomic size
than copper. The value of $\tau$ for Cu+10at.% Au is found to
be similar to that for Cu+12at.% Al (see chapter 6) which
is in agreement with the original prediction by Klemens.
However, if the solute distribution according to Bullough
and Newman is used in the calculation, then a value of $\tau$
for copper-gold alloys is predicted which is smaller than that for pure copper.

Further theoretical work is necessary in applying the Bullough and Newman type of solute distribution to the problem. The assumption that the dilatation field around an edge dislocation is symmetrical is incorrect and hence the atmosphere formation will itself be asymmetrical. The phonon scattering will then be drastically altered.

It is difficult to correlate the thermal conductivity results obtained from the torsionally deformed specimens before and after ageing with the formation of solute atmospheres. For both specimens the conductivity increased very slightly (approximately 0.6%) as a result of the ageing process although on the theoretical model proposed by Klemens it should have decreased significantly. It is highly probable that the atmospheres of solute atoms had almost completely formed around the dislocations in the time between deforming the specimens and cooling them down to liquid nitrogen temperature. Information about the time necessary for the formation of solute atmospheres may be obtained by considering the rate at which impurities segregate to the dislocation core. These impurities affect the mechanical properties of the material and give rise to effects such as yield point phenomena in solid solutions. In this case an initial maximum in the stress-strain curve is recoverable after strain ageing and has been ascribed to the pinning of dislocations by solute atoms (Ardley and Cottrell, 1953; Koppenaal and Fine, 1961; Hendrickson and Fine, 1961). It has been found that for Ag+6at.%Al approximately 50% of the initial yield
drop is recovered after ageing for as little as one minute at room temperature. Similarly, ten minutes ageing was required for a Cu+14at.%Al single crystal. Recently, Devaux, 1967, found that for a strained single crystal of Cu+12at.%Al the yield point returned after only five minutes ageing at room temperature.

The concentration distribution of solute during atmosphere formation calculated by Bullough and Newman, 1962, shows that the rate of depletion of solute at large distances (~100Å) from the dislocation is similar to the rate of accumulation of solute atoms at the core itself. Thus it is reasonable to conclude that the solute atmosphere had already formed around the dislocations when the deformed specimen was cooled to liquid nitrogen temperature.

The fact that for both torsionally deformed specimens the values of the thermal conductivity increased after ageing is almost certainly due to the production of vacancies during the rapid deformation. These could anneal out during the period between the two thermal conductivity measurements (Rider and Foxon, 1966). Vacancies would affect the electronic and not the lattice contribution to the thermal conductivity at liquid helium temperatures and hence the K/T versus T graphs for the aged sample lies parallel to, but displaced from, that of the unaged specimen. The value of L/σ for the aged 10Au specimen was in good agreement with the intercept on the K/T axis at T=0 and by considering these intercepts for both specimens the change in residual electrical resistivity with ageing was calculated. It is generally accepted (Ziman, 1960) that 1 at.% of vacancies give rise to a residual electrical
resistivity of approximately \( 1.5 \mu \Omega \text{cm} \). Hence we may conclude that in these specimens the atomic concentration of vacancies annealed out during the ageing process was 0.1\% and 0.03\% for the 12ÅAl and 10ÅAu respectively.

The results of Solomon and Otter (1967) show that the lattice thermal conductivity of In+40at.%Pb alloy, slightly cold worked, in the superconducting state decreased after annealing for two weeks at room temperature. Thus the change in thermal conductivity with ageing for their material was in the opposite sense to that found in this work and hence could not be explained on the basis of the production of vacancies during cold work. Klemens, 1961, attributes the change to the formation of Cottrell atmospheres but this would appear unlikely as the rate of diffusion in this case would be much higher than in the copper alloys. Further investigation is necessary before the applicability of the theory can be established.
### Table 4.1

**Thermal Conductivity Results for 30Zn.**

<table>
<thead>
<tr>
<th>Strain $%$</th>
<th>$\frac{L/K \times 10^3}{\text{cm}^{-1} \text{mm}^{-2}}$</th>
<th>$\beta_a$ $\mu \text{cm}$</th>
<th>$W \frac{A g}{T^2 \text{cm} \text{deg}^3}$</th>
<th>$W \frac{gT^2}{\text{cm} \text{deg}^3}$</th>
<th>$A \times 10^3 \frac{W}{\text{cm} \text{deg}^2}$</th>
<th>$\tau$ $Kg/mm^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ann.</td>
<td>4.4</td>
<td>3.39</td>
<td>2.70±50</td>
<td>1660±30</td>
<td>602±012</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.35</td>
<td></td>
<td></td>
<td>518±006</td>
<td>7.00±002</td>
</tr>
<tr>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2

Thermal Conductivity Results for specimens Deformed in Torsion.

N.B. Comparison of these results with those of similar annealed specimens is difficult as the size-factor of the twisted specimens was not accurately known.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( A \times 10^2 ) W cm(^{-1}) deg(^{-1})</th>
<th>( B \times 10^2 ) W cm(^{-1}) deg(^{-2})</th>
<th>( L/\rho \times 10^2 ) W cm deg(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Al (single) annealed</td>
<td>3.13(\pm)0.02</td>
<td>2.18(\pm)0.02</td>
<td>2440(\pm)25</td>
</tr>
<tr>
<td>12Al (single) twisted, unaged</td>
<td>4.00(\pm)0.05</td>
<td>4.38(\pm)0.01</td>
<td>2500(\pm)40</td>
</tr>
<tr>
<td>12Al (single) twisted, aged</td>
<td>4.58(\pm)0.06</td>
<td>4.41(\pm)0.02</td>
<td>2180(\pm)30</td>
</tr>
<tr>
<td>10Au (poly.) annealed</td>
<td>4.00(\pm)0.04</td>
<td>38.30(\pm)50</td>
<td>3770(\pm)80</td>
</tr>
<tr>
<td>10Au (poly.) twisted, unaged</td>
<td>265(\pm)0.06</td>
<td>265(\pm)0.06</td>
<td></td>
</tr>
<tr>
<td>10Au (poly.) twisted, aged</td>
<td>265(\pm)0.06</td>
<td>265(\pm)0.06</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.1

Graphs of $K/T$ vs. $T$ for the 30Zn specimen in the annealed condition and after 4.4% tensile strain.
Fig. 4.2  Graphs of $K/T$ vs. $T$ for the 12A1 single crystal deformed in torsion.

$K/T/(10^3 \text{cm}^2 \text{K}^{-2})$

- △ Aged Specimen
- ○ Unaged Specimen
Fig. 4.3  Graphs of $K/T$ vs. $T$ for the 10Au polycrystal deformed in torsion.
Graphs of $\sigma$ against composition for copper-aluminium (Salter, 1965) and Zn specimens. The lines on the diagram are explained in the text.
Fig. 4.5

The jet electro-polishing technique.

(a) The correct profile after polishing with a jet of electrolyte.

(b) The jet assembly.
The concentration distribution of solute atoms around a dislocation due to Bullough & Newman (solid line) and that assumed by Klemens (dashed line).

$C(r)$ is the concentration at radius $r$ from the dislocation core and $C_0$ is the average solute concentration.
A typical dislocation arrangement observed in the 30Zn specimen after 4.4% tensile strain. Magnification x 80,000.
Plate 4.2

3 electron micrographs illustrating various arrangements of dislocations observed in the 4.4% strained 30Zn specimen. Magnification of each micrograph is x 40,000.
5.1 Introduction.

In this chapter the thermal conductivity results for alloys 2Al, 12Al and 10Au are presented and the form of the K/T against T graphs is discussed. The results of the residual electrical resistivity measurements are also included here but a full analysis of the combined results is postponed until chapter 6.

5.2 Results of Electrical and Thermal Conductivity Measurements.

The effect of plastic deformation on the K/T versus T graphs has been demonstrated in chapter 4 for the 30Zn specimen. Figs. 5.1 to 5.7 show these graphs for the polycrystalline specimens 2Al, 12Al and 10Au in the annealed condition and after various amounts of deformation in tension: different symbols are used on a given graph to indicate experimental points when more than one set of measurements was made on the same specimen in a certain state of strain. It is seen that, instead of being straight lines many of these graphs show a curvature or kink which occurs at approximately 3°K, irrespective of the particular alloy. The significance of this is discussed in the later sections of this chapter but certain points are obvious from inspection of the K/T versus T graphs. All of the results of K/T versus T are linear
within experimental error for annealed specimens and this also applies in the early stages of deformation for specimens 2Al and 10Au. The departure from linearity for these alloys does not become apparent until the specimens have been strained approximately 8% in tension whereas for specimen 12Al the initial tensile strain of 1.8% produced a graph which exhibited a very definite kink. Fig. 5.8 shows the K/T versus T graphs for a Cu+12at.%Al single crystal annealed and also in various stages of deformation. The stress-strain curve for this single crystal and the orientation of the annealed specimen in the standard stereographic triangle are shown in Figs. 5.13 and 5.14 respectively. The stress-strain curve exhibits behavior typical of a metal single crystal and it is usual to divide it into three main sections called stages I, II and III. Stage I is the region of easy glide in which very little hardening takes place and occurs when the crystal is so oriented that one glide system predominates. Stage II is a region of rapid work hardening where the stress-strain curve takes on a linear form and finally stage III is where the rate of work hardening begins to decrease and the curve becomes parabolic. This behavior is reviewed and interpreted in detail by Seeger, 1957. In Fig. 5.13 stages I and II are easily identified: the points at which the deformation was interrupted to take thermal conductivity measurements are indicated by vertical arrows. The final set of measurements was taken at the end of stage II at the onset of stage III. In the case of the annealed specimen and also after it had been strained into stage I it is difficult to decide whether
the K/T versus T graphs are completely linear. However, in stages II and III the kinks in the graphs become very noticeable.

The variation of residual electrical resistivity, $\rho_0$, with stress for the polycrystalline specimens is shown in Figs. 5.9 to 5.11. One result in which specimen 10Au differs from the other specimens is that, up to 4% strain, the value of $\rho_0$ apparently decreases. Although this could be accounted for by errors in the size factor it is quite possibly due to short range ordering in the alloy and will be discussed in chapter 6.

Fig. 5.12 shows the variation of flow stress with strain for each increment of deformation of the polycrystalline specimens. A very striking feature is the correspondence of the results for the 12Al and 10Au specimens for strains up to 12%.

Tables 5.1 to 5.3 give the values of $A$, the intercept of the K/T versus T graph of slope $B$ on the K/T axis, together with the corresponding values of $\rho_0$ for the specimens after various amounts of deformation. In the case of a graph which displayed a kink, the values of $A$ and $B$ refer to that part of the curve in the higher temperature region above the kink. Also included in these tables are values for the grain size of these specimens measured using the A.S.T.M. comparative method; they were obtained after the final conductivity experiments had been completed on each alloy.

The form of the results of the thermal and electrical conductivity measurements are discussed in section 5.4. The deductions made from these results concerning the mode of plastic deformation of the alloys are discussed in Chap. 6.
5.3 **Evidence that the Kink is Real.**

In order to ascribe any physical significance to the kink in the graphs of K/T versus T, it must be shown beyond reasonable doubt not to be some form of systematic error. This section presents the evidence and results from many experiments which establish the physical reality of the kink.

As stated above, the kink was first reported in the K/T versus T graphs of a Cu+12at.%Al deformed single crystal, (Charsley, Leaver and Salter, 1967). In order to confirm this unexpected effect, the thermal conductivity was re-measured on a different cryostat, using different thermometers and heater. The two sets of results agree extremely well as can be seen in Fig. 5.15. Following this experiment, all the measurements on the 2Al, 12Al and 10Au polycrystals were made and the existence or otherwise of a kink or curvature in the K/T versus T graphs was noted. The important facts that emerged from these results were that no annealed polycrystalline specimen gave a kink and that the 2Al and 10Au alloys showed no kink until approximately 8% tensile strain.

If the kink was, in fact, the result of some experimental error, then this could arise either from a fault in the apparatus or in the method of calibration. The latter would not appear to be the case as the two initial experiments on the Cu+12at.%Al strained single crystal, with different thermometers having different calibration characteristics, gave an identical kink. In addition, the calibration curves for annealed polycrystalline specimens, for which the K/T versus T graphs were linear, were
similar to those of strained alloys which showed a kink. As described in Chapter 3, the shape of the individual calibration curves and the form of the kink were not dependent upon which thermometer was at the top of the specimen. Finally, more evidence for the reliability of the calibration was afforded by comparing some of the results with those obtained using the computed calibration method of Sousa (1968), which was described in section 3.6. The results (Figs. 3.2 and 3.3) show good agreement between the two methods.

The possibility of some fault in the apparatus being responsible for the kink was then thoroughly investigated. The most probable source of trouble was a large heat input to the specimen. A heat input down the leads could have given rise to non-linearity of the thermal conductivity graphs, (Charsley et al., 1965), but this is a most unlikely explanation as the leads were thermally anchored at 4.2°K and individually anchored at the specimen temperature. Furthermore, the difference in the results for annealed and strained alloys and the similarity in the measurements from two cryostats, make it most unlikely that poor thermal anchoring of the leads was responsible for the kink. It was considered possible that the kink might have been due to a trace of helium exchange gas in the specimen space. This would have had the effect of reducing the temperature difference between the thermometers when a heat current was passed along the specimen, thus giving falsely high values for the thermal conductivity. The most obvious place for a helium leak was the indium ring seal on the thermal anchor block (C) (Fig. 2.1). If this
seal leaked only when surrounded by helium liquid and not by gas, which is characteristic of small leaks at these temperatures, then the heat input would be reduced when the liquid level in the outer dewar fell below the block. In the process of a normal run, this occurred after about one third of the readings had been taken and corresponded to a similar temperature in each run, so it was thought that it could have been a possible explanation of the kink. This was shown to be unlikely since runs with different helium levels did not result in kinks at different temperatures. However, in order to investigate this fully, a series of carefully controlled thermal conductivity experiments was carried out on a Cu+2at.%Al polycrystal which had been strained 9% in tension. The K/T versus T graphs for these experiments are shown in Fig. 5.16. The first experiment (run B63) was performed in the usual manner and the thermal conductivity plot exhibited a kink. The specimen was then measured again (run B68), but this time the readings were commenced at 3°K instead of 4.2°K so that the lower part of the temperature range could be studied while the helium levels in the dewar and in the small pumped can corresponded to those normally associated with the upper temperature region above the kink: the results agreed very well with the first experiment. Two more sets of measurements (runs B69 and B70) were then taken in which the conditions of run B68 were reversed; readings were taken only in the temperature range 4.2° - 3.0°K, the helium can was only half filled and the liquid helium level in the outer dewar was kept below the anchor block at all times. The results agree fairly well with
those from the first experiment and from these, combined with the other evidence from annealed specimens and different cryostats, it was concluded that stray helium gas was not responsible for the kink. Some time after these runs were performed, a helium leak detector became available which was capable of detecting leaks as small as $10^{-6}$ cc/sec: no leaks were detected in the system.

All the above evidence points to the fact that the kink has its origins in a real physical effect and from henceforth it will be considered as such.

5.4 Discussion of the Thermal Conductivity Results and the Interpretation of the Kink.

In sections 5.2 and 5.3 the existence of a kink in the K/T versus T graphs for certain specimens was reported and its physical reality has been established. This kink is not present for any of the annealed polycrystalline alloys investigated. For the 2A1 and 10Au specimens the kink was not apparent until after 5% and 8% tensile strain respectively, but the results for the 12A1 displayed a kink at the initial deformation (1.7% strain). A few experiments performed on strained 30Zn indicated that it behaved in a similar fashion to the 12A1, the smallest value of tensile strain for the 30Zn being 3.3%.

A possible explanation of this kink in the K/T versus T graphs could arise from the scattering of phonons from dislocation dipoles which are commonly found in these alloys, or less specifically from groups or pairs of dislocations which are closely spaced compared with the mean
separation of dislocations in the material. Steeds and Hazzledine, 1964, studying the dislocation configurations in a Cu+10at.%%Al alloy found many groups of dipole dislocations after deformation. A study of the deformation of annealed single crystals of Cu+8at.%%Al was carried out by Mitchell et al., 1967, who established that in the early stages the deformation proceeded by the formation of localised bands of slip. The dislocations in these bands were present in the form of interleaved pile-ups of parallel positive and negative dislocations of near-edge orientation; the distance between the glide planes on which these adjacent groups of dislocations of opposite sign were found varied from 50Å to several microns. Similar examples of dislocation pairs have been observed by Thomas, 1963, in polycrystalline copper-zinc alloys. These were common in specimens containing more than 24% zinc, and the density of such pairs increased thereafter with increasing zinc content.

In this work dislocation dipoles have been observed during the electron microscopy investigation of 30Zn strained to 4.4% in tension. Plate 5.1 shows an example of pairs of dislocations at 'A' lying on nearly parallel slip planes and exhibiting fringe contrast which appears on one side of all the dislocations on one plane and on the opposite side for the other plane. Such a configuration arises from the low stacking fault energy which tends to confine dislocations to their slip planes. During deformation dislocations of opposite sign will, on passing each other, form dipoles with the exception of those of mainly screw character which will mostly cross-slip and
annihilate. There is a certain maximum separation for the pairs of edge dislocations in any given material; for separations greater than this the dislocations could pass each other under the influence of the applied stress. This mechanism of dipole formation has been referred to by Seeger, 1963, as the "encounter mechanism". A second method responsible for the formation of long dislocation dipoles observed in copper in the early stages of deformation is suggested by Hirsch & Steeds, 1963, in which dipoles result from the formation of jogs. The jogs are created when dislocations on the slip plane intersect forest dislocations, and if such jogs are larger than one atomic plane spacing the dislocations can behave separately as single ended sources. In this manner a dipole consisting of two edge dislocations with the same Burgers vector but of opposite sign is formed.

Moss, 1965, has discussed the effect of dipoles on the lattice thermal conductivity and states that it depends on the relative values of the dipole spacing, \( d \), and the dominant phonon wavelength given by \( \lambda = 0.6a\Theta/T \) where \( 'a' \) is the lattice constant and \( \Theta \) the Debye temperature (Carruthers, 1961). When \( \lambda \) is small compared with \( d \) the scattering is similar to that from two dislocations acting individually and the relaxation time for dislocation phonon scattering, \( \tau \), is proportional to \( 1/q \) where \( q \) is the phonon wave-number. However, when \( \lambda \) is large compared with \( d \) the dipole is equivalent to lines of point defects which scatter with \( \tau \propto q^{-3} \) and the scattering is then less effective than that from two isolated dislocations for the same phonon wavelength. This is further discussed in section 5.5.
Consider an isolated dipole of fixed spacing \(d\) or more generally a pair of dislocations in the material whose separation is comparable with the phonon wavelength at liquid helium temperatures. As the temperature is lowered the dominant phonon wavelength increases and at a certain point the phonons become sensitive to the dipole nature of the dislocation arrangement. The scattering then begins to decrease from the value expected from a random arrangement of dislocations with large separation which would account for the scattering at higher temperatures. Thus the values of \(K/T\) begin to lie above the line extrapolated from high temperatures. It has been suggested by Moss, 1965, that a change will occur in the slope of the \(K/T\) versus \(T\) curves when \(l = 2d\). In the alloys investigated in this research the temperature at which the kink occurred was about 3°K when the dominant phonon wavelength is approximately 200\(\AA\). Thus the dipoles must have a spacing of about 100\(\AA\) to account for the effect and this is indeed consistent with the electron microscope evidence outlined above. At lowest temperatures the \(K/T\) versus \(T\) graphs would be expected to tend to a line the slope of which corresponds to phonon scattering by electrons and the residual density of randomly distributed dislocations. A sketch of the \(K/T\) versus \(T\) graph displaying this behavior is shown in Fig. 5.17. The difference between the slope of this line and that of the graph in the upper temperature region above the kink would then be an indication of the proportion of dislocations which are present in dipole formation. From the electron microscopy investigation of alpha-brass strained 4.4%, a rough estimate would place
the number of dislocations in dipole formation at approximately 20%. The fact that the effect of dipoles on the K/T against T graphs for specimens 2Al and 10Au does not become apparent until approximately 8% strain, is not unexpected. In these alloys, which have a high stacking fault energy, tangling of dislocations occurs as the specimen is deformed and the dislocations will tend to arrange themselves in such a way as to minimize their long range strain field. It is suggested that this arrangement of dislocations is beginning significantly to affect the phonon-scattering when the kink appears in the graphs at approximately 8% strain.

Gruner, 1968, has calculated the thermal resistivity due to the scattering of phonons by edge dislocation dipoles. He finds that there are deviations from the usual quadratic temperature dependence for dislocation phonon scattering which occur when $l > d$. Towards higher temperatures the resistivity due to dipoles approaches asymptotically that which is due to isolated dislocations; the temperature at which the dipole resistivity differs by less than 10% from the asymptotic value is given by $T = 370(\hbar / d)^0 K$ where $b$ is the Burgers vector. This result was obtained using the material constants of copper. If the value of $T = 30^0 K$ is taken for the temperature at which the kink occurs then this theory suggests that the dipole spacing will be of the order of $300\AA$ which is not greatly at variance with the experimental observations.

On the model described above to account for the kink in the K/T versus T graphs, it is reasonably certain that dipole scattering was present in the measurements of
Salter, 1965, and Lomer and Rosenberg, 1959. The reason why a kink has been detected in this work and in the later work of Salter (Charsley et al., 1967) when it had hitherto remained unnoticed is because the present measurements of the thermal conductivity exhibit considerably less experimental scatter on the K/T versus T graphs and the presence of the kink thus becomes evident.

In the light of the above interpretation of the kink, certain aspects of the K/T versus T graphs will now be discussed. For the Cu+2at.%Al alloy the kink is most pronounced in the specimen in which it first appears, i.e. 2Al(8%). After 24% strain the graph is almost a straight line probably because at this degree of deformation any dipole nature of the dislocation arrangement is lost as the irregular dislocation tangles observed by Swann and Nutting, 1961, are formed. From Figs. 5.6 and 5.7 it is seen that the 10Au specimen behaves in a manner very similar to the 2Al in so far as no kink appears in the K/T versus T graphs for either alloy until 8% strain. This is not surprising as the copper-gold alloy is expected to have a stacking fault energy of approximately 30ergs/cm² (Kear and Wilsdorf, 1962) which is similar to that for Cu+2at.%Al.

For 12Al, the K/T versus T graphs display a kink in all cases except for the annealed specimen. For any given strain, the dislocation density in this alloy is much lower than that in specimen 2Al (see Chapter 6) and the extended dislocations will be confined to their slip planes as a result of the low stacking fault energy. The dipole nature of the dislocation configuration will
then persist throughout the range of strains studied and the kink remains apparent in the K/T versus T curves. The results for the single crystal specimen (Fig. 5.8) show that the kink becomes more prominent with increasing deformation. This is to be expected on the "encounter mechanism" of dipole formation described above as groups of dislocations on one slip plane will pass similar groups on parallel planes under the influence of the applied stress. As the applied stress increases the groups will tend to re-align on adjacent planes to form dipoles with decreased separation. The fact that the kink becomes far more pronounced as the deformation of the single crystal is increased indicates that a high proportion of the dislocations introduced are in the form of dipoles. This is entirely consistent with the results obtained by electron-microscopy of copper-aluminium single crystals (Hirsch and Steeds, 1963) and is strong evidence that the kink is indeed due to dislocation dipoles.

Tables 5.1 to 5.3 show the values of \( (L/\ell_0 - A) \) for each of the three polycrystalline alloys studied. For specimens 2A1 and 12A1 this value is positive and indicates that there is a small negative linear term in the temperature dependence of the lattice thermal conductivity. The presence of this term was explained for the case of annealed single crystals by Salter, 1965, using Pippard's theories of ultrasonic attenuation (Pippard, 1955, 1960) to calculate the mean free path for electron-phonon scattering. Consideration of the difference between values of \( (L/\ell_0 - A) \) for single and polycrystals indicated that in the latter case grain boundary scattering of
phonons was taking place (Salter and Charsley, 1967) although this was only important for specimens having a grain size of less than 0.1mm. The mean grain size of both specimens 2A1 and 12A1 was 0.09mm and hence the effect on the lattice thermal conductivity due to the scattering of phonons by grain boundaries is not expected to be significant.

On the basis of the Pippard theory

\[-\left(\frac{L}{\rho_o} - A\right)/B \approx -0.06 \rho_o\]

where \(\rho_o\) is measured in microhm cm.

For specimens 2A1 and 12A1 the value of \(-C/B\rho_o\) is 0.2±0.02 and 0.02±0.01 respectively where \(C = (A - L/\rho_o)\). These values are identical with those found for similar alloys by Salter, 1965.

For the annealed 10Au polycrystal, \(-C/B\rho_o = -0.08\).

For this alloy all the specimens, with the exception of the specimen strained 13% have values of \(L/\rho_o - A\) which are either negative or zero within experimental error. It was thought that this was possibly associated with a change in electrical resistivity in the temperature range investigated (Ziman, 1960). Accordingly, the electrical resistance of this alloy was measured at 0.2 degree intervals over the temperature range 4.2°K to 1.8°K. However, it was found that the value of \(\rho_o\) remained constant to better than 0.04% of its value at 4.2°K and it seems very unlikely that this can account for the effect. The grain size of the 10Au specimen was 0.12mm which was slightly greater than that of the 2A1 and 12A1 specimens but the difference is not able to account for the variation in the value of \(L/\rho_o - A\) between the alloys. The reason for this variation is not known.
In this chapter the thermal conductivity results have been analysed and the results of other measurements made on the alloys have been reported.

The deductions made from the combined results are analysed and discussed in the next chapter.
<table>
<thead>
<tr>
<th>Strain %</th>
<th>$\tau$</th>
<th>$A \times 10^3$ W cm$^{-1}$ deg$^{-1}$</th>
<th>$B \times 10^3$ W cm$^{-1}$ deg$^{-3}$</th>
<th>$W_e T^2$ W cm deg$^{-3}$</th>
<th>$W_T T^2$ W cm deg$^{-3}$</th>
<th>$N_p \times 10^{-4}$ cm$^{-2}$</th>
<th>$L_c$</th>
<th>$\frac{\rho}{L} \times 10^3$ Wcm$^{-1}$ K$^{-2}$</th>
<th>$\frac{\rho}{L} - A$</th>
<th>Grain size = 0.09 mm</th>
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<td>ann.</td>
<td>-</td>
<td>11.35±0.01</td>
<td>.742±0.004</td>
<td>1350±10</td>
<td>-</td>
<td>-</td>
<td>2.080</td>
<td>11.70</td>
<td>+.35</td>
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<tr>
<td>2.03</td>
<td>7.64</td>
<td>11.11±0.04</td>
<td>.606±0.010</td>
<td>1650±30</td>
<td>300±40</td>
<td>4.3±0.6</td>
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<td>11.70</td>
<td>+.59</td>
<td></td>
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<tr>
<td>5.09</td>
<td>12.77</td>
<td>11.16±0.03</td>
<td>.473±0.009</td>
<td>2110±40</td>
<td>760±50</td>
<td>10.9±0.7</td>
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<td>11.70</td>
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<td>16.93</td>
<td>10.98±0.07</td>
<td>.409±0.021</td>
<td>2920±150</td>
<td>1570±160</td>
<td>15.7±1.6</td>
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<td>11.14±0.04</td>
<td>.317±0.010</td>
<td>3160±100</td>
<td>1810±110</td>
<td>25.8±1.6</td>
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<td>11.60</td>
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<td>16.5</td>
<td>24.06</td>
<td>11.10±0.04</td>
<td>.290±0.020</td>
<td>3450±250</td>
<td>2100±260</td>
<td>30.0±3.7</td>
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<td>11.60</td>
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<td>.287±0.030</td>
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<td>2130±370</td>
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Thermal Conductivity Results for alloy 2A1.
Table 5.2
Thermal Conductivity Results for alloy 12Al.

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<tr>
<th>Strain</th>
<th>$\tau$</th>
<th>$\sigma$</th>
<th>$c_{0}$</th>
<th>$N_{\nu} \times 10^{-1}$</th>
<th>$W_{g} T^{2}$</th>
<th>$W_{g} T^{3}$</th>
<th>$W_{g} T^{4}$</th>
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<td>ann.</td>
<td>1.77</td>
<td>16.38</td>
<td>3.02±0.02</td>
<td>.369±0.004</td>
<td>2790±45</td>
<td>80475</td>
<td>340±85</td>
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<td>4.03</td>
<td>20.80</td>
<td>2.93±0.02</td>
<td>.359±0.006</td>
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<td>850±80</td>
<td>1370±110</td>
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<td>5.70</td>
<td>24.10</td>
<td>2.96±0.01</td>
<td>.328±0.006</td>
<td>3560±50</td>
<td>4080±80</td>
<td>1960±180</td>
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<td>8.16</td>
<td>28.67</td>
<td>2.97±0.02</td>
<td>.281±0.005</td>
<td>450±50</td>
<td>4670±150</td>
<td>2150±180</td>
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<td>9.94</td>
<td>31.74</td>
<td>2.97±0.02</td>
<td>.245±0.005</td>
<td>640±80</td>
<td>4860±150</td>
<td>3710±110</td>
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<td>2.87±0.02</td>
<td>.244±0.007</td>
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<td>I</td>
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<td>.153±0.002</td>
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<td>70±45</td>
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<td>III</td>
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<td>6.73</td>
<td>2.94±0.01</td>
<td>.138±0.006</td>
<td>690±100</td>
<td>6420±80</td>
<td>190±15</td>
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Grain size = 0.09mm
Table 5.3
Thermal Conductivity Results for alloy 10Au.

<table>
<thead>
<tr>
<th>$\frac{\gamma_t}{\beta}$ $\times 10^3$</th>
<th>$C_0$ $\mu_0$ cm</th>
<th>$N_p$ $\times 10^{-7}$ cm$^{-2}$</th>
<th>$A \times 10^3$ W cm$^{-1}$ deg$^{-1}$</th>
<th>$B \times 10^2$ W cm$^{-2}$ deg$^{-1}$</th>
<th>$\tau$ Kg/mm$^2$</th>
<th>$%$</th>
<th>Grain size = 0.12mm</th>
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<td>4.386</td>
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<td>39.08</td>
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Fig. 5.1
Graphs of $K/T$ vs. $T$ for specimen 2A1 in the annealed condition and after certain amounts of strain.
Fig. 5.2
Graphs of $K/T$ vs. $T$ for specimen 2A1 for further amounts of strain.
Fig. 5.3

Graphs of $K/T$ vs. $T$ for specimen 2A1 for further amounts of strain.
Fig. 5.4

Graphs of $K/T$ vs. $T$ for specimen 12A1 in an annealed condition and after certain amounts of strain.
Fig. 5.5

Graphs of $K/T$ vs. $T$ for specimen 12A1 after further amounts of strain.
Fig. 5.6  Graphs of K/T vs. T for specimen 10Au in an annealed condition and after certain amounts of strain.
Fig. 5.7  Graphs of K/T vs. T for specimen 10Au after further amounts of strain.
Graphs of $K/T$ vs. $T$ for 12Al single crystal in various stages of deformation.

- **Annealed**
- **Stage I**
- **Stage II**
- **Stage III**
Fig. 5.9
Graph of $\rho_o$ versus $\gamma$ for specimen 2Al.
Fig. 5.10
Graph of $\rho_0$ versus $\tau$ for specimen 12A1.
Fig 5.11
Graph of $\rho_0$ versus $\tau$ for specimen 10Au.
Fig. 5.12.
Stress-strain curves for polycrystalline specimens.
Fig. 5.12

Load-elongation curve for single crystal 12A1. Vertical arrows indicate the points at which the deformation was interrupted to take thermal conductivity measurements.
Fig 5.14

The initial orientation of the tensile axis of the single crystal of Cu+12at.%Al.
Fig. 5.15
Graphs of $K/T$ vs. $T$ for a deformed single crystal of Cu+12at.\%Al measured in two different cryostats.
Fig. 5.16  The effect of different experimental conditions on the thermal conductivity results. (See text for details).
A sketch of the expected behaviour of a graph of $K_g/T$ versus $T$ when there is significant scattering of phonons by dislocation dipoles. (See text).
Plate 5.1
An array of dipole dislocations at 'A' in specimen 30Zn strained 4.4% in tension. (x 80,000)
6.1 Introduction.

In this chapter the results of the conductivity measurements on the specimens are used to obtain information about the mode of plastic deformation of the alloys. The power of this experimental technique as a means of investigating defects in materials becomes immediately obvious as the density of these defects is so high that conventional methods such as electron microscopy cannot be used to study them.

6.2 Results derived from Thermal and Electrical Conductivity Measurements.

In the previous chapter the $K/T$ versus $T$ graphs for specimens 2A1, 12A1 and 10Au after successive amounts of tensile strain, were presented. In accordance with the theories developed in chapter 5 for the case of a graph which was kinked, the value of the slope corresponding to the higher temperature region was taken as being indicative of the dislocation-phonon scattering. From consideration of the change of the slope of these graphs with strain, values for the dislocation densities, $N_p$, for specimens 2A1 and 12A1 were calculated from the relationship $N_p = \frac{W_p T^2}{\sigma}$. The values taken for $\sigma$ were not those obtained by Salter, 1965, but the modified values as
calculated in chapter 4 of this thesis. For convenience, the values of $N_p$ are included with the other numerical data in tables 5.1 to 5.3.

Figs. 6.1 and 6.2 show the variation of $\sqrt{W_pT^2}$ and $\sqrt{N_p}$ respectively with the stress $\tau$. The relationship between $N_p$ and strain is given in Fig. 6.3. In Figs. 6.2 and 6.3 the results of work on alpha-brass by Lomer and Rosenberg, 1959, are also plotted. In this case the graph reproduced here is the smooth curve fitted to their points; there is, in fact, considerable scatter for the actual experimental points. The significance of Fig. 6.4, illustrating an aspect of the electrical resistivity measurements is discussed in section 6.

6.3 Dislocation-Phonon Scattering in the Copper-Gold Alloy.

Initially, it was intended to determine the dislocation density in a deformed specimen of 10Au using transmission electron microscopy in a manner similar to that employed for the copper-aluminium and copper-zinc alloys. However, copper-gold is not an alloy that is easily electro-polished and after lengthy experimentation with different polishing techniques, this method of approach was abandoned. Instead, a value of $\sigma$ for the 10Au alloy was determined by comparing the thermal conductivity measurements and work hardening characteristics of this alloy with those of the copper-aluminium system.

Any theory of work hardening is an attempt to derive
an expression to fit the experimentally observed form of the stress-strain curves for single and polycrystalline specimens. Most workers (e.g. Taylor, 1934; Seeger, 1957; Basinski, 1959) agree that for metals and alloys the relation between stress \( \gamma \) and dislocation density \( N_p \) is of the form

\[
\gamma = \gamma_0 + \alpha G b \sqrt{N_p}
\]  

(6.1)

\( \gamma_0 \) is the so-called "friction stress," \( G \) is the shear modulus, \( b \) is the magnitude of the Burgers vector and \( \alpha \) is a numerical constant.

The stress-strain curves (Fig. 5.13) for specimens 10Au and 12Al are coincident within experimental error for strains up to 12%: the divergence of the curves at higher strains is discussed later. The value of \( \gamma_0 \) for both alloys is similar. Of the other quantities in the work hardening relation (6.1) the values of \( G \) and \( b \) are not widely different for the two materials and the constant \( \alpha \) will later be shown not to depend directly on the stacking fault energy, \( \gamma \). The macroscopic physical dimensions of both specimens are very similar and the grain sizes are of the same order of magnitude. In view of the close agreement between 10Au and 12Al outlined above it is not unreasonable to assume that, for a given amount of deformation, the dislocation density will be similar for both specimens.

In order to determine the value of \( \sigma \) for 10Au, the variation of \( W_p T^2 \) with deformation must be known. From Fig. 6.1 it is seen that the relationship between \( \sqrt{W_p T^2} \) and \( \gamma \) is identical within experimental error for
specimens 12A1 and 10Au. Thus for a given deformation both these alloys have similar values of \( N_p \) and also \( W_p T^2 \) and it is concluded that \( \sigma \) is the same for 10Au and 12A1. It should be pointed out that if, for some reason, the values of \( N_p \) are not the same for both specimens, then \( \sigma \) will indeed be different. However, this difference will have to be such as exactly to cancel out the difference in \( N_p \) in order that values of \( W_p T^2 \) are still in agreement. This is regarded as being exceedingly unlikely.

6.4 Work Hardening in Copper Alloys.

The variation in \( N_p \) with deformation and alloy type and concentration is best studied by considering the graphs of \( \sqrt{N_p} \) versus \( \tau \) (Fig. 6.2) and the stress-strain relation (Fig. 5.12). The variation of \( N_p \) with strain (Fig. 6.3) then follows from these.

The first two of the above-mentioned graphs give values of \( \tau_0 \) in equation (6.1). For alloys 12A1 and 10Au this value is approximately 12.5 kg/mm\(^2\) but for 2A1 the graph of \( \sqrt{N_p} \) versus \( \tau \) indicates a very small value of \( \tau_0 \). Comparison with the intercept on the \( \tau \) versus strain curve is difficult as the yielding behaviour is not precisely known for this specimen below 2\% strain. The value of \( \tau_0 \) for Cu+30at.\%Zn is approximately 7 kg/mm\(^2\) and a study of Lomer and Rosenberg's, 1959, results for Cu+7at.\%Zn gives a value of \( \tau_0 \approx 1 \) kg/mm\(^2\). The grain size for both the alpha-brass specimens is
expected to be similar as the same preparation and annealing procedure was used in each case. These values for alpha-brass are in very good agreement with those of Feltham and Copley, 1960. These authors studied the yielding of a series of alpha-brasses as a function of temperature and solute concentration. They found that $\tau_0$ increased with increasing solute content and decreasing temperature and suggested that this could be interpreted in terms of changes in the Peierls-Nabarro force resulting from the diminution of core widths of partial dislocations. Thus for both copper-aluminium and copper-zinc alloys, $\tau_0$ increases with increasing solute content. This is in agreement with the results of Koppenaal, 1963, who attributed changes in $\tau_0$ to a source strengthening, as opposed to a friction strengthening, mechanism. He claims good correlation between the change in $\tau_0$ with solute concentration and the change in the length of unpinned dislocations where pinning is due to forest dislocations. However, there is also the possibility that the alloys with larger solute concentrations will, in the annealed state, have a greater density of 'grown-in' forest dislocations which would increase $\tau_0$.

For most of the range of deformations studied the graphs of $\sqrt{N_p}$ versus $\tau$ are linear, indicating that the work hardening relation (6.1) is well obeyed in these alloys. However, at higher strains there appear to be significant departures from the accepted relation. Taking the linear part of the graphs, values of $\alpha$ in equation (6.1) can be calculated. For copper-aluminium
alloys it is found that $\chi$ increases with increasing solute concentration, having a value of 0.44 for 2A1 and 0.8 for 12A1. The value for 10Au is obviously the same as that for 12A1. In the case of pure polycrystalline copper, $\chi = 0.35$ (Rider and Foxon, 1960), which is consistent with the steady reduction in $\chi$ with solute content. However, a value of $\chi = 0.3$ is deduced from Lomer and Rosenberg's results for both Cu+30at.%Zn and Cu+7at.%Zn. The atomic radii of copper and zinc are very similar and it appears that the value of $\chi$ for this alloy system is independent of solute concentration. For copper-aluminium alloys, however, where there is a difference in atomic size between solute and solvent, $\chi$ appears to be dependent upon solute concentration. The conclusions drawn by Venables, 1962, are thus probably incorrect. For a range of single crystals of copper-aluminium containing between 2 and 12at.% aluminium as solute, Venables found a value of $\chi$ of 0.5 which was independent of solute concentration. However, careful examination of his work indicates that a variation in $\chi$ with solute concentration is indeed consistent with his results.

From the stress-strain curves for the polycrystalline alloys it is seen that alloy 12A1 hardens more rapidly than 2A1. Remembering that both these alloys had a similar grain size, the obvious difference between them is in the dislocation arrangement. The more rapid increase in hardening in specimen 12A1 compared with 2A1 is undoubtedly due, at least in part, to the high concentration of dipole dislocations, as discussed in chapter 5, which require a
comparatively large applied stress to force them past one another on adjacent slip planes. This is consistent with the early kink formation in the graphs of K/T versus T for this alloy.

From the data discussed above, graphs of Np versus strain can be drawn (Fig. 6.3). These curves illustrate several important features. The fact that there are two distinctly separate curves for specimens 2A1 and 12A1 indicates that copper-aluminium deforms in a manner different from copper-zinc for which points of Np versus strain lie on a universal curve irrespective of the alloy composition (Lomer and Rosenberg, 1959). For large deformations in specimen 2A1 the values of Np increase less rapidly with strain as the applied stress becomes such that abundant cross-slip occurs for this alloy. The same effect is expected to take place in 12A1, but at larger deformations, because the low stacking fault energy results in widely dissociated dislocations requiring a high value of the applied stress to bring the two partials together so that cross-slip can occur. The fact that the curves for 12A1 and 10Au coincide is a necessary consequence of the correspondence of the behaviour of these two alloys as noted earlier and indeed, in the disordered state, the dislocation arrangement for 10Au is similar to that of 12A1 (Kear, 1964). The reason for this similarity, in spite of the large difference in stacking fault energy, is that in the 10Au a dislocation moving on its slip plane destroys the short-range order, thus facilitating the passage of further dislocations along the same slip plane.
However, the much higher stacking fault energy of 10Au results in comparatively early cross-slip occurring which is the most likely explanation for the divergence of the stress-strain curves for 12Al and 10Au for strains in excess of 12%. From Fig. 6.3 it is also noted that Lomer and Rosenberg's curve of $N_p$ versus strain for alpha-brasses with a wide range of stacking fault energies $\gamma$, lies very near to that of 2Al having a relatively high $\gamma$

It thus appears that the relationship between $N_p$ and strain is not dependent directly upon the stacking fault energy of the material. Lomer and Rosenberg attributed the universallity of their curve to the fact that the zinc atoms fit in well in the copper lattice. Aluminium and gold atoms have similar radii which are greater than copper and it has been shown in this work that a roughly similar atomic percentage of each as a solute in copper yields similar relationships for $N_p$ as a function of strain.

In the light of all the above experimental evidence it is concluded that the relative sizes of solute and solvent atoms play a decisive role in the mechanism of deformation of copper alloys. It is of interest to note that Dorn et al., 1950, found that the strength of alpha-phase aluminium alloys was largely determined by the atomic diameter of the solute element but Allen et al.1951, found, in contrast, that for copper alloys the electron concentration was the predominant factor. As the stacking fault energy is very strongly dependent upon the electron concentration the results of this research are in obvious disagreement with the latter.
Further evidence for the importance of the atomic size of the solute element is afforded by the work of Thomas and Nutting, 1956, in which the deformation of polycrystalline alpha-phase Al-Cu, Al-Mg and Al-Ag alloys was studied. These authors found that only aluminium-silver alloys deformed in a manner similar to pure aluminium, this being explained by the fact that the silver atoms fitted well into the aluminium lattice whereas the magnesium and copper atoms introduced mechanical strains. It was suggested that these strains interfered with the cross-slip process. The mechanism by which this could take place has been outlined by Seeger, 1957. His argument is that, in a pure metal, dislocations piled-up against a barrier are straight but deviations from straightness will occur when solute atoms, surrounded by strain fields, are present. The straightening out of the dislocations so that cross slip can take place requires the applied stress to do additional work and hence the apparent activation energy for cross-slip increases.

The values of $W_p T^2$ for alloy 2A1 as a function of strain are of interest as they help to indicate the source of error in the original determination of $\sigma$ for this alloy, (Salter, 1965; Charsley et al., 1968). In that work, $W_p T^2$ and $N_p$ were measured for two specimens, one of which had been strained by 3% in tension, the other by 10%. In the former case a value of $\sigma$ of $1 \times 10^{-7}$ watt cm deg$^{-3}$ was calculated while for the latter $\sigma$ was 2.5 times greater. It was assumed that the second value was in error as the result of a spurious low value of $N_p$ determined by electron
microscopy. This present work suggests an alternative explanation; instead of \( N_j \) being too small, \( W_p \) was too large. The value of the latter was quoted by Salter as being 2880 watt\(^{-1}\) cm deg\(^3\) which value is never attained by the 2Al specimen investigated here even for strains of 24%. A further indication that the slope of Salter's \( K/T \) versus \( T \) graph may have been in error (giving a false value of \( W_p T^2 \)) is that \( (L/p - A) \) for his specimen was quoted as +0.05 whereas for other strains on the same specimen these values were between +0.32 and +0.36. If the value for \( W_p T^2 \) from the present research, for 10% strain, is combined with Salter's value of \( N_j \) then the value of \( \sigma \) is approximately 1.0x10\(^{-7}\) watt\(^{-1}\) cm deg\(^3\) which is in excellent agreement with the original result for the specimen strained 3%. Careful examination of Salter's \( K/T \) versus \( T \) graph shows that it exhibits a form of kink and if the slope of the higher temperature region alone had been taken then the value of \( W_p T^2 \) would be much reduced.

6.5 Discussion of the Results of the Electrical Resistivity Measurements.

Figs. 5.9 to 5.11 show the variation of residual electrical resistivity with deformation. From the graph for alloy 10Au it is seen that the value of \( \rho \) decreases with increasing \( \tau \) until a minimum value is reached after which it increases again. This initial decrease is attributed to the destruction of short-range order (S.R.O.) with deformation. The specimen was prepared by annealing
the "as received" alloy for 14 hours at 750°C after which it was furnace cooled: thus, it is fairly certain that S.R.O. was present in the annealed sample. The fact that $\rho_0$ decreases with decreasing S.R.O. is in agreement with the results of Damask, 1956(b), who found the same effect in a specimen of Cu$_3$Au after quenching from various annealing temperatures to obtain differing degrees of S.R.O. Obviously, in specimen 10Au the real decrease in $\rho_0$ due to the decrease in S.R.O. is somewhat masked by the increase due to the introduction of dislocations.

The graph of $\rho_0$ versus $T$ for specimen 12Al is very definitely non-linear. The reason for this is undoubtedly due to the scattering of electrons by stacking faults in this alloy which are not detected by lattice thermal conductivity measurements at liquid helium temperatures and hence the ratio of the change in $\rho_0$ with deformation to $N_p$ can be used as a measure of the variation of stacking fault widths with deformation and solute concentration. This ratio is plotted as a function of $T$ for the three alloys in Fig. 6.4. For specimen 2Al the ratio is almost constant and using the value for the electrical resistivity of a unit dislocation density in copper at 4.2°K (Rider and Foxon, 1967), the effective dislocation density as determined by electrical and thermal measurements can be compared. For 2Al the dislocation density calculated from electrical measurements is approximately 10 times greater than that determined by thermal measurements. The constant value of the ratio $\Delta \rho / N_p$ in Fig. 6.4 shows that the stacking fault width in this alloy does not vary
with deformation. For alloy 12A1 the stacking fault energy $\gamma$ is smaller than that for 2A1 by a factor of 10. The value $\Delta \rho_0/N_\rho$ is correspondingly larger for 12A1 by a factor of approximately 10 but the ratio increases with increasing deformation. At large deformations, cross-slip must be taking place but those partials which are not being brought together under the influence of the applied stress are obviously forced further apart as the dislocation density increases.

For the 10Au alloy the value of $\Delta \rho_0/N_\rho$, for deformations larger than that giving the minimum in $\rho_0$, are of especial interest. $\gamma$ for this alloy is similar to that for 2A1 and hence both alloys would be expected to have similar stacking fault widths and hence similar values of $\Delta \rho_0/N_\rho$. However, for small deformations, $\Delta \rho_0/N_\rho$ for 10Au is some 6 times greater than that for 2A1 but the ratio decreases rapidly with increasing deformation. It is probable that the S.R.O. in the 10Au alloy gives rise to the occurrence of super-lattice dislocations consisting of a pair of extended dislocations separated by an anti-phase boundary. The width of the stacking faults is still dependent upon $\gamma$ and hence the initially large value of $\Delta \rho_0/N_\rho$ must be ascribed to anti-phase boundaries. These are removed as the S.R.O. is destroyed with increasing deformation and the value of $\Delta \rho_0/N_\rho$ is expected to level off at a similar value to that for 2A1.
Graphs of $\sqrt{W_p T^2}$ versus $T$ for specimens 2A1, 12A1 & 10Au.

---

**Fig. 6.1**

Graphs of $\sqrt{W_p T^2}$ versus $T$ for specimens 2A1, 12A1 & 10Au.
Fig. 6.2
Graphs of $\sqrt{N_p}$ versus $\Upsilon$ for specimens 2A1, 12A1 & 10Au.
The dashed line indicates Lomer & Rosenberg's results for Cu+30 at.% Zn.
Fig. 6.3

Graphs of $N_p$ versus Strain for specimens 2A1, 12A1, 10Au.

The dashed line represents Lomer & Rosenberg's universal curve for alpha-brass.
Fig. 6.4

Graphs of $\Delta \rho / N_0$ for the specimens.

$10^9 \Delta \rho / N_0$

ohm cm$^3$

$T$ kg/mm$^2$
Conclusions

1. The dislocation-phonon scattering, defined as 
\[ \sigma = \frac{W_p T^2}{N_p} \], has been measured for Cu+30at.%Zn and 
found to be \[ 0.4 \times 10^7 \text{ W cm deg}^3 \] which is approximately 
3 times smaller than \( \sigma \) for Cu+2at.%Al and 5 times 
smaller than \( \sigma \) for Cu+12at.%Al.

2. Dislocation-phonon scattering has been shown to be 
independent of the type of dislocation arrangement 
but dependent upon the relative masses and possibly 
sizes of the solute and solvent atoms.

3. The lattice thermal conductivity in the temperature 
range 1.6\(^\circ\) to 4.2\(^\circ\)K has been shown to exhibit depart-
tures from the usual \( T^2 \) dependence which have been 
attributed to phonon scattering by dislocation 
dipoles.

A value for the dislocation-phonon scattering in 
Cu+10at.%Au has been deduced by comparison with 
dislocation-phonon scattering in other copper alloys 
and without recourse to a direct measurement of \( N_p \). 
The value of \( \sigma \) for this specimen is \[ 2.8 \times 10^7 \text{ W cm deg}^3 \].

The work hardening of copper alloys has been shown
to depend strongly on the sizes of the solute atoms relative to those of copper and not on the electron-atom ratio.

Measurements of the residual electrical resistivity of the specimens of Cu+2at.%Al, Cu+12at.%Al and Cu+10at.%Au have provided information about the relative widths of stacking faults in these alloys as a function of deformation. In the case of copper-gold the destruction of short-range order is the explanation of the observed decrease in electrical resistivity with increasing deformation.
Suggestions for Further Work.

1. It would be of interest to measure the dislocation-phonon scattering in an alloy of copper-gold, more dilute than that studied in this research, so that the variation of $\sigma$ with solute content in this alloy could be established.

2. It would obviously be highly desirable to confirm the value of $\sigma$ for $10Au$ by direct measurement of the dislocation density. This would necessitate considerable research into a suitable electro-polishing technique.

3. A very much more detailed study of solute atmosphere formation around dislocations would be worthwhile and the theory proposed by Klemens might then be revised so that dislocation-phonon scattering as a function of solute concentration and type could be predicted with certainty.

4. In addition to a theoretical investigation into solute atmosphere formation around dislocations, an experimental study would be valuable. A cryostat would need to be constructed so that specimens could be deformed at liquid helium temperatures and the dislocation-phonon scattering could then be determined when no atmospheres are present.
APPENDIX

A paper has very recently been published by Kusunoki and Suzuki* reporting measurements of the lattice thermal conductivity at liquid helium temperatures on an alloy of Cu+15at.%Al deformed by various amounts. Their results are of interest as the K/T versus T graphs for all their deformed specimens display a curvature at approximately 3°K similar to that reported by Charsley et al., 1967, and also in this thesis. The curvature in their graphs is interpreted by assuming resonance scattering due to vibrating edge dislocations in their Cottrell atmospheres. The conductivity calculated on a theoretical model is compared with the experimental results but agreement is poor for larger deformations.

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An Experimental Investigation of Dislocation-Phonon Scattering in Some Copper Alloys

By
P. Charsley, J. A. M. Salter, and A. D. W. Leaver

The thermal conductivities of polycrystalline copper alloys, containing 2, 8, and 12 at% aluminium and 30 at% zinc, have been measured between 1.5 and 4.2 °K in the annealed state and after tensile deformations up to 12%. Measurements of the dislocation densities in the alloys were made by transmission electron microscopy. It has been found that the scattering power of phonons by unit dislocation density increases linearly with the atomic concentration of aluminium. It would appear that the effect of zinc additions is negligible and that changes in the arrangements of the dislocations does not affect the effective scattering power.

1. Introduction

Work in recent years has shown that measurements of the lattice thermal conductivity of solids, at sufficiently low temperatures, are sensitive to the presence of dislocations. A great deal of this work (see Moss [1]) has been confined to insulators—mainly alkali halides. Dislocation densities have been determined by etch-pit techniques and correlated with the thermal conductivity measurements. As a result of this work the theoretical estimates [2, 3, 4] of the scattering of phonons by dislocations have been shown to be too small by factors of between 20 and 500 in these materials.

In the case of metals, Lomer and Rosenberg [5] have shown that lattice thermal conductivity measurements can be valuable in giving information on dislocation density changes resulting from the plastic deformation of alloys. The advantages of this technique are that it is non-destructive, that it can be used up to high dislocation densities and, in addition, that the effects of dislocations and point defects can be separated. To be of real value, however, it is essential to know the scattering power of individual dislocations and the effect, if any, of the concentration and type of solute.

A direct comparison between dislocation densities as determined by transmission electron microscopy and by lattice thermal conductivity measurements was made by Lomer and Rosenberg [5] in a deformed Cu–30 at% Zn alloy. In this work only a rough comparison was made; there was no attempt at a de-
tailed study. Work on Cu-32at% Zn and Cu-0.4 at% As alloys, heavily deformed in torsion, has been carried out by Kemp et al. [6]. In this work the dislocation density was estimated from the stored energy measurements of Clarebrough et al. [7, 8, 9] on similar materials; the results are dependent, therefore, upon a theoretical estimate of the stored energy for a single dislocation. In addition there are complications of interpretation which, it is supposed, arise from energy release as a result of dislocation rearrangement. The results of these studies were that the theoretical estimates of dislocation-phonon scattering were too small by a factor of about 6.

In the present work we have attempted to obtain a more reliable correlation between lattice thermal conductivity and dislocation density than has hitherto been attained in alloys. Initially this study was concerned with a range of α-aluminium bronzes but the results indicated the need for further measurements on α-brass. Dislocation densities and arrangements have been determined by transmission electron microscopy; this technique is the most direct and is the most suitable one available for the measurement of dislocation densities of the magnitudes encountered in these studies. The results show that both the solute type and concentration can significantly affect the scattering of phonons by dislocations.

2. Experimental Techniques

2.1 Preparation and analysis of alloys

Both the copper-aluminium alloys and the α-brass were prepared by International Research and Development Co. Ltd.; the preparation of the copper-aluminium alloys has been described previously [10]. The α-brass was produced by induction melting under an argon atmosphere in a drop cast furnace. The alloys were supplied in rods 3 mm in diameter produced from the original ingots by swaging and drawing. Chemical analyses were carried out by I.R.D. Co. Ltd. on lengths cut from the two ends of each rod. In some cases this was adjacent to a specimen, but in most cases only the mean composition of the rod from which a specimen was cut is known. In the latter cases the value given for the composition in Table 1 is followed by an 'm'.

2.2 Thermal conductivity specimens

Approximately 10 cm lengths were cut from the rods as supplied, annealed at 750 °C for about 15 h and furnace cooled. The copper-aluminium specimens were annealed in graphite tubes in vacuo. With α-brass, in order to avoid the loss of zinc, the specimens were wrapped in brass foil of a similar chemical composition and annealed in evacuated, sealed silica tubes. After annealing, copper thermometer tags were brazed onto the specimens about 6 cm apart. The resulting polycrystalline specimens had a grain size of the order of 0.1 mm.

The cryostat used and the methods of measuring the thermal conductivity and residual resistivity of the specimens have been previously described [10]. The deformation of the specimens was in tension at room temperature at a constant strain rate of about 2 × 10⁻³ s⁻¹.

2.3 Preparation of specimens for electron microscopy

When thermal conductivity and electrical resistivity measurements had been completed on a deformed specimen it was cut into 2 cm lengths by spark
machining. Care was taken to avoid including regions near the specimen tags or the ends of the specimen. These lengths were chemically or electrolytically polished to a diameter of 2.3 mm, and then discs of 0.5 mm thickness were cut from the lengths by spark machining. The discs were thinned for electron microscopy using a combination of jet machining and a P.T.F.E. holder [11]. After thinning the discs were immediately mounted in a Valdré holder and viewed at 100 kV in a Siemens Elmiskop I electron microscope.

2.4 Measurement of dislocation densities

Three methods were used to obtain dislocation densities from the electron micrographs:

(i) The counting of dislocation intersections with planes perpendicular to the foil surface, as described by Ham [12].

(ii) The counting of dislocation intersections with the foil surfaces, as described by Ham and Sharpe [13].

(iii) The direct measurement of the projected line length of the dislocations. This method was only used for the regular arrays seen in the 12 at% copper-aluminium alloy and the α-brass.

Methods (i) and (iii) require a knowledge of the foil thickness. This was obtained either from one slip trace and the orientation of the foil normal as determined by electron diffraction, or from two or more slip traces of different widths and/or directions. In the latter case the tables prepared by Crocker and Bevis [14] were used.

In cases where methods (i) and (ii) could be applied to the same micrograph, the values of dislocation density obtained usually agreed to within 10%. The dislocation densities quoted in this paper are measured in line length per unit volume. To obtain these by methods (i) and (ii) the numbers obtained must be multiplied by 2 as shown by Schoeck for random dislocation arrangements, [15]. In addition allowance was made in all three methods for the invisibility factor [16].

3. Thermal Conductivity Results

3.1 Analysis of the thermal conductivity

In the temperature range 1.5 to 4.2 °K the total thermal conductivity of all the specimens is well represented by the relation

\[ K = A T + B T^2. \]  

The separation of the electronic and lattice contributions has been described previously [10, 17]. Briefly, the validity of the Wiedemann-Franz law is assumed and the results are analysed by a plot of \( K/T \) against \( T \). Any departures from a horizontal line passing through \( L/\rho_0 \) on this plot are due to lattice thermal conductivity, where \( L \) is the Lorenz number and \( \rho_0 \) is the residual electrical resistivity. The value of \( L/\rho_0 \) was not used as an experimental point in the determination of \( B \), although this practice was adopted by Lomer and Rosenberg [5]. For both annealed and deformed specimens the lattice thermal conductivity is well represented by the equation

\[ K_g = C T + B T^2, \]  

where the quadratic term is dominant and the linear term, which has a negative coefficient, has been explained in terms of a combination of grain boundary and
electron scattering of phonons [17]. Before deformation the lattice conductivity is limited mainly by electron–phonon scattering. The relaxation time for dislocation–phonon scattering is expected to be inversely proportional to the phonon wave number as, to a good approximation, it is for electron–phonon scattering. Therefore, the expected effect of introducing dislocations into a given specimen is to reduce the value of $B$ in equations (1) and (2). In fact, both $C$ and $B$ were observed to have changed after deformation. For the purpose of this investigation we have neglected changes in $C$, because they were small, and have followed the earlier convention (see for example [18, 19]) of defining a lattice thermal resistivity $W_g$ by

$$W_g T^2 = B^{-1}.$$  \[(3)\]

Then differences between $W_g T^2$ for an annealed and strained specimen give values of $W_D T^2$ where $W_D$ is the increase in thermal resistivity due to the dislocations introduced by the deformation. This procedure may be questioned since Salter and Charsley have shown that the grain size can affect the value of $B$ [17]. However, this effect will not be significant unless the grain size is rather less than 0.1 mm.

### 3.2 Results

Figs. 1 and 2 show the results for the copper–aluminium alloys plotted as graphs of $K/T$ against $T$. Fig. 3 shows the results for the $\alpha$-brass plotted in a similar fashion. The graphs for the annealed specimens 8 and 12 can be seen in [10]. Straight lines were fitted to the points by the method of least squares, and values of $A$ and $B$ of equation (1) evaluated with their mean square deviations. Table 1 gives values of $A$, $(L/q_0)$, $(W_g T^2 = B^{-1})$, $W_D T^2$, and the results of the chemical analyses. In the table the copper–aluminium specimens are referred to by their nominal compositions in at% of aluminium and the $\alpha$-brass as $\alpha$–B, followed, where relevant, by a figure in brackets giving the tensile strain. The strained specimens were not always originally the annealed

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition</th>
<th>$\frac{L}{q_0}$ (W cm$^{-1}$ deg$^{-2}$ × 10$^9$)</th>
<th>$A$ (W cm$^{-1}$ deg$^{-2}$ × 10$^9$)</th>
<th>$W_g T^2$ (W$^{-1}$ cm deg$^3$)</th>
<th>$W_D T^2$ (W$^{-1}$ cm deg$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.09</td>
<td>11.53</td>
<td>$11.21 \pm 0.02$</td>
<td>$1310 \pm 20$</td>
<td>$-$</td>
</tr>
<tr>
<td>2(2.9%)</td>
<td>2.09</td>
<td>11.53</td>
<td>$11.17 \pm 0.04$</td>
<td>$1800 \pm 90$</td>
<td>$400 \pm 110$</td>
</tr>
<tr>
<td>2</td>
<td>1.93m</td>
<td>11.64</td>
<td>-</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>2(10%)</td>
<td>1.93m</td>
<td>11.34</td>
<td>$11.29 \pm 0.03$</td>
<td>$4190 \pm 260$</td>
<td>$2880 \pm 280$</td>
</tr>
<tr>
<td>8</td>
<td>9.12</td>
<td>3.69</td>
<td>$3.66 \pm 0.02$</td>
<td>$2330 \pm 50$</td>
<td>$-$</td>
</tr>
<tr>
<td>8(6%)</td>
<td>9.12</td>
<td>3.65</td>
<td>$3.55 \pm 0.02$</td>
<td>$3720 \pm 190$</td>
<td>$1390 \pm 240$</td>
</tr>
<tr>
<td>12</td>
<td>11.25</td>
<td>3.39</td>
<td>$3.33 \pm 0.02$</td>
<td>$2480 \pm 60$</td>
<td>$-$</td>
</tr>
<tr>
<td>12(6.2%)</td>
<td>11.25</td>
<td>3.39</td>
<td>$3.21 \pm 0.02$</td>
<td>$3450 \pm 150$</td>
<td>$970 \pm 210$</td>
</tr>
<tr>
<td>12</td>
<td>11.60m</td>
<td>3.35</td>
<td>-</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>12(12.8%)</td>
<td>11.60m</td>
<td>3.29</td>
<td>$3.07 \pm 0.04$</td>
<td>$4550 \pm 320$</td>
<td>$2070 \pm 380$</td>
</tr>
<tr>
<td>$\alpha$B *)</td>
<td>27.2m</td>
<td>7.21</td>
<td>$6.93 \pm 0.04$</td>
<td>$1660 \pm 30$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\alpha$B(4.4%)</td>
<td>27.2m</td>
<td>7.30</td>
<td>$7.00 \pm 0.02$</td>
<td>$1930 \pm 20$</td>
<td>$270 \pm 50$</td>
</tr>
</tbody>
</table>

*) $\alpha$-B = $\alpha$-brass.
Dislocation-Phonon Scattering in Some Copper Alloys

Fig. 1. Graphs of $K/T$ against $T$ for annealed and deformed 2 at.% copper-aluminium specimens.

Fig. 2. Graphs of $K/T$ against $T$ for deformed 8 and 12 at.% copper-aluminium specimens.

Fig. 3. Graphs of $K/T$ against $T$ for the annealed and deformed α-brass specimen.

Fig. 4. This figure shows values of $V_{s\alpha}^2T^4$ for the 2 and 12 at.% copper-aluminium alloy plotted against flow stress. The full circles refer to the 2 at.% alloy. For each alloy, a straight line may be drawn through the origin to fit the points.
specimens for which thermal conductivity data are given. Where this was not the case the value of \( L/\theta_0 \) obtained from measurement prior to deformation is given in Table 1 immediately above the data for the relevant strained specimen.

For both the annealed and deformed specimens no significant systematic deviations of the experimental points from the lines fitted by least squares on the \( K/T \) against \( T \) plots were observed.

Fig. 4 shows the results of the deformation of the 2 and 12 at% copper-aluminium alloys plotted as graphs of \( \sqrt{W_D T^2} \) against flow stress. For each alloy the points lie close to a straight line passing through the origin.

### 4. Dislocation Densities and Combined Results

For the 2 and 12 at% copper-aluminium alloys a few foils were prepared from annealed specimens. The dislocation densities found were less than \( 2 \times 10^8/cm^2 \) on average. Table 2 gives the dislocation densities of the deformed specimens:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( \tau ) (kg mm(^{-2}))</th>
<th>( m )</th>
<th>( g )</th>
<th>( N_D ) (cm(^{-2})X10(^{-9}))</th>
<th>( \sigma ) (W(^{-1})cm(^3) deg(^3)X10(^7))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(2.9%)</td>
<td>7.3</td>
<td>43</td>
<td>23</td>
<td>4.7 ( \pm ) 0.4</td>
<td>1.0 ( \pm ) 0.3</td>
</tr>
<tr>
<td>2(10%)</td>
<td>17.3</td>
<td>31</td>
<td>17</td>
<td>11.3 ( \pm ) 1.0</td>
<td>2.5 ( \pm ) 0.5</td>
</tr>
<tr>
<td>8(8%)</td>
<td>20.9</td>
<td>43</td>
<td>24</td>
<td>8.4 ( \pm ) 1.0</td>
<td>1.7 ( \pm ) 0.5</td>
</tr>
<tr>
<td>12(3.4%)</td>
<td>7.3</td>
<td>18</td>
<td>10</td>
<td>1.6 ( \pm ) 0.4</td>
<td>—</td>
</tr>
<tr>
<td>12(6.2%)</td>
<td>18.3</td>
<td>20</td>
<td>11</td>
<td>4.7 ( \pm ) 0.7</td>
<td>2.1 ( \pm ) 0.8</td>
</tr>
<tr>
<td>12(12.8%)</td>
<td>27.5</td>
<td>11</td>
<td>7</td>
<td>9.8 ( \pm ) 1.1</td>
<td>2.1 ( \pm ) 0.7</td>
</tr>
<tr>
<td>( \alpha-B(4.4%) )</td>
<td>12.2</td>
<td>31</td>
<td>14</td>
<td>6.6 ( \pm ) 1.1</td>
<td>0.42 ( \pm ) 0.18</td>
</tr>
</tbody>
</table>

*) \( \alpha-B \) = \( \alpha \)-brass.

In this table \( m \) is the total number of micrographs analysed in each case, and \( g \) is the number of separate grains for which dislocation densities were obtained.

The values of \( N_D \) are the mean of the \( g \)-values obtained for the dislocation densities of the separate grains for each specimen. The quoted errors in \( N_D \) are the standard deviation of the mean of the \( g \)-values.

In Fig. 5 points for \( \sqrt{N_D} \) against flow stress \( \tau \) for the 2 and 12 at% copper-aluminium alloys are shown. In Table 2 values of \( \sigma \) are given defined by the

![Fig. 5. This figure shows values of \( \sqrt{N_D} \) for the 2 and 12 at% copper-aluminium alloys plotted against the flow stress. The full circles refer to the 2 at% alloy. While an acceptable straight line can be drawn through the points for the 12 at% alloy, this is not the case for the 2 at% alloy.](image)
5. Discussion

Before considering the interpretation of the results presented above it is necessary to consider the reliability of the individual values of $\sigma$. Firstly, it should be noted that for copper–aluminium $\sigma$ is independent of $N_D$ for the 12 at% alloy but apparently not for the 2 at% alloy. For small or moderate strains it would not be expected that $\sigma$ was dependent upon $N_D$ and certain aspects of the results indicate that this is correct.

There is a considerable body of evidence (see for example [20]) that the dislocation density in deformed polycrystalline metals and alloys increases as the square of the flow stress. If this is accepted as applying to the cases of the 2 at% and 12 at% copper–aluminium alloys then the linearity of the curves in Fig. 4 shows that $\sigma$ is independent of $N_D$ for both alloys. For this reason the values of $N_D$ for the 2 at% alloy must be viewed with suspicion.

In a plot of $\sqrt{N_D}$ versus $\tau$ an extrapolation of the line through the points must necessarily intersect the $N_D = 0$ axis at a zero or positive stress. As can be seen in Fig. 5 the results obtained for $N_D$ are consistent with this requirement in the case of the 12 at% alloy but not in the case of the 2 at% alloy. The only satisfactory explanation is that the value of $N_D$ for specimen 2 (10%) is too low by an appreciable factor.

This is not unexpected in view of the suggestion of Foxon and Rider [21] that, where dislocation tangling occurs, there is an apparent loss of dislocations, above a certain maximum strain, which increases with strain. This ‘loss’ probably arises from a combination of a true loss together with an overlapping of the dislocation images in those parts of the specimen where the density is high. We will, therefore, discard the results obtained for specimen 2 (10%).

The possibility of a loss of dislocations from the thin foils of the other specimens cannot be ignored but we consider it to be small. In general it is to be expected that a true loss of dislocations from a dilute alloy specimen will be smaller than from the corresponding pure metal due to the friction stress experienced by the dislocations. In the case of pure aluminium the results of Foxon and Rider [21] suggest that there is virtually no loss of dislocations for small deformations. Furthermore, that observations of Valdré and Hirsch [22] on stainless steel indicate that in the particular case an upper limit of 30% must be placed on the dislocation loss. We would expect that, since both stainless steel and Cu–12 at% aluminium have very low stacking fault energies, the Valdré and Hirsch estimate is applicable to our 12 at% alloy; a similar argument can be used for specimen $\alpha$–B. For these various reasons we consider that dislocation loss, except for specimen 2 (10%), can be ignored for the purposes of further discussion.

The remaining results for the 2, 8, and 12 at% copper–aluminium alloys indicate a linear increase of $\sigma$ with solute content, as can be seen in Fig. 6. In view of these results the values of $\sigma$ suggested by Lomer and Rosenberg [5] and by Kemp et al. [6] for $\alpha$–brass appeared surprising; for this reason an indepen-
dent set of measurements was made by the present authors. As can be seen in Table 2, the results obtained were in very good agreement with the earlier work. However, since no measurements have been made on more dilute Cu–Zn alloys, there remains some uncertainty in any attempt to build a consistent empirical picture embracing both sets of alloys. The following two extreme possibilities are suggested:

(i) If the best straight line is drawn through the values of $\sigma$ for the Cu–Al alloys a value of $8 \times 10^{-8} \text{ W}^{-1} \text{ cm}^2 \text{ oK}^3$ for pure copper is deduced. This implies that the value of $\sigma$ for the Cu–Zn alloys decreases with increasing zinc content. This possibility is indicated by the solid lines in Fig. 6.

(ii) If the maximum estimated errors for the individual values of $\sigma$ for the Cu–Al alloys are considered a minimum value of $\sigma = 3 \times 10^{-8} \text{ W}^{-1} \text{ cm}^2 \text{ oK}^3$ for pure copper is deduced. This leads to the conclusion that $\sigma$ is virtually independent of zinc content in the $\alpha$-brasses. This possibility is indicated by the dotted lines in Fig. 6.

The second possibility seems to be the most likely in view of some of the results of Lomer and Rosenberg [5]. These authors found that the dislocation densities, as deduced from the thermal conductivity values of deformed, polycrystalline Cu–Zn alloys containing 7, 15, and 30 at% Zn fell on a universal curve when plotted against strain, for small strains. The simplest explanation of these results is to suppose that the dislocation density varies with strain in approximately the same way with all the alloys and that $\sigma$ is independent of zinc content. Without further work it is not possible to be certain about this point; nevertheless it is clear that $\sigma$ does not depend strongly on zinc content.

Whichever of the two possibilities is accepted it seems unlikely that the dislocation arrangements significantly affect the values of $\sigma$. For both Cu–Al and Cu–Zn alloys the stacking fault energy decreases with increasing solute content; correspondingly the dislocation arrangements change from the tangled type seen in pure copper to the more regular arrays seen in the low stacking fault alloys (see for example [23, 24]). Cu–12 at% Al and Cu–30 at% Zn are very similar in the way they deform and in the dislocation arrangements in the deformed alloys. The values of $\sigma$, however, vary in a quite different manner with
increasing solute in the two alloy systems. For this reason the discrepancy by about one magnitude between the experimental and theoretical values of $\sigma$ for pure copper is unlikely to arise from coherent scattering from groups of dislocations.

The fact that the solute type and concentration can have a significant effect upon $\sigma$ is an unexpected result. An obvious difference between aluminium as opposed to zinc dissolved in copper is that, in the former case, there is a large mass difference between solute and solvent; this difference is very small in $\alpha$-brass. In this connection recent measurements of $\sigma$ for a Cu-6.8 at% Ga alloy, due to Zeyfang at Stuttgart [25], are of interest. The mass difference between Cu and Ga atoms is small and the value of $\sigma$ is very close to that obtained in $\alpha$-brass. However, mass difference scattering would be expected to be negligible at liquid helium temperatures (see for example [26]); this view is strengthened by the quadratic temperature dependence of $K_g$ for both annealed and deformed alloys. It is also worth noting that, in the case of annealed alloys, the lattice thermal conductivity values at liquid helium temperatures appear not to be correlated with the mass difference between solute and solvent atoms. In these cases there would appear to be a good correlation between the lattice thermal conductivity and the electron mean free path (see Lindenfeld and Pennebaker [27] and Charsley and Salter [10]). Since the frequency dependence is the same for both electron-phonon and dislocation-phonon scattering it would seem reasonable to conclude that mass difference scattering is not playing a part in the latter case. It follows that if the mass difference between solute and solvent is important in dislocation-phonon scattering then it must arise as a result of an interaction between the dislocations and the solute atoms.

An effect which may be of importance could arise from a segregation of solute atoms to the neighbourhood of the dislocations. This could give rise to an additional scattering of phonons by cylindrical regions of markedly different density from the matrix. Such regions could have diameters of the order of the phonon wavelengths at liquid helium temperatures. A quite different possibility, however, is that the anharmonic terms in the interatomic forces are significantly affected by the addition of solute atoms; in this way the strain field scattering of phonons by the dislocations could be affected. This mechanism is not dependent on the mass of the solute atoms. Much more experimental work, on carefully chosen alloy systems, is required to distinguish between the various possibilities.

In conclusion, it is worth remarking that the use of lattice thermal conductivity measurements to deduce comparative dislocation density changes in different alloys can be misleading. Thus the values given by Tainsh et al. [28] for dislocation densities in deformed Cu-Si alloys may well be in error. If the mass difference between the solute and solvent atoms is the important factor then this will certainly be the case. However, further work should make the low temperature thermal conductivity technique very valuable in the future for the study of deformed alloys.

6. Conclusions

1. The scattering of phonons by dislocations has been found to increase linearly with solute concentration in $\alpha$-aluminium bronzes. A change in the atomic concentration of aluminium from 2% to 12% causes a change in the
scattering per unit dislocation density from \((1.0 \pm 0.3) \times 10^{-7}\) to \((2.1 \pm 0.5) \times 10^{-7}\) \(\text{W}^{-1} \text{cm}^{-3} \text{K}^{-4}\).

2. The change in the scattering power of dislocations with zinc concentration in \(\alpha\)-brass is probably negligible.

3. The scattering power per unit dislocation density in pure copper lies between \(4 \times 10^{-8}\) and \(8 \times 10^{-8}\) \(\text{W}^{-1} \text{cm}^{-3} \text{K}^{-4}\).

4. The scattering of phonons by dislocations in these alloys is proportional to the reciprocal of the phonon frequency.

5. There appears to be no change in the dislocation–phonon scattering arising from differences in dislocations arrangement in the as-deformed alloys.

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References


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Measurement of Dislocation Phonon Scattering in Alloys

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Measurement of thermal conductivity between 1.5 and 4.2°K combined with the determination of dislocation density by transmission electron microscopy yielded values for dislocation phonon scattering in three copper aluminium alloys, and one copper zinc alloy. The results indicated that dislocation phonon scattering in copper alloys depends on both the type and amount of solute, and that the effects of dislocation arrangement are small. More careful experiments to detect any effect due to dislocation arrangements have been carried out. An experiment to measure the thermal conductivities of a deformed 12 at.% copper aluminium alloy while held under tension near its flow stress, and while released, indicated no difference between the two cases. In an experiment on a deformed single crystal of a 12 at.% copper aluminium alloy, a small effect ascribed to an anisotropy in the scattering of phonons by screw dislocations has been found. In both these experiments the \( \lambda / T \) against \( T \) graphs showed a kink at about 3°K. This may be explained by considering the scattering of phonons from edge dislocation dipoles.

Key Words: anisotropy, copper alloys, dislocations, lattice conductivity, phonon scattering.

1. Introduction

At liquid helium temperatures the thermal conductivity of annealed copper alloys with residual resistivities less than about 0.1 \( \mu \Omega \)m can be well represented by

\[
\lambda = AT + BT^2
\]

where the quadratic term is entirely due to lattice conduction; its magnitude is limited by electron-phonon scattering which has the same dependence on phonon wave number \( q \) as the expected scattering due to individual dislocations. So the effect of plastic deformation is to reduce the value of \( B \) in eq (1). Changes in \( B^{-1} \) give values of \( W_{\ell}T^2 \) which is a measure of the extra thermal resistivity due to the dislocations introduced.

From measurements of \( W_{\ell}T^2 \) combined with the determination of dislocation densities \( N_d \) using transmission electron microscopy we have obtained values for

\[
\sigma = \frac{W_{\ell}T^2}{N_d}
\]

for some \( \alpha \) phase copper aluminium alloys. The results, which have been submitted for publication elsewhere (1), were that \( \sigma \) varied from \( 1.0 \pm 0.3 \times 10^{-13} \text{ W}^{-1} \text{ m}^3 \text{ deg}^3 \) for a 2 at.% alloy to \( 2.1 \pm 0.7 \times 10^{-13} \text{ W}^{-1} \text{ m}^3 \text{ deg}^3 \) for a 12 at.% alloy. We thought that this variation was due to the marked changes in dislocation structures with aluminium content which is observed in these alloys (2). The 12 at.% alloy has a low stacking fault energy and the dislocation structure is quite regular with the frequent occurrence of rows of dislocations of the same sign. In the 2 at.% alloy the dislocations are very tangled. It seemed possible that the higher value of \( \sigma \) in the 12 at.% alloy was due to the effect of dislocation pile ups. This was suggested previously by Klemens (3) as a possible explanation of the discrepancies which exist between theoretical and experimental values of \( \sigma \). However, 70-30 \( \alpha \) brass has a dislocation structure in the deformed state very similar to that found in our 12 at.% copper aluminium alloy, and the value of \( \sigma \) obtained by Lomer and Rosenberg was about \( 0.5 \times 10^{-13} \text{ W}^{-1} \text{ m}^3 \text{ deg}^3 \), (4). Believing this might be in error we made a similar measurement and

\[\text{Figures in brackets indicate the literature references at the end of this paper.}\]
obtained a value for α of 0.4 ± 0.2 x 10^{-11} W^{-1} m^{-3} deg^{-3}. We therefore suggested that the values of α obtained in copper alloys depend upon both the type and amount of solute present, and that they appear to be substantially independent of dislocation arrangement.

Because this conclusion seems at variance with the strain field model for dislocation-phonon scattering we have carried out some further experiments to investigate the effect of pile ups and dislocation arrangements on the lattice thermal conductivity of a 12 at.% copper-aluminium alloy.

2. The Specimens

The alloy of nominal composition 12 at.% was prepared and analysed by the International Research and Development Co. as described previously (5). The mean composition of the ingot from which all the specimens were made was 11.3 at.% aluminium in copper.

Single crystals were grown in graphite moulds using the Bridgman technique. The polycrystalline specimens used in the under stress experiment described below were turned out from as received material and annealed for about 15 hours at 750°C before use.

3. The Experiment to Detect Pile-Ups

3.1 The Idea

The strain field of a dislocation pile-up depends upon the spacing of the dislocations in it. This can be altered by applying an external stress. The phonons are scattered by the strain field, so that if pile-ups in any number are present one might expect to find a difference between the lattice thermal conductivities of a deformed specimen while in a relaxed state and while held under tension. Since the effect of a stress is to decrease the average spacing between dislocations in a pile-up it is to be expected that a specimen under stress will have a lower conductivity than a relaxed specimen.

To perform such an experiment the specimen must be constrained by a jig, and at the same time the thermal conductivity measured.

3.2 The Techniques Used in the Under-Stress Experiments

It was decided to use a jig of very high thermal conductance and to supply the heat to the specimen from the centre. Thus the two ends of the specimen are maintained at equal temperatures. The jig is shown in figure 1. Stainless steel threaded end pieces E were brazed on to the specimen S, these served both to take the nuts N, and to enable the specimen to be fitted into a tensile machine. The thermal contact from the ends of the specimen to the copper jig J were made by soldering copper wires W between them and the jig corners. The connection of the jig to the heat sink was made by a 3 mm diameter copper wire W from the centre of the cross piece B. The specimen, with a heater H and thermometers T1 and T2 attached as shown, was fitted in the jig and then mounted in a tensile machine. After a suitable amount of plastic deformation, and with the stress still applied, the nuts N were tightened until the stress registered on the tensile machine had dropped to zero.

The specimen is then held in the jig under tension near the flow stress, and when mounted in the cryostat and cooled to 4.2K remains in this condition. We believe this to be the case because:

(a) Separate experiments in the tensile machine indicated that after an initial load drop of about 2% of the flow stress no load relaxation in the specimen and end pieces occurred over periods of up to 12 hours.

(b) The differential contraction between specimen and jig which occurs on cooling is of such a sign as to cause further plastic deformation.

The cryostat was similar to one previously described (5). Measurements of Q and ΔT, the temperature difference down one half of the specimen, were made between 1.5 and 4.2K. The system was then warmed to room temperature, the nuts N loosened and removed, and the measurement of Q and ΔT repeated. For a symmetrical arrangement λ is easily calculated since half the heat produced in the heater goes in each direction; but in any case λ may be calculated knowing the size factor of the gauge length and the relative size factors of the two halves of the specimen between the heater tag and the points where the wires W are attached. A comparison of the values of λ determined in this way for a relaxed specimen in the jig with the values obtained by the standard method for the same specimen removed from the jig gave results which agreed to within 1% of λ.
4. The Experiment to Detect Anisotropy

4.1 The Idea

This is similar to the experiment carried out by Moss (6) on non-metallic crystals. We tried to prepare from a deformed single crystal specimens in which the angle between the heat current and the dislocation lines differed. This experiment is very difficult in a face centred cubic material because one must limit plastic deformation as much as possible to one slip system. This in turn limits the dislocation densities which can be introduced, and one is trying to detect small changes in $W_d T^2$ against a relatively large background of electron-phonon scattering.

4.2 Specimen Preparation

Figure 2 shows diagrammatically a single crystal of 12 at.% copper-aluminium of dimensions $0.2 \times 10 \times 2.5$ cm. The operative slip plane containing the primary burgers vector $b$ is shown. $b$ made an angle of $10^\circ$ with the trace of the slip plane on the thin face of the crystal. This crystal was deformed in tension as much as possible consistent with only one slip system operating. This was judged from the absence of a significant number of slip lines on any but the primary system. (In this connection it is worth noting that Steed and Hazzledine (7) measured the relative densities of primary and secondary dislocations in a 10 at.% copper-aluminium alloy after 45% shear strain. They found that the density of the primary dislocations was about four times that of the secondary dislocations.) Then the directions in the crystal of the primary edge and screw dislocations may be determined. Two specimens of the shape shown in figure 2 complete with thermometer tags $T$ were obtained by cutting perpendicular to the large face $ABCD$ of the crystal. This was done by spark machining. In one specimen, referred to here-after as cross 1, the orientation of the cross was chosen such that the primary edge dislocations made equal angles with both arms $A_1 A_2$ and $B_1 B_2$. The angle between the screw dislocations and these two directions however differed. In cross 2 the situation with regard to the edge and screw dislocations was reversed. Thus a comparison of the thermal conductivities of the two arms of cross 1 or of the two arms of cross 2 will show any anisotropy in the scattering of phonons by screw and edge dislocations respectively.

One arm of each cross made an angle of about $30^\circ$ with the tensile axis so that it is reasonable to assume equal mean dislocation densities and the same dislocation structures for both arms of any one cross.

5. Results

5.1 The Jig Experiment

The results for the measurements done in the jig are shown in figure 3. The upper set of points is for the single crystal. This had been deformed about 20% in tension to a stress of 7 kg mm$^{-2}$. The lower set of points is for the polycrystal which was deformed by about 5% at a stress of 20 kg mm$^{-2}$. For both specimens the open circles refer to the relaxed condition. Note that the ordinates for the two specimens are shifted relative to one another.

The vertical arrows on the graph indicate $\pm 1\% \lambda/\Gamma$ and within this range, (a) there is no significant difference between the measurements under stress or relaxed for either the poly or the single crystal, and (b) straight lines may be drawn through the points. However, the scatter on the individual curves is considerably less than $\pm 1\%$, and in the case of the polycrystal the relaxed measurements give lower values throughout the temperature range. This is the opposite of what one would expect for pile-ups, and any change in size factor caused by the elastic deformation of the specimen under tension can only increase this difference. Moreover, if one joins up the points the $\lambda/\Gamma$ against $T$ plots appear as a curve for the single crystal under stress, but more like a kinked straight line for the remaining three sets of points.

5.2 The Anisotropy Experiment

The flat single crystal was deformed about 25% in tension at a flow stress of 6 kg mm$^{-2}$. This took the crystal through stage I of the work hardening curve and into the beginning of stage II. The table below gives the angles between the heat current and the primary edge and screw dislocations for each cross. The edges in cross 1 were not at exactly the same angle due to the rotation of the crystal axis during deformation.
Table 1. The angles between the primary dislocations and the heat flow for the directions measured. The graphical symbols used in figure 4 are also given.

<table>
<thead>
<tr>
<th></th>
<th>Cross 1</th>
<th>Cross 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₁ A₂</td>
<td>B₁ B₂</td>
</tr>
<tr>
<td>Angle to Edges</td>
<td>55°</td>
<td>63°</td>
</tr>
<tr>
<td>Angle to Screws</td>
<td>35°</td>
<td>73°</td>
</tr>
<tr>
<td>Graphical Symbol</td>
<td>O</td>
<td>□</td>
</tr>
</tbody>
</table>

The results of the thermal conductivity measurements are shown in figure 4. The graphical symbols used are indicated in table 1, and the points for cross 2 are shown displaced to the right by 0.6 K. Almost all the points can be made to lie within ± 1% λ/T of the same straight line. Taken at their face value each set of points is better represented by a kinked straight line as drawn in figure 4. The results for cross 2 indicate that there is no detectable anisotropy due to edge dislocations. The vertical difference between the results for the two arms of cross 1 cannot be considered significant since each direction involves the measurement of a different size factor. Nevertheless, for cross 1 in the region above about 3 K, the points for arm A₁A₂ lie on a line of greater slope than those for arm B₁B₂. This would be consistent with an anisotropy in the scattering of phonons by screw dislocations.

5.3 Evidence that the Kink is Real

The drawing of other than straight lines through the points for the λ/T against T plots needs justification. The effect looks like a systematic error. It cannot be due to the superfluid transition in liquid helium because it occurs well above this. We measured cross 1 in the direction A₁A₂ in a different cryostat using different thermometers and heater. The two sets of measurements are shown in figure 5. They agree extremely well. Recent measurements in this latter cryostat of the thermal conductivity of an annealed and deformed 2 at.% alloy gave very good straight lines in both cases with all the points within ± 0.2% λ/T of the lines. We are at present carrying out further test experiments.

6. Discussion

No effect corresponding to the expected behaviour of dislocation pile-ups was observed in the jig experiments. For the polycrystal the difference between the two measurements, under stress and relaxed, could be significant but it is in the opposite direction to that expected.

The limitations on the dislocation density which can be introduced in the anisotropy experiments together with the results obtained indicate perhaps the unsuitability of a face centred cubic alloy. The experiment might be better done using an alloy with a hexagonal close packed structure in which slip only occurred on the basal planes. Nevertheless, considering the results for cross 1 in the temperature region above the kink there is a difference in the slopes of the λ/T against T plots for the two arms. The smaller slope occurs for direction B₁B₂ in which the screw dislocations make a greater angle with the heat flow in agreement with the expected behaviour (6).

There still remains the kink in the λ/T against T graphs which occurs in all the specimens. This kink is not present in annealed and deformed alloys of 2 at.% copper-aluminium. We believe that it may be due to the presence of large numbers of dislocation dipoles in the deformed 12 at.% alloy. The deformation of annealed single crystals of this alloy in the early stages proceeds by the formation of localized bands of slip, separated by regions in which comparatively little or no slip has occurred. As the deformation proceeds the bands get wider and fresh bands appear until at the end of stage I the crystal is uniformly covered with slip. Recently Mitchell et al (8) studied the dislocation structure of these bands in an 8 at.% copper-aluminium alloy in the first few percent of plastic deformation. They found that the dislocations in the bands of deformation were present in the form of interleaved pile-ups of parallel positive and negative edge dislocations. The distance between the glide planes on which the adjacent groups of dislocations of opposite sign occurred varied from about 50 angstroms to a few microns. Steeds and Hazzledine (7) also found large numbers of dipole groups in their 10 at.% alloy.
The effect of dipoles on lattice thermal conductivity has been discussed by Moss (6); it depends upon the relative sizes of the dipole spacing \( d \) and the dominant phonon wave length given by

\[
\xi = 0.6 \frac{\theta}{a}
\]

where \( a \) is the lattice spacing and \( \theta \) the Debye temperature. For \( \xi \ll d \) the phonons see a dipole as separate dislocations giving the usual \( q^{-1} \) wave number dependence for the dislocation phonon scattering relaxation time. For \( \xi >> d \), the phonons see the equivalent of a line of point defects, the relaxation time is proportional to \( q^{-3} \), and the scattering is less effective than that from two isolated dislocations for the same \( \xi \).

For a fixed value of \( d \), as the temperature is lowered, there will come a point where the phonons will begin to see the dipole aspect of the dislocation arrangement. The phonon scattering will then begin to decrease from the value expected for a random arrangement of dislocations sufficient to account for the phonon scattering at higher temperatures. Correspondingly the values of \( \lambda / T \) will begin to lie above a line extrapolated from the higher temperatures.

Moss (6) has suggested that this change will begin when \( \xi = 2d \). In our alloys the kink occurs at about 3 K where the dominant phonon wavelength is about 200 angstroms. So to account for the effect observed, the majority of the dipoles must have a spacing of about 100 angstroms. This is consistent with the available electron microscope evidence. What one might expect to happen at lower temperatures is that the \( \lambda / T \) against \( T \) plots would turn again, but in the opposite direction to a line whose slope would correspond to the scattering from electrons and the residual density of randomly distributed dislocations.

The effect of an external stress on a sheet of dislocation dipoles will be to move one set of dislocations relative to the other but not to change the relative spacing of dislocations of a given sign. Thus a null effect in the under-stress experiment is readily explained on the assumption that the majority of the piled-up groups of dislocations exist in dipole sheets. The effect in the 'wrong' direction might be explainable in terms of an overall decrease in dipole spacings under the action of the applied stress.

With regard to our values for \( \sigma (T) \). Neglecting the existence of the kink in deformed copper-aluminium alloys of the higher compositions could lead to an over estimate of the values of \( \lambda / T \) obtained. At the worst, the values we obtained would be one-and-a-half times too big.

7. References


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Figure 1  The specimen and jig. See section 3.2 of the text for explanation.

Figure 2  The single crystal and specimen shape. The trace of the primary slip plane on the crystal faces is shown. $b$ is the primary burgers vector.
Figure 3: $\frac{\lambda}{T}$ against $T$ for the specimens measured in the jig. The open circles are for the relaxed condition. The lower set of points and the right hand $\frac{1}{T}$ axis refer to the polycrystal.

Figure 4: $\frac{\lambda}{T}$ against $T$ for the cross shaped specimens. The lower temperature scale refers to the right hand set of points which are for the two directions of cross 2. For a further indication of which points refer to which directions see table 1 in section 5.2.
Figure 5 \( \frac{\lambda}{T} \) against \( T \) for the direction \( A_1A_2 \) of cross 1 measured in two different cryostats. The triangles refer to the second cryostat.