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The Electrical Resistivity of Dislocations in Aluminium.

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Abstract

Aluminium foil was extended by tensile deformation at room temperature by amounts up to about 15% plastic strain. The flow stress (σ), the change in electrical resistivity (Δρ) and the dislocation density (N₁) were measured as a function of plastic strain and subsequent annealing. The change in electrical resistivity was measured at liquid Helium temperature and the dislocation density was measured by thin film transmission electron microscopy. The change in electrical resistivity and the dislocation density were both proportional to the plastic strain and hence to one another. The annealing of the extended specimens was found to occur in three stages. The first, which occurred at room temperature was due to the annealing out of point defects; an activation energy of 0.65eV was obtained for this process. The second stage took place above about 70°C and during this process both a re-arrangement and loss of dislocations occurred. The third stage was recrystallisation. The resistivity of dislocations in the deformed state was found to be:

\[ \Delta \rho = (18 \pm 1) \times 10^{-20} \text{ N}_1 \text{ ohm cm.} \]

and after the second annealing stage:

\[ \Delta \rho = (17 \pm 2) \times 10^{-20} \text{ N}_1 \text{ ohm cm.} \]

These results have been compared with experimental values
obtained by other authors and with various theoretical estimates. It is suggested, that the loss of dislocations during the preparation of thin foils was negligible, that the scattering of conduction electrons by the core of a dislocation compared with that of the long range strain field was not negligible in contributing to the electrical resistivity and that the theoretically calculated value of the stored energy of a dislocation in Aluminium $^{38}$ was correct within $\pm 25\%$. 
To Mum & Dad,

with thanks for all that you have done to make this possible.

Your loving son,

Tom.

February 1965.
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Chapter 1. Historical Survey and Proposed Programme.

1.1 An outline of the current theories of work-hardening.

When a metal specimen is deformed by applying a tensile stress to it, the stress-strain curve departs from Hooke's Law at a certain point which is usually referred to as the elastic limit (see A on fig. 1.1). If the specimen is deformed beyond this point, say to a stress $\sigma_1$ (see B on fig. 1.1), then when the stress is removed the metal does not fully recover its initial length. The permanent increase in length per unit length is referred to as the plastic strain. If the specimen is reloaded, then to cause a further amount of plastic strain, an increased stress must be applied to the metal (see eg. C on fig. 1.1). This phenomenon is known as work-hardening and occurs in most of the common metals at room temperature. The stress required to cause a small increase in plastic strain after work-hardening the metal is referred to as the flow stress. This is generally less than the maximum stress used to initially deform, or cold work the specimen, by a small amount $\Delta \sigma$ which is also shown in fig. 1.1. This difference is thought to be due to some relaxation of the internal stresses in a metal during unloading.
The study of dislocations arose from the realisation that the so-called perfect crystal model could never fully explain the nature, and in particular the mechanical properties, of metals. The dislocation was proposed independently by several authors and was first studied as a theoretical model to explain the apparently low yield stress of metals. Several works of a complete nature have been published on this subject and the reader is referred to them for a mathematical treatment. A more general treatise will provide a similar account of the nature and properties of the other defects found to be present in metals.

Any dislocation model of work-hardening must first explain how dislocations are generated within the crystal. How this occurs is by no means clear at this present time, but at least one mechanism has been shown to exist and this is the Frank-Read source. Fig. 1.2 shows such a source operating. The dislocation is pinned at both ends, and under the action of a stress will bow out until an unstable configuration is reached, when the dislocation will break away in the form of a loop, leaving an identical dislocation pinned as before. This new dislocation is free then to bow out again and so repeat the process. The source is thus free to act until some sort of
reverse stress is built up, due e.g. to a pileup of dislocations.

Any complete theory of work-hardening must be able to predict several other things. It must predict the dislocation arrangement of the cold worked metal, the value of the flow stress necessary to cause dislocations to move through the postulated structure and it must relate these two things to the plastic strain produced in the crystal. None of the present theories does this completely, but all go some way to predicting the behaviour of metals under stress. These various theories have been recently reviewed in an article by Spencer and Holt to which the reader is referred for a detailed treatment of the subject. The present author will describe only the more complete theories.

Of the various theories which try to account for the flow stress in terms of the long range stress associated with dislocation pileups, the most complete is that due to Seeger et al. In this theory it is assumed that the dislocation sources are limited by two components of reverse stress. The first, temperature independent term, is due to the interaction of dislocations in the slip plane with piled-up dislocation groups in parallel slip planes. In this
model it is proposed that barriers are created due to the locking of dislocations on different slip planes. The most commonly proposed lock of this type is the so called Lomer-Cottrell barrier in which two dislocations on different (111) planes interact to produce a wedge-shaped stacking fault ribbon bounded by two partial edge dislocations and a partial edge dislocation of the stair-rod type. This whole system is sessile and it is against this sort of barrier that Seeger et al. picture a piledup group of about 25 dislocations of the normally glissile type. They postulate that the number of pileups increases during deformation and that they are distributed in a more or less random manner, with dislocation groups of opposite sign being near neighbours. This last assumption accounts for the fact that the configuration is reasonably stable even after the stress is removed. This interaction gives rise to a component of stress of the form:

\[ \tau_\varphi = \alpha G b N_1^\frac{1}{2} \]

where \( \tau_\varphi \) is the flow stress.

\( G \) is the shear modulus.

\( b \) is the Burgers vector.

\( N_1 \) is the dislocation density.

The second component of flow stress arises from the non-elastic interaction of dislocations in a slip plane with the
so-called forest of dislocations on other planes. Here the stress arises from the constriction that must occur if two extended dislocations are to cut one another without the creation of a region of stacking fault. The form of this interaction is shown schematically in fig. 1.3. This component of the reverse stress is temperature dependent and the effect of the forest becomes negligible at increasing temperatures. We have thus:

\[ \tau = \tau_0 + \tau_s \quad \tau_s \rightarrow 0 \quad \Theta > \Theta_c \]

The model accounts well for the observed slip lines on the surface of deformed metals, but the model pictures the majority of dislocations lying in the slip planes. The various electron microscope studies, however, indicate that this is not so for high stacking fault metals, but does occur in alloys and low stacking fault metals. Seeger's model does, however, account for the low temperature behaviour of the flow stress (see fig. 1.4).

An alternative theory is that the stress arises from the elastic interaction between the dislocations in the glide plane cutting through the dense forest of dislocations. The original suggestion of Cottrell that a forest of dislocations existed within the deformed metal, was later developed into a quantitative theory by several workers.
and this theory has been reviewed recently by Bailey. The theory gives rise to a relation between the flow stress and the average spacing of the dislocations in the forest as follows:

\[ \tau = \alpha \cdot \frac{G \cdot b}{l_f} \]

where \( \alpha \) is \((2\pi)^{\frac{1}{2}}\) for screw and \((2\pi \cdot (1 - \nu)^{\frac{1}{2}}\) for edge-dislocations

\( \nu \) is Poisson's ratio.

\( l_f \) is the mean spacing of the forest dislocations.

If one accepts that the dislocation network in bulk material is similar to that revealed both by transmission electron microscopy of thin foils and etch pit studies, then one can postulate that within a deformed metal most of the dislocations lie within the subgrain boundary walls, with relatively clear regions in between. It is true that the structure may change during electro-polishing of thin foils, but the general picture is most probably correct.

The model does not assume that the dislocations lie in slip planes unlike the Seeger model. Howie reviewed the experimental work of Bailey and Hirsch, Venables, Carrington et al., and Bailey and concluded that the flow stress was related to the dislocation density in all these metals by the relation:

\[ \tau = (0.50 \pm 0.05) \cdot G \cdot b \cdot N_f^{\frac{1}{2}} \]

He showed that this relationship was in agreement with the
predictions of the theoretical model on the assumption that the density of dislocations in the forest was related to the average dislocation density by the relation:

\[ N_{\text{sub-boundary walls}} = N_f = m \cdot N_{\text{average}} = (1_f)^{-2} \]

Bailey and Hirsch attempted to measure the value of this constant \( m \) experimentally and found that: \( m \approx 5 \).

Substituting this value into the equation gives:

\[ \gamma = 0.45 \text{ G.b.} N_{\text{average}}^{1/2} \]

Clearly there is good agreement between this quasi-theoretical model and the experimental values. Thus whilst this theory accounts well for the observed relation between the flow stress and the dislocation density for Copper and Silver, it does not give an explanation of the slip line observations and does not present a realistic picture of the dislocation configurations observed at low strains, where a well-developed substructure is not present (see e.g. fig. 3.5). It is also true that the theory does not take into account the production or movement of jogs which must give rise to a component of the flow stress.

Hirsch and Warrington\(^{14}\) observed that in Copper the flow stress of a deformed specimen decreased with temperature in the manner illustrated in fig. 1.4. Hirsch\(^{16}\) put forward the hypothesis that in most metals vacancy jogs move with
the creation of a row of vacancies and that this leads to a component of flow stress which is temperature independent below the second drop illustrated in Fig. 1.4. Interstitial jogs on the other hand are glissile at normal temperatures and so give rise to a contribution to the flow stress only at low temperatures. This theory has been reviewed by Mott\textsuperscript{17} and will not be discussed here in detail. The calculated relation between the flow stress and the dislocation density is:

\[ \gamma = (2K)^{-1} \sigma b/\ell \]

where \( K \approx 0.8 \)

This is clearly identical with that predicted by the earlier forest theory, but this later theory has the advantage that it predicts the presence of slip lines of about the observed length. The theory postulates that the observed network of dislocations is produced by secondary slip. The secondary slip also produces hardening by forming glissile and non-glissile jogs which, when stressed sufficiently, move and thus unlock the original dislocation sources. The theory is thus able to account for most of the observed features of work-hardening of the common face-centred cubic metals, but does not explain in detail how the complex dislocation networks arise which are observed in the electron microscope. The theory also predicts that vacancies rather than interstitials will be produced during plastic deformation.
at room temperature. It is also pertinent to point out that this theory predicts well the behaviour of single crystals of copper in the linear hardening region of the stress strain curves.

Clearly there will be some differences in the behaviour of polycrystalline materials and single crystals, but the authors of the forest theory and the jog theory have compared their theories to measurements made on polycrystalline materials. Seeger does not explicitly refer to polycrystalline material, but the predictions of his theory should hold for the relation between the stress and the dislocation density.

It might also be said that none of the theories completely explains the relation between the two properties, flow stress and dislocation density and the degree of plastic strain produced during cold work; except for the linear hardening portion of the stress strain curve of single crystals.
1.2 The properties of point defects in metals.

As has been stated in the previous section, Van Bueren\(^3\) has reviewed in detail the properties of point defects. It is, however, useful to summarise some of the properties of point defects here in order to interpret correctly the measurements of the resistivity of dislocations by previous workers. In general, the theories of work-hardening predict that such defects will be produced by moving jogs during plastic deformation. Since the likely migration energy for interstitials is very low, vacancies are the defects which are expected to be produced by cold work at room temperature and they have a number of effects upon the properties of a metal. In particular, they give rise to an increase in the internal energy of a metal and this energy, usually referred to as the stored energy, will be released when these defects anneal out. These defects also cause the density of a metal to decrease by a small amount. The presence of vacancies also gives rise to an increase in the electrical resistivity of the metal. As all of these properties are also affected by the density of dislocations present in a deformed metal, then to separate the contributions due to dislocations alone, it is necessary to know, either that all the vacancies have annealed out of the
crystal, or the exact magnitude of the contribution of vacancies to these various properties. Dawson has shown that for Copper, Silver and Gold deformed at -195°C there are several distinct annealing stages for the point defects produced, at least one of which in each case occurs above room temperature.

As the temperature of a metal increases the equilibrium concentration of vacancies created by thermal energy also increases. Several authors tried to measure the activation energy for migration of vacancies in Aluminium by quenching metals heated to near the melting point. In all these studies, the recovery of electrical conductivity was measured as the defects annealed out. Panseri et al., Desorbo et al., Bradshaw et al. and Wintenburger obtained respectively 0.58 ± 0.03 eV, 0.52 ± 0.04 eV, 0.44 ± 0.03 eV and 0.58 ± 0.05 eV. Although some discrepancy exists between the various estimates, the mean value is probably 0.55 ± 0.05 eV, if all the defects were in fact identical.

The jump frequency for vacancies is related to the atomic vibrations of the lattice by the relation:

\[ \nu_d = A \nu_0 e^{-Q/kT} \]
where $\nu_0$ is the jump frequency of the defects.

$A$ is a constant approximately equal to 1.

$\nu_0$ is the atomic vibrational frequency (10^{13}/sec at 20°C).

$Q$ is the activation energy for migration.

$k$ is Boltzmann's constant.

$T$ is the temperature in degrees Kelvin.

Then using the normal laws of diffusion we can relate the diffusion distance to the jump frequency as follows:

$$L = (4.\nu_0 kT)^{\frac{1}{2}}$$

$L$ is the diffusion distance.

$D$ is the diffusion constant.

$t$ is the time.

where $D = (1/12)\nu_0 a^2$

and $a$ is the jump distance.

Substituting for the probable activation energy of 0.55 eV gives:

$$\nu_0 \approx 10^3 / \text{sec at 20°C}.$$ 

The average spacing between dislocations is related to the dislocation density and in deformed foils this density is likely to be in excess of $10^8$/cm$^2$; thus the average distance between dislocations will be less than $10^{-4}$cm. Since the likely sinks for vacancies are dislocations we might expect that when the diffusion distance was approximately equal to the average distance between dislocations, then the
vacancies would be absorbed. If we assume that the jump distance is one atomic spacing, then vacancies will be expected to travel a distance of $10^{-4}$ cm. in about three hours.

Even if a vacancy were not absorbed by the first dislocation it met, there was every probability that after deforming Aluminium, the number of vacancies left after two days would be extremely small. For an exact calculation, however, it would be necessary to know the dislocation cross-section for vacancy absorption. As an additional guide, therefore, it is essential to measure simultaneously the flow stress of the metal, which is not affected by the presence of vacancies and one of the properties e.g. electrical resistivity, which is sensitive to the presence of such defects during annealing experiments, to obtain a value for the decay time of vacancies. Such an experiment is described in Chapter 3.

1.3 The scattering of conduction electrons by dislocations.

As has been shown in 1.1 dislocations are expected to affect the work-hardening properties of metals and in this section their effect on the electrical resistivity of a metal is considered. Conduction electrons travelling through
a crystal are scattered by the strain fields associated with the dislocation. In the case of dislocations which dissociate to leave two partial dislocations separated by a region of stacking fault, this stacking fault region may also scatter dislocations. The scattering due to these two defects gives rise to a contribution to the resistivity of a metal. This may be stated as follows:

\[ \rho = \rho_0 + \rho_0 \]

where \( \rho \) is the total resistivity of the metal at any temperature, \( \rho_0 \) is the contribution to the resistivity caused by the lattice thermal vibrations and \( \rho_0 \) is the resistivity due to the presence of defects which scatter the conduction electrons present in the crystal e.g. impurity atoms, interstitials, vacancies and dislocations. It is the latter term which is studied in this thesis and in particular the contribution of un-dissociated dislocations to this term.

On a simple picture of the atom, electrons exist in a closed shell round the nucleus, the inner shells being completely filled whilst the outer shells are either empty or partially filled. The electrons in the partially filled states are referred to as valence electrons. When an electric field is applied to the system, it is assumed that the inner complete shells are unaffected and that in a conductor, the
valence electrons in the outer shell may be free to act as conduction electrons. On this simple picture of the electron states, the effect of both electron-electron and electron-nuclei interactions are neglected. These assumptions lead to the Sommerfeld free electron theory of metals, which is outlined in Chapter 2 of Ziman's book\textsuperscript{22}. The valence electrons, usually referred to as free electrons, interact weakly with the lattice and therefore the effect of the periodic lattice structure on the electron states in a metal, may be derived by considering this interaction as a perturbation upon the free electron states predicted by the Sommerfeld theory. Applying this approach to the one-dimensional lattice, leads to a picture of the energy states of the electron being split into bands or zones with discrete energy gaps in between, in which no electron may permanently exist. Bloch's theorem, also discussed in Ziman's book, applied to the three-dimensional case, leads to the representation of the wave function of an electron as the product of a plane wave function and a function having the periodicity of the lattice. Bloch considered the effect of the displacement of atoms or nuclei from their rest positions and in this way was able to calculate correctly the effect of the lattice thermal vibrations upon the electrical resistivity of the metal. Koehler\textsuperscript{23} (1949), Mackenzie and Sondheimer\textsuperscript{24} (1949) and Dexter\textsuperscript{25} (1952)
tried to apply this approach to the case for the dislocation, but the approximation is poor, for the dilatations round a dislocation are large compared to the lattice dimensions and there is also a discontinuity in the lattice surrounding a dislocation.

Hunter and Nabarro\textsuperscript{26}(1953) were the first to consider the metal as being replaced by a continuum in which the potential of each region depended only upon the strain in that region. Using the Born approximation and simplified expressions for the strain field surrounding a dislocation, they obtained a value for the resistivity of a random array of dislocations in copper of: $\Delta \rho = 0.4 \times 10^{-20} \text{N}_1 \text{ohm cm.}$ where $\Delta \rho$ is the resistivity due to dislocations.

Klemens\textsuperscript{27}(1956) attempted to account for the scattering by analogy with the scattering of phonons by dislocations. He calculated the change in the electron distribution function in terms of the phonon scattering and used values of the temperature thermal resistance to calculate the phonon scattering. The calculation is, of course, indirect and the value taken for the phonon scattering may have been incorrect.
Harrison (1958) pointed out that none of the previous calculations had allowed for the scattering due to the atomic displacements near to the core of a dislocation. Using the approximation that the core of a dislocation could be represented by a hollow cylinder, he deduced a value for the electrical resistivity of the core of a dislocation in copper:

\[ \Delta \rho = 5 \times 10^{-20} \text{ N}_1 \text{ ohm cm.} \]

This value was much greater than any of the previous workers had anticipated and is surprisingly large in view of the fact that a large fraction of the energy of a dislocation lies in the long range strain field.

Broom (1952) had suggested that much of the resistivity of dislocations in face-centred cubic metals arose from the dissociation of the dislocations into partials. Howie (1960) used a wave matching calculation, in which the various crystal waves that propagate in the perfect region of crystal, on either side of the stacking fault, were matched, so that the wave function and its derivative normal to the fault were continuous across the boundary. The calculation in fact considers only the case for two waves and Howie stated that the calculation might be improved if more waves were considered. Howie derived a value for the resistivity of stacking faults in Copper of:
\[ \Delta \rho = 10^{-12} B \text{ ohm cm.} \]

where \( B \) is the total stacking fault area / cm\(^2\).

If it is postulated the dislocations are separated into partials, at a distance apart of 10 Burgers vectors, then we have:

\[ B = 25 \times 10^{-3} \cdot N_1 \text{ cm}^{-1} \]

and therefore

\[ \Delta \rho = 25 \times 10^{-20} N_1 \text{ ohm cm.} \]

Heine\(^{31}\) considered the Fermi surface of Aluminium and postulated a model for this metal, in which the inner band of electrons is completely filled, the second band contained approximately one electron per atom and the third and fourth bands contained almost no electrons. This picture of Aluminium approximates very closely to the free electron model of metals.

Howie used this suggested model for Aluminium, to calculate the likely effect of stacking faults in this metal and found by the same method a value of:

\[ \Delta \rho \approx 10^{-13} B \text{ ohm cm.} \]

If again we assume that the separation distance of the partials is approximately 2 Burgers vectors, then we may deduce the contribution due to resistivity as:

\[ \Delta \rho < 10^{-20} N_1 \text{ ohm cm.} \]

It should be pointed out however that the magnitude of the
scattering from stacking faults is still far from certain, but the calculations of Howie probably represent an upper limit. In the same calculation Howie also postulated that there existed a diffraction effect from undissociated dislocations, similar to those associated with stacking faults. There is a phase change produced by this diffraction, which is not abrupt, as in the case of the stacking fault, but continuous over a large distance. This gives rise to a contribution to the electrical resistivity of the dislocations, which he calculated to be approximately:

\[ \Delta \rho = 5 \times 10^{-20} N \text{ ohm cm for Aluminium.} \]

Seeger and Bross\textsuperscript{32} (1960) criticised the original calculation of Hunter and Nabarro for their use of the first Born approximation, which they postulated did not take into account the fact that the core of an edge dislocation no longer remains neutral, but becomes negatively charged, due to the surplus of electrons in the dilated regions around the core of the dislocation. They found that the second order terms in the Born approximation, yielded contributions to the electrical resistivity of the type:

\[ \Delta \rho = Q_{\text{se}} \frac{\hbar}{2} \left\{ k_f \left( \frac{R}{R_c} \right) \right\} \]

where \( k_f \) is the wave number at the Fermi surface, \( R \) is the cut off radius beyond which the strain field associated with
the dislocation was assumed to have vanished and $r_0$ is the radius of the core of the dislocation assumed in the calculation to have been $b/3$. These terms they thought represented the magnitude of the scattering due to the charged core. Their calculated value for the electrical resistivity of an edge dislocation is shown in fig. 1.4. Seeger and Stehle\textsuperscript{33}, by a similar method, had also calculated the effect upon the electrical resistivity of a screw dislocation. In this case, however, the result is convergent and yields an answer of:

\[ \Delta \rho \]

Dalitz\textsuperscript{34}(1951) compared the results of calculating the scattering of a charged particle by a screened Coulomb potential by an exact solution of the Schrödinger equation, the first Born approximation and also by classical mechanics. The solutions of all three calculations agreed. He went on to show that the second and third Born approximations gave rise to terms of the type: $\log R$, $(\log R)^2$ respectively. He thus showed that these terms did not give rise to a term in the scattered intensity, but gave rise to a phase change. Nabarro and Ziman\textsuperscript{35} compared the terms in the Seeger-Bross calculation to those in the work of Dalitz and concluded that it was not at all certain whether the $\log_2 \left[ \frac{h}{k, \left( \frac{R}{r_0} \right)} \right]$ term in
the Seeger-Bronss calculation gave rise to a contribution to
the electrical resistivity of a dislocation or merely to a
phase shift of the diffracted electrons. They concluded
that if their interpretation was correct, then the best
estimate of the resistivity of an undisassociated dislocation
should come from a calculation of the Huntar Nabarro type,
together with a correction for the resistivity of the core.

Basinski et al.\textsuperscript{36}(1963) again considered the effect of
the atomic displacements in the same manner as Klemens, but
did not attempt to obtain an absolute value for the resis-
tivity of a dislocation. Instead, they took the formula
they evolved and which may be expressed as follows:
\[ \Delta \rho / \rho_{i} = \alpha b^{2} V^{2/3} M \Theta \rho_{i}(T)/T \]
where \( V \) is the atomic volume.
\( M \) is the atomic mass.
\( \Theta \) is the Debye temperature and \( \rho_{i} \) the ideal resistivity
and adjusted the value of the constant \( \alpha \) to match the work
of Blewitt et al.\textsuperscript{37} and Clareborough et al.\textsuperscript{45}. Both of these
values are based on indirect measures of the resistivity of
a dislocation and so the accuracy of this estimate
must be in some doubt. (For a discussion of the results of
Blewitt et al. and Clareborough et al. see section 4.5). They showed nevertheless, that for a wide range of metals,
their predicted and measured values of the resistivity of dislocations agreed to within the experimental error. It is interesting to note that these authors, one of whom was Howie, did not refer explicitly to the calculated value of the resistivity of dislocations due to the postulated diffraction effect of undissociated dislocations. They also concluded that the core of a dislocation must contribute only a small fraction to the total resistivity of a dislocation; about 20%.

Ziman\textsuperscript{39}(1964) calculated that the scattering of electrons by dislocations would give rise to an increase in resistivity of approximately:

\[ = 10 \text{ to } 20 \times 10^{-20} N_1 \text{ ohm cm.} \]

In this calculation, he used the so-called method of Neutral Psuedo-atoms. The assumption is that the metal may be treated as if the ion plus the surrounding screening charge, might be regarded as a composite independent entity. In relating this approach to the case for dislocations, he has considered the effect of only a few atoms near to the core of the dislocation. He considered, however, that the likely result for a metal, such as idealised copper, would be approximately equal to this first estimate. It is clear also that this method is capable of calculating the effect of the
entire dislocation as such and not as previously treating the core of the dislocations in isolation from their long range fields.

To sum up it is fair to say that there is no general agreement at present as to the total resistivity due to undissociated dislocations and further more, the contribution due to dislocations splitting into partials has not been agreed upon. The relative contributions of the core and long range strain field are unknown, different models of the core yielding different apparent values. Finally, there is no agreement as to whether the resistivity of a dislocation is a function of the arrangement of dislocations or not. Seeger et al. would argue that the arrangement is of paramount importance, whereas Ziman, Nabarro and others would say that this is not so.

Factors influencing the measurement of the electrical resistivity of dislocations.

We have seen that there have been various theoretical estimates of the electrical resistivity of dislocations in section 1.3; in order to make an experimental comparison with these estimates, it will be useful to bear in mind the following points:
a) A method must be established for introducing and counting a number of dislocations.

b) A method must be established for measuring the change in electrical resistivity of the specimens containing dislocations.

c) A method must be established for measuring the flow stress of the specimens containing the dislocations (also to compare with estimates of this quantity given in 1.1).

To fulfill condition a) above

i) The counting method must give directly the number of dislocations present in the crystal, not a figure that is proportional to this.

ii) The counting method must establish the arrangement of the dislocations and, in particular, be able to distinguish between a pileup model, such as that envisaged by Seeger (see 1.1), and a forest model or relaxed model.

To fulfill condition b) above

i) Account must be taken of the increase in electrical resistivity due to defects other than dislocations, which are produced during cold work. (There is some evidence that these defects anneal out at room temperature in several hours. See section 1.2 for a discussion.)
ii) Dislocations in a metal also affect and are affected by the lattice thermal vibrations of the metal. Since none of the theoretical estimates of the likely resistivity due to the presence of dislocations takes this into account, it is obviously important to know the magnitude of this variation, or to conduct the measurements at low temperatures, where the atoms are "at rest". (The magnitude of the variation has been measured by Blasinski et al.\textsuperscript{36} for Copper, Silver and Gold, who found that the resistivity of dislocations in these metals increased by 60%, 80% and 30% respectively between 4.2°C and 80°C).

1.4 A review of the available methods of determining the density of dislocations.

Measurements of the density of dislocations in a metal may be subdivided into two categories. In the first category are those which reveal the individual dislocations or their sites, and in the second category are those which give only a numerical estimate of the density, usually in terms of some other known parameter. It will be useful to summarise these methods here and to discuss the inherent limitations of each technique.
The etchpit technique falls into the first category. A dislocation raises the free energy of a surface that it intersects at, or near, its core. Therefore an etchant which is sensitive to this property will dissolve away metal at a different rate in the neighbourhood of a dislocation. In general, the rate of dissolution is raised by the presence of dislocations, but other factors, such as the presence of impurities, can affect the etchant to a much greater extent. An early method of showing up the dislocations, used this enhanced dissolution rate at impurities. The dislocations were revealed by doping the metals with a small amount of impurity and then inducing the impurity atoms to take up preferential sites along dislocations, usually by heating the specimen. The method is open to criticism on two counts; firstly, that there is no reason to suppose that all the dislocations will be equally attractive to impurities, and secondly, that during the migration of the impurities, rearrangement of the dislocations might well occur. More recently a number of etchants have been developed which appear to etch up undecorated dislocations of certain low index planes\(^{40}\). When estimating the density of dislocations intersecting a surface, the greatest density that can be resolved is limited by the smallest size of etch pit that can be recognised as such. The diameter of the pit must
obviously be small compared to the average distance between the dislocations. Using modern replica techniques and very short etching times, the method can be used to count dislocation densities in the range $10^5$ to $10^9$ dislocations per square centimeter. Some doubt still exists as to the correlation between the number of sites etched and the number of dislocations present in the crystal. This method has the advantage of simplicity, but it is questionable to what extent any count of dislocation density on the free surface of a metal can be typical of the bulk value. (For a further discussion of the problem see Chapter 4.2.) It is additionally well known that, even with such etchants, pits can arise at other than dislocation sites.

Surrounding a dislocation there is an associated strain field in the lattice; the orientation of the lattice is also changed in the regions either side of a dislocation site. Both of these phenomena combine to alter the Bragg reflecting conditions of a crystal in the neighbourhood of a dislocation; thus the contribution to a particular Bragg reflection may be altered in that region and contrast arises in any picture that is taken using that reflection. This mechanism is used in transmission electron microscopy \(^{10,41}\), which consists essentially of looking at a particular Bragg reflection from
a small region of crystal and magnifying the image by electromagnetic lenses, until the individual dislocations can be seen. The criterion for contrast for a particular Bragg reflection depends, amongst other things, on the relationship between the directions of the Burgers vector and the normal of the reflecting planes, but this is in general a calculable factor. The method has the advantage that densities in the range $10^6$ to $10^{11}$ dislocations/sq. cm. can be resolved. This makes it a particularly suitable method for investigations into the work-hardening properties of metals. The method also gives an indication of the structure of the deformed metal. The limitation of the method lies in the fact that the thin films may be atypical of the bulk specimens from which they are prepared and that during this preparation, some rearrangement and loss of dislocations may occur.

Using the same contrast principles, a number of techniques for microbeam transmission or reflection micrography have been developed. The advantages of this technique are, that relatively large samples may be used, but the magnification available is such that the maximum resolvable dislocation density is approximately $10^6$/sq. cm., which is applicable only to lightly deformed specimens. A review of
these methods is given in the St. Louis conference report.\textsuperscript{42}

Into the second category come the various measurements of the stored energy of deformed metals, in which the energy of dislocations is measured as they are allowed to anneal out. The dislocation density is calculated from the release of stored energy, using the calculation of Cottrell p.38, who gives an expression for the free energy of a dislocation as:

\[ E = \frac{G \cdot b^2}{4 \cdot \pi \cdot R} \log_e \left( \frac{R}{r_0} \right) + E_{\text{core}} \]

and \( K = 1 \) for screw, \( = 1 - \) for edge dislocations.

The contribution due to the core of the dislocation cannot be calculated exactly, but has been estimated by Bailey and Hirsch\textsuperscript{11} to be approximately:

\[ E_{\text{core}} = \frac{G \cdot b^2}{10} \]

Seeger and Schoeck\textsuperscript{43}(1955) have made a more detailed calculation which modifies to some extent the value given above, but the value essentially depends upon the cut-off radius chosen. Bailey and Hirsch\textsuperscript{11} and Bailey\textsuperscript{7} attempted to compare the theoretical estimates above with their own experimental results on polycrystalline silver and copper. They found that a discrepancy existed between the theoretical predictions and their results, of a factor of about 3, where the practical results indicated a higher value of the stored energy. They calculated that this could be entirely due to
interactions between neighbouring pairs of dislocations seen in the thin foil electron microscope specimens, which were used to estimate the density of dislocations. They pointed out, however, that the estimation of dislocation density might be in error for the two reasons indicated in the previous section. The present author would like to point out that there is also a distinct possibility that unobservable clusters of point defects or small loops might have been present in the foil and that the discrepancy might, in part, have been due to this. Seeger and Kronmuller have, however, argued that the calculation of Bailey and Hirsch, of the likely effect of the relaxation of dislocations, was in error due to an incorrect interpretation of the nature of dislocation pileups. The present author would like to point out, however, that the likely presence of clusters of vacancies, means that the forest theory could give a correct interpretation of the results of Bailey and Hirsch's experiment. It would seem to the present author, that there might, therefore, be a systematic error in the determination of the density of dislocations from measurements of stored energy and this error might well be as high as 100%.

A second parameter which is affected by the presence of
dislocations is the density of a metal. A calculation by Seeger and Stohle\textsuperscript{33} yields a value for the change of density due to the presence of dislocations, but this calculation is also open to criticism for the exact nature of the dilatations of atoms at, or near, to the core of dislocations is unknown. Clarebrough et al.\textsuperscript{45,46} have used these figures in their work and have found that the density of dislocations estimated by this method is greater than that estimated by the stored energy technique, by a factor of two.

A number of attempts have been made to estimate the density of dislocations produced by cold work, by postulating theories of work-hardening, but as we have seen in section 1.1, the state of our knowledge of dislocation theories cannot yet give an exact quantitative answer of this type.

1.5 Estimates of the resistivity of dislocations in Aluminium and other face-centred cubic metals.

Experiments were carried out on Aluminium by Clarebrough et al.\textsuperscript{38} using stored energy technique. They measured the change in electrical resistivity upon annealing metal which had been deformed 75\% in compression. They also measured the Vickers Hardness Number, which they found
decreased in the same manner as the resistivity during annealing. As has been remarked in section 1.2, if vacancies were present, they would contribute to both the increase in stored energy and the electrical resistivity. If this is so, then any result computed from these figures will be in error. Clarebrough, et al. argue that since the point defects are not expected to contribute to the Vickers Hardness Number, but will contribute to the resistivity, then the fact that the curves for decrease in Vickers Hardness and resistivity are similar, indicates that there are no vacancies present. Rider and Brooks\textsuperscript{47} working on Copper, found that there was a single-valued relationship between the resistivity and Vickers Hardness Number, but failed to find a similar relationship in Aluminium. This must cast some doubt onto the assertion of Clarebrough et al. that no vacancies were present. From the stored energy measurements, Clarebrough et al. obtained an estimate of the density of dislocations of $N = 4 \times 10^{10}$ dislocations/cm$^2$ and they deduced a value for the resistivity of dislocations $\Delta \rho = 33 \times 10^{-20} N_1$ ohm cm.

Silcox and Whelan\textsuperscript{48} measured the density of dislocations in thin foils by transmission electron microscopy, the dislocations in this case having been introduced by quenching foils from very high temperatures, to retain an above
equilibrium number of vacancies, which were then allowed to aggregate by annealing at room temperature. These aggregates collapse to form the dislocations commonly observed in this type of specimen in the electron microscope. They compared their results with those of Panseri and Federighi who had measured the change in resistivity of similarly quenched foils and so obtained an order of magnitude estimate for the resistivity of dislocations, in the form of loops, of \( \Delta \rho \approx 30 \times 10^{-20} \text{ N}_\text{cm} \text{ cm}. \) The error in this calculation is, however, liable to be very great, as the specimens used in the two experiments were completely different.

A third indirect estimate was obtained by Gondi et al. (1961) who measured the change in resistivity of specimens deformed by 99% cold-rolling. Two methods were used to estimate the dislocation density, the first relied on a theoretical estimate of the relation between dislocation density and flow stress and the second estimate was obtained from the mis-orientation of subgrain boundaries viewed in the electron microscope. The error in this last type of measurement is very high, the mis-orientation varying from 0.07 to 0.12 radians. In this case as in the previous two measurements, the resistivity changes were measured at liquid nitrogen temperatures. They also investigated the annealing
of Aluminium, which they found to take place in two distinct
stages; the first of which was characterised by an activation
energy of approximately 1.1 eV. The second stage was re-
crystallisation. Their deduced value for the resistivity of
a dislocation was:

$$\Delta \rho = 40 \times 10^{-20} N_1 \text{ ohm cm.}$$

Wintenburger\(^2\) (1960) attempted to estimate the resis-
tivity of dislocations by measuring the change in residual
resistivity, as a function of plastic strain, but he had to
assume a dislocation model to estimate the density of the
latter. His derived value of: $$\Delta \rho = 2 \times 10^{-20} N_1 \text{ ohm cm},$$
is therefore of doubtful significance.

Cotterill\(^5\) (1963) used a similar method to that of
Silcox and Whelán, but in this case measured both the change
in resistivity and the dislocation density on the same
specimens. The resistivity measurements were made at 80^0K
and the dislocation density was obtained as in the previous
experiments, by transmission electron microscopy. The
possibility of there having been unseen small aggregates of
vacancies cannot be ruled out. He deduced a value for the
resistivity of dislocations in the form of loops of 300^0A
diameter of: $$\Delta \rho = (70 \pm 20) \times 10^{-20} N_1 \text{ ohm cm.}$$
A recent estimate by Yoshida et al.\textsuperscript{51}, who in 1963 studied both deformed and quenched Aluminium, was made by deforming wire specimens in tension and measuring the change in electrical resistivity at liquid nitrogen temperatures. The dislocation densities were measured in the electron microscope, by deforming thin foil specimens by similar amounts. They did not publish their stress strain curves for the two materials at that time and it is not clear whether the flow stresses of the wire specimens and the foil specimens were the same or not. They stated that the measurements of the change in specific resistivity were not decisive and that more accurate results were required. They obtained a result for the resistivity of dislocations of:

$$\Delta \rho = (65, 61 \& 66) \times 10^{-20}N_1 \text{ ohm cm.}$$

in the range 0 to 14\% plastic deformation. Yoshida et al. stated that one day was allowed to elapse between deforming the specimens and measuring the change in resistivity, to allow the vacancies to diffuse away. With the then accepted value for the activation energy for vacancy migration, this was a reasonable assumption in the absence of any other experimental evidence, but as will be shown in this thesis, the quoted values were in fact in error, probably due to the presence of large numbers of divacancies in the quenched foils. The half life of the vacancies produced by cold
working the Aluminium used by the author of this thesis, was approximately 4 days. In the same series of experiments Yoshida et al. also measured the density of stacking faults present in quenched foils using different specimens. They were able to deduce a value for the resistivity of both stacking faults, which they found to be negligible and vacancies, which they found to disagree with the earlier estimates of Simmons and Balluffi\textsuperscript{52}.

It is difficult to compare these practical results with the various theoretical estimates, for, as has been pointed out earlier, there is every reason to suppose that the resistivity of dislocations at 80°K, will differ from the value at 0°K. This will, however, be discussed further in Chapter 4.

Clarebrough et al.\textsuperscript{45,46} have also measured the stored energy, the increase in density and the decrease in electrical resistivity as dislocations anneal out of Copper, Silver and Gold. All the measurements of the resistivity were carried out at liquid nitrogen temperatures. They obtained values for the resistivity of dislocations of the metals respectively:

\[
\Delta \rho = (28, 34 \& 35) \times 10^{-20} N_1 \text{ ohm cm.}
\]
The density of dislocations was in the range $10^{11}$ to $3 \times 10^{11}$ dislocations/cm$^2$.

Basinski et al.$^{36}$ have used the value derived by Clarebrough et al., described above, to calculate the resistivity of dislocations at $4.2^\circ$K, by using their own experimental results, in which they measured the resistivity of a deformed specimen at different temperatures and were able to deduce the contribution due to plastic deformation at the different temperatures. They deduced values for the resistivity of dislocations in Copper, Silver and Gold of respectively:

$$\Delta \rho = (17, 19, 26) \times 10^{-20} \text{ohm cm}.$$ 

Clarebrough et al.$^{45, 46}$ also concluded that the contribution of the stacking fault term to the resistivity of dislocations was negligible. In doing so, however, they used a value for the stacking fault energy of Copper of 163 ergs/cm$^2$. A second estimate of this quantity was made recently by Bowie and Swann$^{70}$, using a direct observation technique of the nodes of dislocations in copper alloys. From the dislocation geometry, they deduced a value for the energy of the stacking fault. Their value is 40 ergs/cm$^2$, which, if it is correct, casts some doubt upon the conclusion of
Clarebrough et al. It would be proper to say, therefore, that the situation is unresolved at this present time.

Blewitt et al. measured the change in the electrical resistivity of deformed copper specimens at 4.2°K, or liquid helium temperature, and found that the relation between the flow stress and increase in resistivity could be given by:

$$\Delta \rho = 1.3 \times 10^{-10} \tau^2 \text{ ohm cm.}$$

$\tau$ is the resolved shear stress.

After annealing for 16 hours at 300°K, or approximately room temperature, they found that the relation changed to:

$$\Delta \rho = 0.9 \times 10^{-10} \tau^2 \text{ ohm cm.}$$

The difference they ascribed to vacancies. With this value and a knowledge of the nature of the stress strain curve, they postulated a dislocation model and derived a value for the resistivity of dislocations in Copper of:

$$\Delta \rho = 23 \times 10^{-20} N_1 \text{ ohm cm.}$$

As has been pointed out in section 1.1, there is still no general agreement between the various models of work-hardening and so the calculated dislocation density may well be considerably in error.

Livingston measured the dislocation density in deformed copper, by an etch pit technique, and deduced a
relation between the dislocation density and the flow stress of:
\[ \gamma_r = \frac{3}{2} G b N_1^2 \]

Using the results quoted by Blewitt et al., he was thus able to deduce a value for the resistivity of dislocations of:
\[ \Delta \rho = 23 \times 10^{-20} \text{N}_1 \text{ohm cm} \]

which is in good agreement with that derived by Blewitt et al. using the theoretical model. It is pertinent to point out, however, that the specimens were entirely different.

Feltham\textsuperscript{53} in a recent paper, measured the change in electrical resistivity of Silver after deformation and deduced that the relation between the flow stress and the increase in resistivity after annealing was given by:
\[ \Delta \rho = \alpha \gamma_r^2 - \gamma_{\rho_0}^2 \]

Kovacs et al.\textsuperscript{54} have deduced a value for the resistivity of dislocations in silver using these results, together with those of Bailey and Hirsch\textsuperscript{11}, who measured the change in dislocation density and flow stress in deformed silver foils. Again, however, the specimens used were different and a more serious objection is, that they were deformed by different techniques and as the flow stress density relation may well be a function of the dislocation arrangement, the value must be regarded with some caution. Their deduced value was:
\[ \Delta \rho = 20 \times 10^{-20} \text{N}_1 \text{ohm cm} \]
To sum up, the results for Aluminium indicate a difference between the values for the resistivity of dislocations, as measured by the stored energy techniques of Clarebrough et al.\textsuperscript{38,45,46}, and those measured by the electron microscope techniques of Cotterill\textsuperscript{50} and Yoshida\textsuperscript{51}. There are several factors which could account for the difference. It could be a genuine difference in the resistivity of the dislocations due to different arrangements, of the sort predicted by Seeger and Bross; there could have been a loss of dislocations in the thin foil preparation; the use of different specimens by Yoshida et al., for the measurement of change of electrical resistivity and dislocation density, might have introduced errors; and the stored energy calculation might well be in error. There are no experiments which prove that there is a one-to-one correlation between the increase in dislocation density and the resistivity after the specimens have been annealed at room temperature, thus all the above measurements might have been affected by small vacancy clusters. Finally, there are no reliable measurements of the resistivity of dislocations at 4.2\textdegree K, as has been discussed before.

In the case of the other metals, no experiments have been carried out, in which the measurements of the change
in electrical resistivity and dislocation density were made on the same specimen. The only exception being the experiments of Clarebrough et al., whose calculations contain an unknown systematic error;

1.6 Proposed Programme.

In the light of what has been said in the previous section, it is clear that in 1961, when this project began, there were no reliable measurements of the resistivity of dislocations. The values obtained since then, can also be criticised for various reasons. In particular, none of the measurements gives a clear indication of whether the resistivity of dislocations is a function of arrangement, or not. Finally, there were no reliable measurements of the relation between the flow stress and the dislocation density in the range $10^6$ to $10^9$ dislocations/cm$^2$.

Accordingly, the author proposed to make measurements of the flow stress, electrical resistivity and dislocation density as a function of plastic strain. The dislocations were to be produced by tensile deformation, since this offered the advantage that a simultaneous load extension curve could be obtained, from which the flow stress could
be derived. Two methods were devised for measuring the change in electrical resistivity. The first relied on the assumption that the ratio of the electrical resistivities of two specimens is related to the ratio of their electrical resistances. It was felt that, by monitoring the latter, as the dislocations annealed out of the material, the resistivity of the dislocations could be deduced. This method, however, was not sensitive enough to measure the small change in resistivity produced upon deforming the material used.

The second method adopted, consisted of measuring the change in the residual resistivity upon deforming the metal. It was felt that electron microscopy offered the best available method of measuring the dislocation density in the range of densities $10^6$ to $10^{10}/\text{cm.}^2$.

Since the contribution of stacking faults to the electrical resistivity of dislocations was unknown when the project started, it was felt that the best material to use would be Aluminium, since this has the highest stacking fault energy of any of the common metals. Thus the width of the partial dislocations would be as narrow as possible, and therefore the contribution of the stacking fault to the resistivity of a dislocation would be relatively small. This metal had the additional advantage of being one of the
easiest to electro-polish. Since there was no previous experience within the College of thin film electron microscopy, this choice was expedient. For the same reason, the author also decided to work entirely on foil specimens. The choice of material also ruled out the possibility of using an etch pit technique for determining the dislocation density. The various techniques developed, are fully described in the following chapter.

It was felt that there were two simple ways of trying to find out if the resistivity of dislocations was a function of arrangement or not. The first, was to measure the resistivity of dislocations over as great a range of dislocation densities as possible. The second, to measure the resistivity of dislocations arranged in subgrain, or low angle boundaries, and to compare the results with similar measurements on dislocations in random arrangements. Both these approaches were used in this project.

Three series of measurements were proposed. The first consisted of measuring the flow stress, electrical resistivity and dislocation density of the foils, as a function of plastic strain. The second consisted of measuring these same parameters for foils strained a known amount and annealed
at different temperatures. The third consisted of measuring the resistivity and flow stress of deformed foils during isothermal anneals, to obtain estimates of the activation energy for any annealing stages found in the second series of experiments. The results of all these measurements are described in Chapter 3.

It was hoped that these measurements would provide a reliable estimate of the resistivity of dislocations and, moreover, an indication of any variation with arrangement, if this exists. It was also felt, that the measurements of flow stress would provide a useful addition to the knowledge of the relation between this parameter and the dislocation density, and that this information would throw some light on the validity of the various work-hardening theories currently proposed.
Figure 1.1 Stress-strain curve.

Figure 1.2 Frank-Read source.
Figure 1.3 Crossing of extended dislocations (Segger).

Figure 1.4 Variation of flow stress with temperature (Hirsch and Warrington.)
Fig. 3. Resistivity of edge-dislocations in copper as a function of the cut-off radius $R_0$ ($k_F = \text{wavenumber at the Fermi surface for } 1 \text{ cm dislocation length per } 1 \text{ cm}^2$). $\Delta \rho_{yy}$ gives the resistivity perpendicular to the glide-plane; $\Delta \rho_{xx}$ gives the resistivity in the direction of the Burgers vector. The two sets of calculated points refer to different evaluations of the third-order elastic constants. H.—N. denotes the value for $\Delta \rho_{yy}$ found by Hunter and Nabarro [69].
Chapter 2. **Experimental Methods used for the Measurement of the Flow Stress, Electrical Resistivity and Dislocation Density of Deformed Polycrystalline Aluminium Foil.**

Aluminium sheet 0.004 inches thick was used throughout these experiments and was obtained in two grades, commercial purity and 99.996% purity.* Sheet material was chosen because the author wished to make all the measurements on the same material and sheet material was necessary to facilitate easy production of thin films for electron microscopy. The resistance of a specimen is given by:

\[ R = \frac{\rho l}{w t} \]

where \( \rho \) is the resistivity of the material,
\( l \) is the length of the specimen,
\( w \) is the width of the specimen,
\( t \) is the thickness of the specimen.

and \( R \) the resistance of the specimen.

To obtain the necessary accuracy in measuring the change in resistivity of the deformed specimens during annealing, the room temperature resistance had to be approximately 1 milli-ohm. Further, to make effective use of the hot zone in the furnace, the overall length of the specimens had to be about

* This aluminium was kindly supplied by British Aluminium Co. Ltd..
10 cms, and therefore the distance between the potential terminals had to be approximately 6 cms. The resistivity of Aluminium, at room temperature, is approximately 2.7 micro-ohm cms. These figures mean, therefore, that the total width of the specimens was limited to 1.5 cms. The ratio of the width to the thickness was 150 to 1 and this was about the optimum figure for easy preparation of the specimens for the thin film electron microscopy. With these specimen dimensions, the portion for electron microscopy could be cut from the same strip as that used for the resistivity measurements.

Two other possibilities were considered. The first alternative would have been to use different specimens for the measurements of the change of resistivity and dislocation density, but this was rejected as unlikely to give a reliable value, for the reasons discussed in the last chapter. The second alternative was to measure the change in resistivity on relatively large specimens and to prepare specimens for electron microscopy from these. This was rejected because any mechanical reduction in thickness could have caused a degree of damage to the specimen and so introduced further dislocations, whereas any chemical or electro-chemical means used to fulfil the same purpose might have produced specimens
of non-uniform thickness.

Accepting the use of this sheet material, initial measurements were made of the thickness of the two samples. In both of them the thickness varied by less than \( \pm 3\% \). Any measurements made involving the thickness would therefore be limited to an accuracy of between 0.1\% and 1\%.

2.1 Measurement of the flow stress and plastic strain of the deformed specimens.

The specimens used throughout these measurements, were deformed in a tensile testing machine, which had a built-in load extension recorder. Specimens could be extended at a constant rate, which could be varied from 1/2 to 4 inches per minute. The load was measured by the extension of a series of calibrated springs. Loads of between 5 lbs and 1 ton could be measured. The grips used were of the self-actuating type. The machine was provided with an alternative hand drive to initially align the specimens.

The material was first cut into strips approximately 1/4 ins wide, using a guillotine. The strips were then placed between a pair of ground steel gauge lengths, which were
1 inch wide and the surplus metal was cut away with a sharp knife. This left strips which were accurately 1 inch wide. In the initial experiments, the damaged region at the edge of the foil, caused by the cutting, was removed by passing the foils slowly through a flame. In the later experiments, this was achieved by annealing the specimens for 3 hours at 470°C in vacuo.

The strip 1 inch wide, had a pair of parallel lines scribed onto its surface about 10 cms apart. This distance was measured using a pair of vernier calipers. The error in this measurement was less than ± 0.5%. Several measurements of the width were always made, but in general, no variation in the width could be detected. The thickness of the specimens was measured using a micrometer screw gauge, but no difference could be detected from foil to foil, or from one end of a specimen to the other. Accordingly, it was assumed that the thickness of all the specimens of similar composition was the same throughout these experiments. The probable error in this assumption is less than ± 3%. The ends of the specimens were prone to tearing in the grips during deformation. This was overcome by turning over the foil at the ends, to provide a thicker portion of specimen to go into the grips. This procedure resulted in a non-uniform width
of the specimen after deformation, but the extent of the non-uniformity was small. The specimens used for measurements of the change in resistivity and dislocation density, were taken from the central 15 cms of a 25 cm specimen, therefore the non-uniform width did not introduce a significant error. After deformation, the distance apart of the two scribed lines was again measured and the maximum load recorded.

The measured, or engineering, strain was deduced from the measurements as follows:

\[ e_m = \frac{l - l_o}{l_o} \]

where \( l_o \) is the initial distance apart of the lines, \( l \) is the final distance apart of the lines, and \( e_m \) is the measured or engineering strain.

The elongation strain, or true strain, is related to the measured, or engineering, strain by the following:

\[ e_e = \log_e(1 + e_m) \]

\( e_e \) is the elongation strain.

In the range of deformations used, the difference between these two measurements is less than 5%. Throughout this thesis, the strain has been expressed in terms of the engineering strain by:

\[ e = 100 \times e_m \]
The stress was calculated from measurements of the maximum load, thickness, width and plastic strain. It was assumed that the volume of specimens remained constant during deformation. The stress was thus the load, divided by the initial area, multiplied by a correcting factor:

\[ \sigma = \frac{P}{t \cdot w} \left( 1 + e_m \right) \]

where \( \sigma \) is the stress before unloading.

\( P \) is the final load.
\( t \) is the initial thickness of the specimens.
\( w \) is the initial width of the specimens.

An initial experiment was performed to see if the stress strain curve of high purity Aluminium was a function of the strain rate. Fig. 2.1 shows the results of this experiment. The points may all be considered to lie on one curve, within the experimental error.

2.2 A method for measuring the change in electrical resistivity of deformed metals during annealing.

As has been stated in Chapter 1, when a metal is deformed below its recrystallisation temperature, its resistivity increases, due to the introduction of dislocations and other defects. If the specimen is then annealed at a sufficiently
high temperature, the dislocations will anneal out and the resistivity will return to its value before deformation. If, therefore, the change in resistivity is measured at a constant temperature during annealing, both the total change in resistivity produced by the deformation, and the annealing characteristics, may be deduced. The expected change in resistivity for Aluminium was approximately $0.1\%$ of the room temperature resistivity. Since the temperature dependent part of the resistivity is approximately proportional to the absolute temperature, then the temperature of the specimen would have to be maintained constant to 1 part in $10^4$, to measure the small change in resistance due to the annealing out of defects. Clearly, this is a difficult task to achieve at the annealing temperature of Aluminium, which is approximately $350^\circ C$ or $650^\circ K$. The permissible change in specimen temperature would therefore be $\pm 0.06^\circ C$. The temperature stability of a furnace is usually little better than $\pm 1^\circ C$, at such a temperature and the use of a Silicon Oil bath was undesirable, owing to the possible effect of Silicon Oil on the Aluminium used. An alternative method of measuring the change was adopted, by placing the specimen in series with an undeformed specimen, referred to throughout as the dummy, and measuring the ratio of the potential differences across the two. In this way, it was
only necessary to keep the temperature difference between the specimen and dummy constant to 1 part in $10^4$. The theory for this is given in Appendix 1, and leads to the following equation.

$$\frac{\Delta \rho_a}{\rho_d} = \frac{X}{S.S'} - K$$

where $X = \frac{\text{resistance of the specimen}}{\text{resistance of the dummy}}$

where $\Delta \rho_a$ is the resistivity due to defects.

$\rho_d$ is the resistivity of the dummy.

$S.S'$ is a function of the geometry of the specimen and dummy and is approximately equal to 1, provided that the temperature difference between the specimen and dummy is less than 0.1°C.

$K$ is the ratio of the thermal contributions to the resistivity of the specimen and dummy respectively, and is constant to $\frac{\Delta T}{T}$ where $\Delta T$ = change in the temperature difference between the specimens, and $T$ is the mean temperature of the specimens.

If, therefore, the resistivity due to defects anneals out, then the ratio $(X)$ will change. Thus monitoring this ratio reveals the change in resistivity due to the defects annealing out. As is shown in Appendix 3, the effect of a small temperature variation is negligible, provided that
the temperature difference between the specimen and dummy remains constant. The basic assumption throughout, is that the resistivity of the dummy does not vary with time at constant temperature. Clearly, therefore, the change in resistivity can be measured by a potentiometric technique, since, as shown in Appendix 3, the ratio of the resistances of the two specimens is directly proportional to the ratio of the potential differences across the two, provided the thermal e.m.f.'s remain constant during the measurement.

If the temperature difference between the specimen and dummy varies during an anneal, this too will produce a change in the factor $X$, thus indicating an apparent change in resistivity. A sensitive test of the overall error in such a measurement is provided by measuring the ratio of the resistances of two fully annealed specimens during annealing, and changes revealed in this type of experiment, must be less than the change to be measured, due to the annealing out of defects. The expected change was based on the work of Rider and Brooks, who found that the change in resistivity was approximately 0.1% of its value at room temperature. The apparatus, therefore, was designed such that the total apparent change in resistivity, when comparing two annealed specimens, was to be less than 0.01% of
the resistivity of one specimen. Fig. 2.2 shows a schematic arrangement of the apparatus.

An accumulator of 400 ampere hours capacity, which held five gallons of acid, provided an electro-motive force, which was independent of the short term fluctuations in room temperature. The current was fed to the specimens through thick, low resistance leads and an oil-immersed manganin resistor. This latter formed more than 90% of the total electrical resistance of the circuit, and was temperature insensitive. The total electrical resistance of the circuit was unaffected by the normal fluctuations in room temperature. It was thus possible to keep the current stable to less than 1 part in $10^5$, for a period of several minutes, after some time had elapsed. If, however, the circuit was interrupted, the e.m.f. of the cell changed, but recovered after several minutes to give a current, which afterwards varied in an approximately linear manner, increasing by 3 parts in $10^5$ per minute.

The present author found that by cycling the current rapidly, between forward and reverse directions, he could reduce the time required to reach equilibrium from several minutes, to less than 40 seconds. Further, that by this
technique the measurements could be made almost immediately after first drawing current from the cell, compared with the long elapse which previous workers have had to allow.

The potential differences across the specimens were measured on a five dial Diesselhorst potentiometer. The out of balance current was magnified by a Tinsley galvanometer amplifier, which allowed linear interpolation to 0.01 microvolt. The current flowing through the specimens was kept at approximately 1 ampere, thus giving a possible resolution of 0.01 micro-ohm. The galvanometer was mounted upon a platform suspended by long soft springs, which reduced the transmitted vibration to less than one small scale division on the galvanometer.

The specimen holder was designed, such that the specimens were in similar locations within the furnace. Long leads connected the specimens to the external electrical circuits through a vacuum seal, thus keeping the heat loss by conduction from the specimens to a minimum. The mechanical connectors throughout the circuit were designed to give the best thermal conductivity possible between adjacent wires, but to give negligible electrical conductivity. During an experiment the whole of the furnace tube was evacuated to a pressure of
less than 1 mm. of Mercury. This prevented convection currents from being set up, but sufficient air remained to maintain good thermal equilibrium between the specimens and the furnace, provided the heat losses by conduction were small.

All the electrical connectors in the external circuit were of a mechanical type, those between dissimilar metals being immersed in an oil bath. The selector switch used was of the all-copper type. These two precautions ensured that there was a negligible error due to the variations in the thermal e.m.f.'s in the external circuit. As Appendix 1 shows, reversing the currents through both the specimens and potentiometer, allowed the error due to the presence of constant thermal e.m.f.'s to be eliminated.

The specimens themselves were cut from the deformed foils round a jig (see fig. 2.3). The dimensions of this were chosen such that the current flow was linear between the potential terminals and such that the total electrical resistance, at room temperature, was approximately, 1 milli ohm.

Initial tests showed that with the circuit as shown in fig. 2.2, the current could be maintained constant to 1 part
in $10^5$ and that the potentiometer could measure to the required accuracy. Tests were then conducted upon pairs of fully annealed foils at room temperature. These showed that the ratio of resistances could be maintained the same, to within $3 \times 10^{-5}$; measurements being repeated over several days. This was clearly within the designed experimental error. The third series of tests was conducted to investigate the effect of the normal and abnormal handling of the specimens. These showed that, with care, the error could be maintained within that previously quoted.

Tests were then carried out upon pairs of fully annealed foils at various temperatures, within the furnace. The ratio of the electrical potential differences should have been constant and independent of the temperature. Fig. 2.4 shows a typical example of the annealing graph obtained. It can be seen, that the ratio was not constant, but changed systematically by 2 to 3 in $10^5$ per hour, with a scatter between readings of 3 in $10^5$. This variation was attributed to a change in the difference of temperatures of the specimens. This explanation was confirmed by an experiment in which one of the current carrying leads, at the end of the furnace, was cooled by several degrees. This resulted in a change in the ratio of the resistances of the specimens, of 3 in
$10^4$, due, presumably, to an enhanced loss of heat through the cooled lead from that specimen, whose temperature had been reduced. After some time, when the coolant was removed, the ratio of the resistances recovered by $1$ in $10^4$.

The length of an anneal had to be large, compared to the time taken for the specimens to attain thermal equilibrium with the furnace. If this were not so, most of the resistivity due to deformation would have annealed out during this initial period. It seemed, therefore, that a method had been established, which would measure the change in electrical resistivity due to the annealing out of defects during a prolonged anneal, within an overall experimental error of approximately $1$ part in $10^4$.

During these initial experiments, the author of this thesis noted two things of interest. Firstly, the ratio of the resistances of the specimens, after they had attained thermal equilibrium with the furnace, had changed from its value at room temperature. Secondly, a similar change also occurred upon cooling the specimens, after an anneal. The magnitude of these changes lay between the experimental error and $2 \times 10^{-3}$, and no regular pattern was observed, between the ratio of resistances before and after annealing.
The previous tests at room temperature, ruled out the possibility that these changes were merely due to experimental error. They were then, changes in the ratio of the resistances of the two fully annealed foils, caused by the period of heating during which the specimens were in a mixture of air, oil-vapour and water-vapour. It was inferred at the time that, either the physical dimensions of the specimens must have changed, or that their resistivities must have changed. It became clear, from later experiments, that the latter explanation was correct.

The early experiments carried out upon Aluminium, showed no change in the resistivity of deformed specimens upon annealing, of the expected magnitude. Therefore, any change that had taken place must have been comparable only with the experimental error. This experiment, therefore, indicated that the change in resistivity, caused by tensile strain of the foils, was considerably less than that produced by drawing wires a comparable extent. A similar type of experiment on Nickel wires, showed the expected behaviour; the change in that case being rather larger; \( \frac{dR}{R_0} \) was 6 in \( 10^4 \), and thus easily measurable.

The final inference drawn from these experiments, was
that, during a prolonged anneal, the ratio of the resistances of specimens of commercial purity, changed by a greater extent than the same ratio for a similar pair of pure Aluminium foils. This indicated that there might have been a change in the impurity contribution to the resistivity during an anneal.

In conclusion, the author of this thesis feels that the method evolved would work for specimens in which the change in electrical resistivity due to deformation was large, compared with the experimental error of 1 in $10^4$. It is obvious, however, that in the case of deformed Aluminium foils, this condition was not fulfilled.

To have improved the apparatus, to have achieved the desired accuracy of approximately 1 in $10^5$, would have required extensive modifications. Furthermore, the error due to changes in resistivity of the foil on heating or cooling, could not be reduced. As at that time liquid Helium had just become readily available in the department, this seemed to offer a simpler means of making the same measurements.
2.3 A method for measuring the change in the residual resistivity of Aluminium foil due to tensile deformation.

The resistance of a metal decreases steadily with temperature, until a point of inflexion is reached, below which the electrical resistivity is constant. It is then referred to as the residual resistivity and is only a function of the defect concentration and the impurity content of the metal. It was thus possible to measure the increase in residual resistivity due to dislocations, by comparing two specimens of similar dimensions and impurity content, one of which contained dislocations and the other did not. In practice, it was not possible to obtain thin foil specimens of exactly similar dimensions, however, the ratio of the resistances was measured at both liquid helium temperature, which is below the point of inflexion for Aluminium, and room temperature, where the major contribution to the resistivity comes from the lattice thermal vibrations. The contribution due to deformation was then deduced as shown in Appendix 4:

\[
\frac{\Delta \rho_d}{\rho_0} = (T_{02} - 1) \cdot \left( \frac{R^0_d}{R^2_d} \right)
\]

where

\[ T_{02} = \frac{X_0}{X_2} \]

\[ X = \frac{\text{resistance of specimen}}{\text{resistance of dummy}} \]
The suffix (0) refers to measurements made at 4.2°C (liquid Helium temperature), (2) refers to 20°C.

$R_d$ is the resistance of the dummy.

$\rho_d$ is the resistivity of the dummy.

Liquid Helium at atmospheric pressure, exists at a temperature of 4.2°C, and would therefore have boiled off extremely rapidly, unless precautions had been taken, to ensure that the heat input to the liquid, from the surroundings, was negligible. The liquid was contained within a pair of vacuum dewar flasks (see fig. 2.5). The outer surface of the inner dewar was maintained at liquid air temperature (80°C), by filling the outer dewar with this liquid. The presence of even a small amount of gaseous Helium in the interspace of the inner dewar, would have greatly increased the heat input to the liquid Helium, by conduction across this space. To prevent this occurring, the interspace was flushed out several times with air, before the arrival of the Helium container. The tap was sealed with a pressure of 1 mm. of air, left within the interspace; this provided a conduction path for the initial cooling of the apparatus. When the Helium first entered the inner dewar, this residual air was cooled and solidified and a hard vacuum was created. Both the dewars were silvered, with the exception of a small strip through which the liquid levels were observed; this reduced
the heat input to the Helium by radiation via the glass walls of the vessel. The specimens were supported upon a thin-walled, stainless steel tube of low thermal conductivity. Leads to the specimens were as thin as possible, consistent with the required current stability. The copper discs and polystyrene shield reduced the heat input from the mouth of the dewar. The specimens were mounted using mechanical contacts. Paxolin spacers prevented electrical contact between the specimens. Potential contacts were made by clamps manufactured for the purpose, and the specimens themselves were prepared in the manner indicated in the last section (see fig. 2.3).

The specimen assembly was placed inside the inner dewar and this was cooled to liquid Nitrogen temperature, by pouring the liquid into the outer dewar. The period of cooling was typically 40 to 60 mins. and was deemed to have finished, when the electrical resistances of the specimens no longer decreased. Helium was then transferred through a pre-cooled syphon tube. The syphon entered the transport vessel and inner dewar simultaneously and was further cooled by the gaseous Helium, boiled off as the tip of the syphon neared the level of the liquid. After this, the syphon was lowered slowly into the Helium and the latter transferred, by
recompressing some of the Helium boiled off during the initial cooling. This gas had been collected in a previously deflated bladder. The whole system was gas-tight. Helium was then transferred until the desired level was reached. At this point, the pressure was released and the syphon removed.

An initial period had then to elapse during which the thermal e.m.f.'s varied so rapidly, that no useful measurements could be taken. This period lasted from 30 to 45 mins, and was judged to be finished when all the potential differences across the specimens were sufficiently constant.

A current of one ampere was used throughout the experiments, and the electrical potential differences were measured in exactly the same way as described in the previous method. The same precautions, of taking readings with the current in the forward and reverse directions, as before, avoided any errors due to constant thermal e.m.f.'s in the specimen leads.

The measurements were repeated at room temperature by placing the whole specimen assembly into a well stirred paraffin bath. The temperature variation of this was nowhere greater than ±0.1°C. The temperature of the bath was
measured using a standard mercury-in-glass thermometer.

As will be seen in the next section, the current need only be maintained constant to 1 part in $10^4$, but the author's method of reversing the current rapidly before measurements, was still found to be useful in stabilising the cell.

Several sources of error arose in making this type of measurement. Referring to the equation stated previously, it is clear that they may be divided into two categories; those which arose in measuring the ratio of the resistances of the specimen and dummy at liquid Helium temperatures, and those which arose in making the same measurements at room temperature. A further source of error arose at liquid Helium temperature, due to the different impurity contributions to the resistivities of the specimen and dummy. All of these errors will be expressed in terms of an apparent change in residual resistivity, since all the graphical illustrations in this thesis have been plotted in this way. To convert to the equivalent apparent change in room temperature resistivity, it is necessary to divide by the resistance ratio which in these experiments, varied from 202 to 212. The resistivity of Aluminium of 99.996% purity at room
temperature is 2.67 micro-ohm-cm. Therefore, to convert the figures into absolute units, it is necessary to multiply by $1.3 \times 10^{-2}$ micro-ohm-cm.

Three errors arose in comparing the ratio of the resistances of a specimen and dummy at liquid Helium temperature. The first arose from the fact that the resolution of the instrument used to measure the potential was ±0.01 micro-volt. The potential differences across the specimens used in these experiments were greater than 5 micro-volts at liquid Helium temperatures, so the probable contribution to the error was less than ±2 in $10^3$, or ±0.2% of the residual resistivity. The second source of error arose from the fact that it was impossible to make simultaneous measurements of the potential differences across the specimen and dummy. The error here was reduced by making two measurements of the potential difference across the dummy. The probable error in comparing the potential difference across the specimen, to the mean of the potential differences across the dummy, was less than ±2 in $10^3$, or ±0.2% of the residual resistivity. The third source of error arose from the variation in potential differences across each specimen, between measurements made in the forward and reverse direction. Fig. 2.6 shows the results of a series of measurements of the potential
differences across a specimen and dummy. The variation in thermal e.m.f.'s was greatest for readings A and B, taken before 45 minutes had elapsed. After this time had elapsed, the magnitude of the variation in the thermal e.m.f.'s was less than 0.1 micro-volt, between sets of readings. The time interval for measurements between current flowing in forward and reverse directions, was typically 3 minutes, compared with the time interval between sets of readings, of 15 minutes. The probable error in measuring the ratio of the potential differences across a specimen and dummy, was therefore less than 4 in $10^3$, or $\pm 0.4\%$ of the residual resistivity. The total probable error, in any single comparison, is given, therefore, by the square root of the sum of the squares of the three errors, and was thus less than 5 in $10^3$. For a series of measurements such as those shown in fig. 2.6, the total error, therefore, should have been less than 2 in $10^3$, or $\pm 0.2\%$ of the residual resistivity. This was borne out by the statistical variation of the results in the table, which also indicated an error of less than this magnitude.

* In a later design, these errors were reduced to less than 1 in $10^3$, for a set of readings, by reducing the variation in thermal e.m.f. between readings.
The total error which arose in making the measurements of the ratio of the potential differences across a specimen and dummy, at room temperature, was less than 4 in $10^4$. This was negligible compared to those encountered at liquid helium temperatures.

The variation in the impurity distribution between specimens, also gave rise to an apparent change in residual resistivity. Fig. 2.7 was compiled from measurements of the ratio of the resistances of nominally fully annealed foils. In cases B, C and D, the specimens have received nominally similar treatment, yet there appears to be a difference in residual resistivity. The probable variation is calculated from there, to be less than $3 \times 10^3$, or $±0.3\%$ of the residual resistivity, between pairs of specimens having received similar treatment. A second systematic change can be seen in this table. There appears to have been a genuine and repeatable change in the resistance ratio, as a function of the number of times that a specimen had been annealed. A variation of this magnitude was not expected, and is now thought to be due to migration of impurity to grain boundaries, during recrystallisation. No evidence of grain growth had been observed, either by X-ray analysis, or by macroscopic etching of the specimens.
The total apparent change in residual resistivity, due to all sources of experimental error, lies between 3 and 4 in $10^3$, or less than $\pm 0.4\%$. In terms of the resistivity at room temperature, this is an error of less than $\pm 2$ in $10^5$.

At low temperatures, the electron mean free path for bulk material, is comparable with the physical size of the specimens used and this effectively limits the mean free path, thus reducing the conductivity of the specimens. The magnitude of this effect has been calculated (see Appendix 4) and is small compared to the experimental errors involved in this type of measurement.

Variations of the thickness between specimens should have had a small effect on the residual resistivity due to this cause. The magnitude of the size effect has been calculated, however, and the results of this experiment will be discussed in Chapter 3.

An initial experiment was carried out to investigate the magnitude of the change in residual resistivity due to deformation. A specimen deformed 7% and a dummy, were immersed in liquid Helium. This initial experiment was carried out without the use of a room temperature measurement,
in a paraffin bath. It indicated an increase in the residual resistivity of 1.9%, or \(2.5 \times 10^{-4}\) micro-ohm-cm, a change of only approximately 0.01% of the room temperature resistivity, much smaller than had been expected. The probable error in this experiment was higher than that quoted in the previous discussion, owing to the fact that the measurements at room temperature were not made in an oil bath. A similar experiment with a pair of fully annealed foils, indicated that the experimental error might be less than \(\pm 0.5\%\).

A similar set of experiments was carried out at the same time, on Aluminium of Commercial quality. This yielded an apparently sensible result, but this was spurious, as will be seen in Chapter 3.

A comparison of the two methods evolved for measuring the change in resistivity due to deformation.

Both of the techniques the author developed have never previously been used, in connection with this type of work, in this College and so it is pertinent to mention here some of the advantages and limitations of each technique.
The sensitivity of the two methods, when applied to this problem, may best be described by the ratio of the value for the change in resistivity, as a fraction of the experimental error in the measurement. The ratio for the first method described, was 2 for a 10% plastically deformed foil. For the same foil, the same ratio, for the second method, was approximately 9, which is far better.

The first method had a number of distinct advantages which would prove attractive, working on more heavily deformed foils. Firstly, no special materials were necessary. Additionally, the whole of the information about the annealing kinetics, could have been derived at the same time as the change in resistivity was being measured.

2.4 A technique for estimating the number of dislocations in Aluminium.

In Chapter 1 the present author proposed to measure the dislocation density, by thin foil transmission electron microscopy. The mathematical treatment of the contrast, due to dislocations in thin films, is described in Appendix 5. It is sufficient here to say that a certain percentage of the dislocations are, in general, visible in a thin foil
under suitable conditions. The use of this technique as a means of measuring the density of dislocations, is still quite new and since this is the first time that such a method has been used in this College, it is worthwhile recording in detail the technique used, especially as at present no single work contains all the necessary information. A general guide to the techniques used, may be obtained from Thomas's book and Howie's review.

The technique for preparing specimens for electron microscopy cannot yet be called an exact science. The number of factors which influence the polishing conditions, make it very difficult to reproduce immediately a technique used successfully elsewhere. It is, therefore, worthwhile recording in detail the technique used and also some of the difficulties encountered.

The general requirement for a successful polish, is to obtain a specimen shape, which tapers slowly from the edge of the specimen. It would be ideal if the specimen were polished at a uniform rate over its entire surface area, and when sufficiently thin, the polishing stopped. This is, however, impossible for many reasons. Any impurity, grain boundary, area of high free energy, such as the site of a
number of dislocations, or any edge will be preferentially attacked. The best that can be achieved, is to arrange things, so that these influences are minimised.

The technique used was a modification of the window technique due to Tomlinson. The liquids used by the author of this thesis were Glycerol, Analar Alcohol and Perchloric Acid (60 w/w), in the proportions 1:7:2. The addition of Glycerol to the original suggestion of Tomlinson, reduced the rate of attack and so produced a more controllable polish. The voltage and current conditions depended to some extent on the impedance of the source, but it was found that a successful polish was obtained with a current of 1 ampere, for a total specimen surface area of 12 cm$^2$. The cathode used was stainless steel, and was curved to provide a more uniform distribution of field in the electrolute. The specimen was supported in the bath on a crocodile clip, which was also dissolved and acted to some extent as a current stabiliser.

The specimen cut from the foil to be examined, was 4 cm x 1.5 cm in area. This was then lacquered in the manner shown in the fig. 2.8(a). The purpose of offsetting the lacquer, was to provide a strengthened final specimen. This
technique left one surface of the specimen unpolished at the edge. This edge was otherwise most prone to attack, with the result that the whole specimen might have collapsed in the polishing bath.

The specimen was polished in the manner described, for about 2 minutes and then taken out and reversed, in the manner shown in fig. 2.8(b). This contributed to the production of a uniform rate of attack and differences in the dissolution rates from top to bottom and from side to side of the specimen were eliminated. The specimen was washed between each polish in alcohol, and this sequence continued until the specimen became perforated. When the perforation reached a suitable region, about \( \frac{1}{3} \) of the way down from the top was found reasonable, the specimen was removed, with the current still on, and transferred to the bath of Analar Alcohol as rapidly as possible, where the polishing solution was washed off. It was then washed again in a second bath of alcohol and left under this liquid. Failure to do this quickly enough, led to extensive etching of the thinned region.

The actual specimens were obtained either by agitating the foil, when small regions were often dislodged, or by cutting off small areas at the edge with a knife. The first
method was preferred, as little damage to the specimens resulted. The specimens were then mounted upon Copper grids of the right diameter, by one of two methods. The first and standard technique, was to sandwich the specimens between two grids, so that it could not be lost within the microscope. The second method was the one which the present author devised and adopted, chiefly because in the early experiments, the prepared foils had to be transported across the city, to be used in a microscope at Northampton College. In order to reduce the damage to the specimens, they were stuck to the Copper grids and then placed in the standard Siemens container, provided with the microscope. The author used a solution of the adhesive from Sellotape in ether and thinned this solution until the resultant film left on the specimen was insufficient to scatter electrons by any appreciable amount. The grids were first coated with a layer of the solution and this was allowed to dry partially, whereupon the specimen was caught upon the grid and removed from the washing solution. The layer of liquid left upon the grid was enough to allow the specimen to be mobile and by tilting the grid appropriately, the specimen was brought to the centre. The grid was then dried upon lens tissue. The specimens had to be left until the solution was thoroughly dry and then the grid could be manipulated freely, without the
specimen becoming detached. This second method has a number of other advantages. Firstly, the area viewable is less restricted than with two grids, and secondly, the specimens do not suffer any damage as the nose cap of the specimen holder is tightened. In the first method, this tightening tends to lead to a shearing action across the specimen between the two grids.

The chief source of trouble encountered initially, was the use of non-Analar Alcohol in the washing solution. This led to severe etching of the specimen. It was also found that the temperature of the polishing solution affected the profile to some extent, and that the best results were achieved below 20°C.

To compare quantitatively the merits of the original technique and that which the present author has described, is very difficult, but if we compare the figures given by Tomlinson, who claimed that 50% of the prepared foils were useful, giving areas of 0.01 to 0.1 mm. visible, with those of the present technique, which produced small pieces of foil up to 1 mm. across, which were often transparent over the entire area; then clearly the modified method is superior.
There are four chief features which any microscope used for transmission electron microscopy, must possess. They are: The accelerating potential available must be sufficient to allow the electrons to penetrate a thin foil of up to 1 micron thickness, without undue loss due to absorption or inelastic scattering. In general, this means that a potential of 100 kV is required, though work can be done at lower potentials with the lighter metals. The electron beam must also be confined to a small region, for three reasons; firstly, to give adequate contrast in the final image, secondly, to limit the amount of specimen heating and so keep the specimen at about room temperature, thirdly, to reduce the area of contamination which Pashley and Presland have shown is mostly responsible for slip of dislocations. To provide these requirements, the second feature a microscope must possess, is a double condenser lens system. The first lens forms a diminished image of the filament and the second lens projects this image onto the specimen. In the Siemens microscope, the current density is \(5 \times 10^{-2}\) amps/cm.\(^2\) over an area as small as 3 microns. Thirdly, the specimen must be capable of being tilted into a suitable orientation to obtain a strong Bragg reflection. In the early work, the available tilt was limited to \(\pm 5^\circ\) in one direction, but recently the use of a Valdre stage allowed tilts of \(\pm 22.5^\circ\) to
be obtained in two mutually perpendicular directions. The need for the fourth feature arises because the orientation of the foil normal, in the region from which the micrograph is taken, is often required. This need is met by the provision of aperture stops, which limit the electrons contributing to the final image, to those coming from the area in question. These apertures are in the back focal plane of the objective lens. The selected area diffraction pattern is then obtained, by reducing the total magnification of the lens system until the back focal plane of the objective lens is focussed on the final screen.

As is shown in Appendix 5, a dislocation is, in general, only visible in the vicinity of a contour, or, in other words, near to a position in a crystal which is orientated to give a strong Bragg reflection. There are two methods of obtaining this criterion for photographing a specimen; either an area is selected and then tilted to a favourable orientation, or an area which is in contrast must be selected. In general, the two conditions were both used. To obtain maximum contrast, as high a beam current as possible was used, together with as small an objective aperture as possible. To reduce the statistical errors due to variation of density from place to place in the foil, pictures of complete lens system until the back focal plane of the objective lens is focussed on the final screen.
subgrains were taken wherever possible and as far as possible several subgrains within each grain were photographed. (This problem will be discussed in detail in the Appendix to Chapter 3.)

Having photographed the required area, dislocations were induced to slip by the heating action of the beam and the associated contamination. The areas photographed before, were all re-photographed when the slip traces appeared. Slip traces arise from the intersection of a moving dislocation with the specimen surface, or oxide layer and if, as is generally the case, the dislocation slips upon a particular plane, then the trace will be a pair of parallel lines. The width of this trace will be determined by the thickness of the foil and the orientation of the plane to the surface, as can be seen in fig. 2.9. The relation between the parameters being:

\[ w = t \cdot \tan \alpha \]  
(see fig 2.9)

The angle between the foil normal and the slip plane was determined from the selected area diffraction pattern, obtained, as previously explained. In general, the planes on which slip occurred were (111) planes in Aluminium at room temperature, and from a knowledge of the direction of the
foil normal and the width of the slip traces, the foil thick­
ness was deduced.

From the diffraction pattern, it was possible to deter­
rine the sets of planes which gave the strongest Bragg re­
flexion. The apertures used to obtain the selected dif­
fraction pattern are only focussed on the final screen, at
one setting of the intermediate current and, hence, at one
magnification. Therefore, the area from which the diffrac­
tion pattern was to be obtained, was first focussed at the
particular magnitude referred to above. When both were in
focus on the final screen, the image of the apertures in the
objective lens coincided with the specimen plane. Failure
to have done so would have introduced a serious error, due
to the lateral shift of non-axial diffracted rays. These
rays would then have come from an area of the specimen ad­
jacent to that being viewed.

The sequence for all measurements, was thus to select
an area of interest and then to obtain a suitable reflecting
condition. A series of pictures representative of this area
were then taken. After dislocation slip in this area had
taken place in the microscope, more photographs of the same
area were taken and finally a diffraction pattern of the
area was obtained.
The method used to estimate the dislocation density, must do two things. It must first give an estimate of the overall density, either expressed as total line length per unit volume \( N_1 \), or the number of dislocation lines crossing unit area taken at random in the plane \( N_m \). These two quantities are related, as was shown by Schoeck. The counting method must, secondly, give some indication of the type of arrangement to be found in the foils and, in particular, must distinguish, if possible, between a pileup model of the dislocation arrangement and a forest theory model.

The earliest method used to determine dislocation densities, was to measure the total projected line length within a picture and so deduce the total line length per unit volume \( N_1 \). This method was rejected, chiefly because of the labour involved in making such measurements.

The second method, used by several workers, is to estimate the density from the number of dislocations intersecting the foil surfaces. There were, however, a number of reasons for not applying this method to this investigation. As can be seen from Appendix 5, the criterion for the invisibility of dislocations normal to the foil may be given by: \( g \cdot b = 0 \), and in fact most of the dislocations intersecting
the foil normally will be visible, even if for these \( g.b = 0 \). Since, therefore, an unknown number of dislocations intersect the foil normally, any estimate of the density of dislocations, which attempts to take into account the percentage of dislocations invisible, using the above criterion, will overestimate the density by an unknown amount. A second disadvantage of this method in this case, was that it could not take into account the number of loops present in the foil (see eg. fig. 2.10). These do not in general intersect the foil surface and so would not contribute to the measured density of dislocations. It would also be difficult in many instances, to distinguish between the foils intersecting the surface, and those pinned by other dislocations in the bulk of the material.

Smith and Guttman\(^{58}\) showed that a series of lines of random orientation, drawn across a foil, could be used to give an estimate of the dislocation density, in terms of the number of dislocations intersecting unit area of plane. A calculation by Schoeck\(^{57}\) showed that for all the commonly occurring directions of the foil normal, this was related to the density of dislocations \( N_1 \) as measured by the total line length per unit volume by:

\[
N_1 = \beta N_m
\]
where \[ \beta \approx 2 \]

In this calculation, Schoeck assumed that all the dislocations were lying in the principle slip planes, whereas, in fact, a number will not be. This will serve to make the distribution even more uniform than he assumed, so the approximation is better still.

The author of this thesis decided that this last method was the most suitable for the measurements envisaged. A number of lines were drawn on a transparent perspex sheet at 20° intervals, all of 3 cms. length. The micrograph was then placed emulsion side down on the sheet and the number of intersections recorded. The micrograph was illuminated by a source, the intensity of which could be varied to suit the varying density of emulsion of different points on the micrograph.

Having estimated the density of dislocation crossing planes normal to the foil of length 3 cms., it was necessary to know the thickness of the foil, in order to know the total area of plane intersected. This information was obtained from the micrographs of slip traces, which were analysed in two ways. The standard method used was to take the projected
slip trace width from the micrograph and to determine the thickness from the relation:

\[ t = w \cdot \tan \theta \]  
(see fig 2.9)

In this case, the angle \( \theta \) was determined from the diffraction pattern. If any doubt existed as to the nature of the particular slip plane, this could be identified in conjunction with the diffraction pattern. There is, however, a particular relationship between the observed slip trace width and the orientation of the foil relative to the slip trace. If two or more slip traces of the same type are visible, then the orientation of the foil can be deduced from the relative widths of the two traces. The results of this type of analysis, have been computed by Dr. Crocker and Mr. Bevis of this department. The present author compared the results using this method, with those using the standard method. The agreement was, in general, within a few percent, well within the experimental error.

The measurements of the projected width, were carried out using a transparent rule, in contact with the emulsion side of the plate. The error in this measurement was less than that due to the variation of thickness from place to place in the foil. To reduce this error, a number of
measurements of the thickness were always taken and the thickness of the centre of the foil deduced.

The electrons accelerated to 100 kV in the electron microscope had an associated wave length of 0.037 Å, which was small compared to the atomic dimensions of the crystal. Consequently the diffraction pattern produced had the form of a planar section through the reciprocal lattice, normal to the electron beam. The spots so produced could be identified from both the ratio of their distances from the central spot and also from their angular relations. Since the specimens were thin in one direction, the maxima of transmitted electron intensity corresponded with the reciprocal lattice points, but were extended in the direction normal to the foil surface. This resulted in a limitation of the accuracy of determination of the foil orientation, by the means described above, to ± 5°, but had the advantage that a number of familiar patterns arose even when the orientation was in some way removed from the standard orientation for that pattern.

Two methods were used to determine the orientation. In the majority of cases, a comparison with a set of standard patterns allowed the spots to be identified by inspection. In the second case, the identification was carried out using
the two relations described above. To assist in this the present author computed the ratio of the distances of all the low index spots from the central spot, for the face-centred cubic metals.

Two methods are available for determining the orientation of the foil normal with greater accuracy, either the Kikuchi patterns may be studied, or the exact angular relations of the spots in the diffraction pattern may be used. In either case the orientation may be determined approximately ±0.1°. In this case, however, these methods were not necessary.

Several sources of error arose in trying to determine the average density of dislocations by this technique and these are discussed here, with the exception of the error due to the loss of dislocations during specimen preparation. This will be discussed later in the light of experiments conducted by various people, including the present author.

One source of error arose from the fact that a certain percentage of dislocations were invisible in any particular orientation. In Aluminium, which is a face-centred cubic metal of high stacking fault energy, the great majority of
dislocations had Burgers vectors of \( \frac{1}{2}(110) \)\(^1,2,3\). Assuming that the dislocations had Burgers vectors of all the possible types and that the distribution between the types was random, the present author calculated the fraction of dislocations which would have been invisible, with any single set of planes giving a string Bragg reflection. If, as sometimes happened in the electron microscope, two or more sets of planes were reflecting strongly from the region under examination, then the dislocations were only invisible if the criterion for both reflections held. Computations according to the dynamical theory have not been completed for all cases, but it appears that the criterion holds for most cases studied so far, with the exception of dislocations normal to the foil surface. In this present work, however, the dislocations intersecting planes normal to the foil surface will not be of this type. If a counting technique had been used, which counted the density of dislocations intersecting the surface, then no reliable criterion could have been used to calculate the percentage of dislocations invisible.

It is interesting to note that Ham\(^61\) in an early paper found a systematic difference of approximately 20% between dislocation densities counted by these two techniques. In
this study he did not account for the invisible dislocations. It is thus possible that the conclusion he reached, that the difference was due to the rearrangement of dislocations, could be explained by the differing criteria for invisibility. On average, the fraction of dislocations invisible in the first counting method, is at least 20%, in the second method it is certainly less than this amount.

Another possible source of error arose from the introduction of dislocations due to the mishandling of the foil after preparation. It was in fact possible to produce a significant number of dislocations in this way, as can be seen from fig. 2.11. These dislocations, however, had a very characteristic shape and pattern and were easily recognised. If such dislocations were present in a foil being examined, the foil was rejected. Fig. 2.11 shows an interesting example of the changing invisibility of dislocations due to the orientation of the foil slowly varying across the bend. The nodes of the intersecting dislocations are visible at the extreme edges of the photograph, but quite invisible at the centre.
Figure 2.1 The variation of flow stress with strain-rate.
Cell supplying current to specimens. (400 a.h.)
Cell supplying current to potentiometer.
Furnace.
Galvanometer (200 mm/micro-ampere)
Galvanometer Amplifier. (Gain 10 times.)
Manganin resistor in oil bath.
Potentiometer. (resolution ±0.1 micro-volt.)
Pumping line for furnace.
Reversing switch.
Specimen A.
Specimen B.
Selector switch.
Standard Resistor.
Standard Cell. (Reference voltage.)
Vacuum Seal.

Figure 2.2 Apparatus for high temperature annealing experiments.
Specimens are cut from the strip by sandwiching between a Jig and cutting with a sharp knife.

Figure 2.3 Specimen Details
Figure 2.4: Variation of the ratio of the resistances of two annealed specimens during annealing at 400°C
Figure 2.5 Schematic diagram of Apparatus for measuring changes in residual resistivity.
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Average X for C to G = \[ 1.038 \pm 0.002 \]

Suffices:
- F is current flowing normally
- R is current flowing in opposite direction
- d refers to the dummy specimen
- s refers to the deformed specimen
- 1 to the reading taken initially
- 2 to the second reading

Definitions:

\[
X = \frac{\text{resistance of the specimen}}{\text{Resistance of the dummy}} = \frac{(V_s^F + V_s^R)}{(V_d^F + V_d^R) + 2/7\left( (V_d^{2F} - V_d^{1F}) + (V_d^{2R} - V_d^{1R}) \right)}
\]

\(V_d\) the thermal emf is the difference between the potential differences with the current in the forward and reverse directions.

The ratio of the sum of the potential differences across the specimen and dummy gives the ratio of their electrical resistances. (see Appendix 1 for a discussion) The second term in the denominator is a small correction to allow for the fact that the measurements of the potential differences across the specimen and dummy were not made simultaneously. It is apparent that when the thermal differences were constant, (C to G), the resistance ratio was also constant. Large variations in the thermal e.m.f. between readings, (e.g. A & B) lead to an error in this ratio.

Figure 2.6 Variation of thermal e.m.f.'s.
The variation of impurity content from specimen to specimen gave rise to a variation in the residual resistivities of otherwise identical specimens. This gave rise to a probable error when comparing the residual resistivities of a deformed and undeformed specimen of 3 in $10^3$ or ± 0.3% of the residual resistivity of the undeformed specimen.

Figure 2.7 The residual resistivities of fully annealed specimens of high purity Aluminium.
Figure 2.3 Specimens for electron-microscopy

Figure 2.9 Relation between foil thickness and slip trace-width.

\[ \alpha \] is the angle between the slip plane and foil surface
\[ t \] is the foil thickness
\[ w \] is the measured width

Thus \[ t = w \tan \alpha \]
Figure 2.10 Dislocation loops in lightly deformed Aluminium.

X 30,000

Figure 2.11 Dislocations in Aluminium deformed by bending.

X 30,000
Chapter 3. Experimental Programme.

3.1 Measurements of flow stress, electrical resistivity and dislocation density of deformed commercial Aluminium foils.

The present author decided to carry out experiments on Aluminium of commercial quality, for several reasons. Firstly, it was felt advisable to try out the techniques on this material, rather than the limited quantity of high purity material available at that time. Secondly, it was felt that the additional impurity present in the commercial Aluminium might serve to pin the dislocations during the preparation of thin foil specimens for electron microscopy. Thirdly, it was known that deforming thin foils of this commercial purity was easier than deforming foils of higher purity. Because of this, it was felt that more dislocations might be introduced into a deformed commercial foil, than one of high purity.

Several strips 1 inch wide were cut and prepared in the manner described in Chapter 2. They were then deformed by varying amounts and the stress on unloading and plastic strain recorded. Since the flow stress is almost equal to the stress on unloading, these results have been used to plot
a flow stress against plastic strain curve, the results of which can be seen in fig. 3.1. The points plotted in the range 0 to 8%, have been obtained from a load-extension curve, produced during the deformation of one foil. This was necessary, since no foils were deformed by amounts less than 5% plastic strain. In this case, the total plastic strain was deduced in the manner described in Chapter 2. The plastic strain at other loads was deduced from the load-extension curve produced by the tensile testing machine. The results of these experiments indicate that the relation between the flow stress and plastic strain, for commercial Aluminium, is of the form:

\[ \gamma = \gamma_0 + \alpha \varepsilon_p \]

where \( \gamma \) is the flow stress.

\( \gamma_0 \) is the flow stress of fully annealed specimens

\( \varepsilon \) is the plastic strain measured in %

For commercial Aluminium:

\( \gamma_0 = 1.9 \times 10^5 \text{ grm/cm}^2 \)

\( \alpha = 1.7 \times 10^5 \text{ gms/cm}^2 \)

Several foils were then selected, to measure the change in residual resistivity due to deformation. These were prepared exactly as described in Chapter 2. The results of this experiment did not indicate a systematic increase in residual resistivity with increasing plastic strain. It was concluded
that the impurity content varied so much from foil to foil, that its changing contribution to the residual resistivity swamped any change due to deformation. The foils were re-annealed, as it was felt that the impurity content might not be affected by annealing. The decrease in residual resistivity after annealing ought then to have been due to the annealing out of dislocations. The results, however, indicated that the impurity contribution to the residual resistivity changed markedly, even for fully annealed foils. It was impossible, therefore, to deduce the contribution due to deformation.

Several foils were selected to measure the increase in dislocation density, with plastic strain. These were prepared and examined in the way described previously. The results of these measurements are shown in figs. 3.2 and 3.3. Fig. 3.2 shows that a correlation existed between the density of dislocations found and the degree of plastic strain, but it is clear that there is a considerable scatter. In order to obtain the best estimate of the relation between the dislocation density and the plastic strain, the results were expressed as the dislocation density per unit % plastic strain. The results of these calculations indicated that the relation between the dislocation density and plastic strain was:
\[ N_m = (4.05 \pm 0.34) \times 10^8 \varepsilon_p / \text{cm}^2 \]

where \( N_m \) was the dislocation density per unit area
\( \varepsilon_p \) was the plastic strain%

Fig. 3.4 shows a series of micrographs, typical of the dislocation arrangements found at different deformations. The dislocation arrangement varied, from a random arrangement of a few dislocations, to a well formed cell structure. The details of the distribution of dislocations are discussed in the appendix to this chapter, together with similar results for foils of high purity.

3.2 Measurements of flow stress, electrical resistivity and dislocation density of deformed, high purity, Aluminium foils.

Several foils were prepared and deformed exactly as described in Chapter 2. In this case, the stress was not measured upon unloading, instead a portion of each foil was restressed until further plastic deformation commenced. The load, at this point, divided by the area, which was deduced as before, gave the value of the flow stress for each foil. The results of these measurements are shown in fig. 3.5. The results in the range 0 to 3\% plastic strain, have been deduced from a continuous record in the manner described in the previous section. These results can also be fitted by a
function of the type found in the case of commercial Aluminium;

\[ \gamma = \gamma_0 + \delta \varepsilon_n \]

where in this case:

\[ \gamma_0 = 0.68 \times 10^5 \text{ gms/cm}^2 \]
\[ \delta = 0.76 \times 10^5 \text{ gms/cm}^2 \]
\[ \varepsilon_n \] was the plastic strain %

It is important to state that the measurements of flow stress were made some time after the specimens had been deformed, at approximately the same time as the measurements of the change in electrical resistivity.

The foils were stored for 28 days, after deformation, when several were selected, to measure the change in residual resistivity. The measurements were made exactly as described in the previous chapter. Two undeformed dummy specimens were used in this experiment and the change in residual resistivity has been plotted with respect to the mean residual resistivity of the two. The results of these measurements are shown in fig. 3.6. The relation is obviously a straight line one and since the error in determining the residual resistivity of the foil is greater than the error in determining the plastic strain, the straight line has been fitted by a least squares regression on the ordinate. The results of this calculation indicated that:
\[ \frac{\Delta \rho}{\rho} = (3.8 \pm 0.1) \times 10^{-3} \varepsilon_m + 0.0 \]

where \( \Delta \rho \) was the change in residual resistivity.
\( \varepsilon_m \) was the plastic strain in \%. 

The value of the intercept was not statistically significant. 

The standard error was calculated using the normal laws of statistics.

As was mentioned in the last chapter, it was known that, as the size of the specimens decreased due to deformation, there would be an apparent change in residual resistivity due to the 'size effect'. The magnitude of this effect was calculated (see Appendix 4 for a detailed calculation) and indicated an expected change of:

\[ \frac{\Delta \rho}{\rho} = 0.1 \times 10^{-3} \varepsilon_m \]

To check this calculation, the foils used in the previous experiment were fully recovered by heating for 3 hours at 470°C in vacuo. The residual resistivities were again measured by the technique described previously. The results of this experiment have also been plotted on fig. 3.6 and the points were fitted by a straight line, as before, to give:

\[ \frac{\Delta \rho}{\rho} = (0.5 \pm 0.1) \times 10^{-3} \varepsilon_m - 0.0 \]

Again the value of the intercept on the ordinate was not statistically significant. There is quite clearly a difference between the experimental result and the theoretical prediction.
The present author feels that this in part may be due to the fact that the measurements were carried out using polycrystalline material. The effect of the defects introduced by plastic strain, and retained after storing for 28 days, is clearly given by the difference in slopes of the two graphs. Thus

\[ \frac{\Delta \rho}{\rho} = (3.3 \pm 0.2) \times 10^{-3} \xi_m \]

It should be noted that one foil, that deformed to 10.7\% plastic strain, did not behave in the same way as any of the other foils observed throughout these measurements. Its residual resistivity, both before and after annealing, differed significantly from all the others. No account was taken of this foil in the above calculations. The present author is of the opinion that the impurity content of this foil was markedly different in some way. It should be stated that the flow stress measurement was entirely normal.

A single foil was first examined, to investigate the change in dislocation density after plastic deformation. The foil chosen, had been deformed to 7\% plastic strain. This was prepared exactly as described previously and indicated that the dislocation density due to this deformation, was approximately \( N_m = 10^9/cm^2 \). Several foils were then selected for detailed study. In all but the case referred to
above, these were some of the foils used to determine the change in residual resistivity. Fig. 3.7 shows a graphical representation of the relation between the dislocation density and the plastic strain. The relation was obviously a linear one and a straight line was fitted by a least squares regression on the ordinate; this gave:

\[ N_m = (1.4 \pm 0.1) \times 10^8 \varepsilon_m - 0.2 \]

where \( N_m \) was the dislocation density per \( \text{cm}^2 \).
\( \varepsilon_m \) was the plastic strain in \( \% \).

The value of the intercept on the ordinate was not statistically significant. This method, however, did not give the best estimate of the dependence of the dislocation density upon the plastic strain, since the various points were incorrectly weighted. A corrected estimate was obtained by expressing the results in terms of the dislocation density per unit \( \% \) plastic strain, and averaging all the individual results. This calculation indicated that the following relation between the two parameters referred to above existed:

\[ N_m = (1.26 \pm 0.07) \times 10^8 \varepsilon_m \]

where \( N_m \) was the dislocation density per \( \text{cm}^2 \).
\( \varepsilon_m \) was the plastic strain in \( \% \).

The error quoted is the standard error. The values of the dislocation density per unit strain, have been plotted, as a function of foil thickness and the results of this can be
seen in fig. 3.8. On this basis the results for foil thicknesses of less than 2000°A were discarded, as clearly they did not agree with those obtained for greater thicknesses. This point will also be discussed in the appendix to this chapter. Fig. 3.9 shows a set of typical pictures at different strains, together with an example of a slip trace and a diffraction pattern. It is obvious that the dislocation structure again changed, from a few randomly distributed dislocations, to a cell structure. Details of the distribution of dislocations found, will also be discussed in the appendix to this chapter.

3.3 The annealing behaviour of deformed high purity Aluminium as a function of temperature.

The results of the experiments described in the previous section, showed that a correlation existed between the dislocation density produced by plastic strain, and the change in residual resistivity. An unknown fraction of the change in resistivity, however, might have been due to the presence of point defects produced by the deformation. If the only defects generated were similar to those produced by quenching, then, as has been shown in Chapter 1, they would in all probability have annealed out after a few days. To
throw some light on this problem, the author of this thesis decided to conduct a series of experiments to investigate the annealing behaviour of deformed Aluminium, by studying simultaneously the changes in resistivity, flow stress and dislocation density. If any fraction of the resistivity was due to the presence of point defects, then it ought to be possible to observe a change in the resistivity without a change in either the dislocation density, or the flow stress, while the point defects are removed by suitable annealing. Little was known of the likely behaviour of deformed Aluminium during annealing. Therefore it was felt that the most informative experiment to conduct, was one in which the temperature of a deformed specimen was continuously raised, whilst the three parameters, residual resistivity, dislocation density, and flow stress, were simultaneously measured. It would have been ideal if the same specimens had been used throughout the experiment, but such a scheme would have entailed the use of too many experiments involving liquid Helium and the cost was prohibitive. Instead, therefore, several foils were used, and the results of previous experiments invoked to allow for small variations in the degree of deformation of the individual foils.

Several foils were deformed to approximately 10% plastic
strain and placed within a furnace. The current flowing through the furnace was adjusted so that the temperature of the inside wall rose at a constant rate. The temperature of the foils was measured by placing a thermocouple within the furnace, in contact with one of the foils. The heating rate chosen was $100^\circ C$/hour and one foil was removed every thirty minutes. The annealing took place in a vacuum, but this was interrupted for several minutes every half hour to remove the specimens. These were removed as slowly as was practicable, to avoid any possible quenching in of vacancies. After a specimen had been removed, the furnace was again sealed and the vacuum re-established. Two foils were left unannealed and two were completely re-annealed for 3 hours at $470^\circ C$ in vacuo, to act as dummy specimens. This latter procedure was adopted at the time, to avoid any error due to the 'size effect', but as we have seen in Chapter 2, there was a change in residual resistivity with the number of times annealed.

After two days, the foils were cut and parts used to measure the flow stress. This time was allowed to elapse, to ensure that any point defects generated during deformation or annealing, were removed. The object of this experiment, was to establish the flow stress, both before and after deformation. In this case the results have been expressed
as the flow stress after annealing as a fraction of the stress on unloading. In this way, any measurements of the dimensions of the specimens were unnecessary, as these remained constant. The actual measurements made were 'load required to cause further plastic strain' and the 'maximum load that had been measured during the initial deformation of the specimen'. The only systematic error in these measurements arose for different positions of the zeros on the drum recorder, but this error was common to all specimens. The magnitude of this error was less than 45%. It must be recalled that the stress on unloading a deformed foil is somewhat greater than its flow stress.

Further portions of the foils were then selected and the change in residual resistivity measured. As before, the foils were cut from the central portion of the metal strip. Two dummy foils were used for comparison, to improve the accuracy of the measurements and two foils strained by approximately 10% were also used, for the same reason. This it was hoped, would fix accurately, the magnitude of the total change in residual resistivity.

Specimens from foils heated to 20°C, 100°C, 150°C, 250°C and 350°C were selected for electron microscopy.
These were prepared in the normal manner and representative areas were obtained and examined.

Fig. 3.10 shows the variation of flow stress with annealing temperature. This indicated that the annealing took place in two distinct stages, separated by a quite distinct plateau region, where the dislocation configuration cannot have changed markedly. It can be seen, by comparing figs. 3.10 and 3.5, that the foils heated to above $350^\circ$C have fully recovered.

The results of the measurements of the change in residual resistivity, as a function of annealing temperature, can be seen in fig. 3.10. Certain assumptions were used to derive this graph. The dummy specimens used in the experiment had been subjected to one more anneal than the deformed specimens. As has been pointed out, the residual resistivity of an annealed specimen varied according to the number of times it had been annealed (see Chapter 2 page 79 for a discussion). Therefore the residual resistivities have now been compared to a dummy annealed the same number of times. The error in this assumption was negligible, in view of the many measurements which were made on annealed foils. All the foils used in this experiment would not be pulled to exactly the same
plastic strain. In practice, the deformations ranged from 9.5% to 10.5% plastic strain. The measured increase in residual resistivity was corrected, therefore, to the value it would have had for a specimen deformed to 10% plastic strain, thus:

$$\frac{\Delta \rho}{\rho} = \frac{10}{\varepsilon_m} \times \frac{\Delta \rho_m}{\rho}$$

where $\frac{\Delta \rho}{\rho}$ was the corrected change in residual resistivity.

where $\frac{\Delta \rho}{\rho}$ was the corrected change in residual resistivity.

$\rho_m$ was the measured change in residual resistivity.

$\varepsilon_m$ was the deformation in plastic strain %.

It is clear that there are three annealing stages in the change in residual resistivity. The first two corresponded exactly to those found by examining the change in flow stress. It is interesting to note that the foil heated to 350°C had undergone complete recrystallisation and as might have been expected, had the same residual resistivity as the dummies used in the experiment.

The third annealing stage was entirely unexpected and revealed that a dramatic increase in the residual resistivity of foils took place, due possibly to heating in a mixture of air, water vapour and pump vapour. The magnitude of the change produced could not be shown on the same scale, since the increase was approximately 40% of the residual resistivity.
This change was quite sufficient to account for the anomalous behaviour of the specimens heated at high temperatures in the earlier furnace type of experiments. The puzzling feature of these experiments had been that the resistance ratio of a pair of fully annealed foils changed during the initial period of heating (see page 69). It is clear from these results, that of the two possible explanations discussed, the correct interpretation is that a change in the resistivity took place. A suitable mechanism to explain this result has not been found, but it is quite clear that it cannot have been due to the generation of any form of line defect, as these, in general, affect the flow stress. One possibility, is that there was an addition of a great amount of impurity, or alternatively, that the impurity present had been redistributed by the anneal.

In view of the nature of the annealing curves found (fig. 3.10), it was decided that only a limited number of the foils would be examined in great detail by transmission electron microscopy. The emphasis was thus placed on finding the values for the density of dislocations, before annealing, on the plateau region and after the second annealing stage. A preliminary study showed that the dislocation configuration was similar at several points on the plateau (see fig. 3.11).
and so the foils chosen for detailed study were the unannealed foils, those heated to 150°C and 350°C. The foil heated to 150°C was chosen because its residual resistivity lay nearest to the postulated plateau drawn on fig. 3.10.

The two foils deformed approximately 10%, were examined in detail and the distribution of dislocations found will be discussed in detail in the appendix to this chapter. The density of dislocations found in both specimens agreed with the density of dislocations for 10% plastic deformation, found in the previous experiment. The mean dislocation density was: \( N_m = (12.7 \pm 0.6) \times 10^8 / \text{cm}^2 \)

where \( N_m \) was the dislocation density per cm\(^2\).

The number of separate determinations being 25. Fig. 3.12 shows the variation of dislocation density with foil thickness. This is clearly similar to that found previously for thicknesses greater than 2000\(^\circ\)A (c.f. fig. 3.8).

Fig. 3.11 consists of micrographs which are typical of dislocations found at different temperatures and as can be seen, the arrangement changed dramatically after the first annealing stage, to give a totally different subgrain structure, typical of a metal after recovery. The mechanism for recovery is still not clear, but previous work suggests that
This change was quite sufficient to account for the anomalous behaviour of the specimens heated at high temperatures in the earlier furnace type of experiments. The puzzling feature of these experiments had been that the resistance ratio of a pair of fully annealed foils changed during the initial period of heating (see page 69). It is clear from these results, that of the two possible explanations discussed, the correct interpretation is that a change in the resistivity took place. A suitable mechanism to explain this result has not been found, but it is quite clear that it cannot have been due to the generation of any form of line defect, as these, in general, affect the flow stress. One possibility, is that there was an addition of a great amount of impurity, or alternatively, that the impurity present had been redistributed by the anneal.

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indicated that the average density of dislocations in the foil was:

\[ N_m = (6.3 \pm 0.6) \times 10^3 / \text{cm}^2 \]

The third foil examined in detail was the foil heated to 350°C and this showed, as expected, that the specimen had fully recrystallised. The density of dislocations was so much smaller than in either of the two previous cases, that it was negligible and no exact analysis was necessary.

The results of this experiment, however, left several questions only partially answered. The overall change in the residual resistivity, for the specimens that had been deformed to 10% plastic strain, was somewhat greater than might have been expected from the previous experiment. In this case the change in residual resistivity was: 4.5 ± 0.3% (see section 3.2), as compared to 3.3 ± 0.2% in the previous case. It is pertinent to point out, that in the present experiment, the foils had only been stored for 2 days, compared to 28 days in the previous experiment. It became known at that time that Ham (private communication) had postulated that dislocation rearrangement and annihilation took place in heavily cold-rolled Aluminium, from the surface layers of a specimen during electro-polishing. Ham postulated that
the recovery took place from a region near to the surface of depth approximately equal to the subgrain size. In these present experiments, the subgrain size was approximately 5 to 10 microns for 10% deformed Aluminium foil. It was felt, therefore, that some annealing might well have taken place during the prolonged storage of the specimens used in the first experiment. This might account for the discrepancy referred to above. An alternative explanation clearly presented itself and that was that all the point defects generated during the plastic deformation had not annealed out of the specimens in this second experiment.

The second interesting feature of the experiment described above, was that though the experiment agreed with those of Panseri and Federighi, Federighi, Silcox and Whelan etc., in that a recovery stage for Aluminium was found above 50°C, it was observed that the recovery took place at a lower temperature than that found by previous workers. This might simply have been due to different specimen geometry, but this was unlikely. It seemed therefore worthwhile trying to obtain a value of the activation energy for this first annealing stage, to compare with those of previous workers. It is pertinent to point out that all the previous experiments had been carried out upon loops, introduced by quenching specimens
from a high temperature, whereas the dislocations in this case were introduced by tensile deformation. Therefore some difference in the annealing behaviour might well have been expected.

3.4 The annealing behaviour of high purity Aluminium at room temperature.

As has been stated in the previous section, the increase in residual resistivity of deformed high purity Aluminium differed according to the length of time that the specimens had been stored at room temperature. Two possible explanations were put forward for this discrepancy. The first hypothesis, was that a rearrangement of dislocations took place from the surface regions of the deformed foils in the first experiment, during the prolonged storage at room temperature. The second hypothesis, was that a fraction of the point defects generated during deformation was left after two days and that this had disappeared in the earlier experiment, where the time interval was much longer. The experiment to be described was devised to distinguish between these two hypotheses.

The experiment consisted of measuring the flow stress
and the increase in residual resistivity of deformed high purity Aluminium, as a function of annealing time, at room temperature. If the first hypothesis were correct, then a change in both these parameters ought to have been observed, whereas if the second hypothesis were correct, a change in the residual resistivity ought to have been observed without a change in the flow stress. Again it was impractical to carry out the experiment upon a single specimen, as this would have entailed the use of too much liquid Helium. Therefore specimens were deformed at intervals of several days and then stored at room temperature. In this way, when the two experiments were carried out, the specimens had been allowed to anneal at room temperature for differing times.

The change in flow stress was determined, as in the last experiment, by measuring the load necessary to cause further deformation after annealing and the maximum load measured during the initial deformation of the specimens. Again, it should be pointed out that the flow stress is less than the stress on unloading, so the intercept on the axis of the annealing graph is not unity. The results of this experiment are shown in fig. 3.13. It is apparent that, within the experimental error, no change in flow stress took place.
The change in residual resistivity was also measured for the same specimens. In this experiment the dummy specimens used had received the same number of anneals as the specimens. The only corrections applied, therefore, to the results were to allow for the varying degrees of plastic deformation and the 'size effect'. The technique used was exactly as described previously, but a new specimen assembly had been constructed. With this new apparatus the error in these measurements due to the variation of thermal e.m.f.s was reduced, so that the only significant contribution to the total error arose from the variation of impurity content from foil to foil. The probable error in these measurements was therefore less than ± 0.3%. The results of this experiment can also be seen in fig. 3.13 and clearly there was a significant change in the residual resistivity over a period of several days.

Measurements of flow stress and the change in residual resistivity were made as a function of the annealing out of dislocations in the previous experiment, the results of which were shown in fig. 3.10. From these it is clear that the magnitude of the change in residual resistivity, in this third experiment, was such that a measurable change in the flow stress ought to have occurred if the defects that
annealed out in this experiment, had been dislocations introduced by plastic deformation. The decay in residual resistivity must therefore have been due in a large part to the presence of some other sort of defect.

The most likely defect present in deformed foils is the single vacancy, but it is somewhat surprising that these were present after such a period of time, in view of the many measurements which have been carried out, of the migration energy of quenched-in point defects. As we have seen in Chapter 1, the quenched-in defects were always assumed to be single vacancies and the measured values for their migration energies were approximately 0.55 eV. The time taken for a defect with this activation energy to disappear at a dislocation, would be approximately 3 hours (see Ch. 1 page 20 for a discussion). Therefore, if the defects present in the deformed high purity Aluminium were the same as those present in quenched materials, they would almost certainly have annealed out of the foils before any resistivity measurements had been made.

Two conclusions may be drawn from this experiment. Firstly, there is no evidence to show that a major part of the dislocations anneals out at room temperature after two
days. Secondly, that a defect is present in deformed foils which anneals out at room temperature, with a half-life of a few days. Clearly if this defect was present in the case of measurements made by other authors of the resistivity of deformed foils, then these measurements too may be in error.

3.5 The annealing behaviour of deformed high purity Aluminium at higher temperatures.

A last series of experiments was conducted to investigate, in greater detail, the first annealing stage found in the deformed Aluminium. To try to obtain an estimate of the activation energy of this low temperature annealing stage, a number of isothermal annealing experiments were carried out at different temperatures. Again the parameters measured were, the change in flow stress and electrical resistivity as a function of annealing time at the different temperatures.

If the change in a parameter during annealing is due to a single-valued activation energy process, then the relation between the parameter and the annealing time will be given by:

\[ d\phi = \phi_n e^{-\frac{Q}{kT}} \, dt \]

where \( Q \) is the activation energy.

\( k \) is Boltzmann's constant and \( T \) the temperature.
We can integrate this to obtain the perfectly general expression:

\[ \psi_n - \psi_n^0 = -\Lambda t e^{-Q/kT} \]

where \( \psi_n \) is a function and \( \Lambda \) a constant.

This assumes only that the temperature of the specimen is constant with time. If therefore we carry out a series of isothermal anneals and in each case measure the time \( t \) for a change in the parameter \( \psi \) of a chosen amount, say:

\[ f = \frac{\psi_n^0 - \psi_n}{\psi_n^0} \]

then we can calculate the activation energy from the above equation. If \( t \) is the time for the decay of the parameter by the fraction \( f \) of its initial value, then:

\[ \log e t = \left( \frac{Q}{k} \right) \left( \frac{1}{T} \right) + \log e \left( \frac{t \psi_n^0}{\Lambda} \right) \]

This may be expressed graphically by plotting \( \log t \) against \( 1000/T \) and the slope of the graph will give the value of the activation energy. More information may be obtained from the annealing curves, if the nature of the function \( \psi_n \) is known, but this was not so in the case of the change of flow stress. In the case of the change in electrical resistivity, the only work of this nature on Aluminium had been carried out upon dislocation loops, and so again this general analysis was used.
Again the choice of techniques used was limited by the desire to conserve liquid Helium as far as possible and so accordingly a number of foils were deformed to approximately 10% and the results of the previous experiments invoked, on the assumption that the initial change in resistivity was the same in all cases. The foils were deformed only two days before the annealing took place. In the light of the previous experiment this was an unfortunate choice. However these last two experiments were carried out at the same time and therefore the results of the previous one were not available when this second experiment was planned.

The deformed foils were first stored at room temperature for about two days, in order to remove the vacancies present, and were then annealed at three different temperatures. The specimens were placed inside a liquid-tight Copper box. This was maintained at a constant temperature by placing it within an oil bath. The oil bath could be heated to any temperature, within the range 50°C to 150°C. The temperature of the bath was measured using a mercury-in-glass thermometer and the temperature of the inner wall of the Copper block measured using a thermo-couple, which was standardised by immersing it in the oil bath, to compare it with the mercury-in-glass thermometer. The temperature of
the oil bath was maintained constant to approximately $\pm 0.2^\circ C$. During the anneal the thermocouple was attached to a dummy specimen within the Copper box, to measure the temperature of the specimens. The Copper box was shaped and had a narrow mouth, which just projected above the level of the liquid. The mouth of this box was covered during the annealing, except when specimens were removed. The temperature of the specimens dropped after the removal of one specimen, by as much as 3 degrees, but recovered after approximately 5 minutes to its former value. Therefore the mean temperature of the specimens was calculated to be approximately $1^\circ C$ less than that of the oil bath, with an error of $\pm 0.5^\circ C$.

The amount of Aluminium available restricted the number of annealing experiments to three. Temperatures were chosen which would be expected to show a reasonable variation in the annealing times measured. These temperatures were deduced from the measurements of Panseri and Federighi who investigated the annealing of dislocation loops from quenched materials. It was felt that in both quenched materials and deformed materials, the recovery of dislocations took place by the migration of jogs in the dislocations. If this was so, then both processes ought to have had the same activation energy.
The measurements of the change in flow stress, were carried out as in the previous two experiments and the probable errors were as before. Since in this case, the measurement involved only the change in the parameter, the error due to a constant shift in the axes of the recording paper did not contribute. The results of these measurements can be seen in fig. 3.14. It was apparent that the three annealing curves had different forms and this cast doubt upon the use of this technique for measuring the activation energy of the first annealing stage, as the basic assumption was that the form of the annealing curve was the same.

The measurements of the change in residual resistivity were carried out as described in Chapter 2. The results of these measurements can be seen in fig. 3.15. It is clear from the last experiment, that a fraction of the point defects generated by plastic deformation was still present before the specimens were annealed. These defects probably gave rise to the rapid initial drops in the residual resistivity that were observed in the three annealing curves. In each case, part of the decrease in residual resistivity was due to the annealing out of dislocations. This was deduced from the fact that there was also a change in the flow stress measurements during the annealing process. It was not
possible, therefore, to separate these two processes and so no estimate of the activation energy for the dislocation annealing process was derived. The results were used, however, together with the change in residual resistivity during the annealing at room temperature, to derive a value for the activation energy of migration of the other type of defect present.

The annealing curve at room temperature (see fig. 3.13) showed that the total change in resistivity, due to the annealing out of the defects mobile at room temperature, was approximately 0.8% of the residual resistivity of the dummy specimens used. Since the dislocations were not mobile at room temperature, it was reasonable to assume that they were far less mobile at these elevated temperatures, than the other defects present. Accordingly, the initial drop was ascribed to the defects mobile at room temperature. The time for a fraction $f$ of the defects to anneal out was measured, where $f$ was chosen to be 0.5% change in the residual resistivity, and these were plotted on a log scale, in accordance with the theory given earlier in this section (See fig. 3.16).
The activation energy, for migration of the defects that were mobile at room temperature, was approximately 0.65 eV. No figure can be given for the probable error in this determination, but it cannot be large, because an error of 50% in the time measured for the decay would only change the estimate of the activation energy by \( \pm 0.04 \) eV. The activation energy found was thus significantly different to those measured by other authors, which were referred to in Chapter 1 page 18. Defects with an activation energy of 0.65 eV would have annealed out of deformed Aluminium at a much slower rate than the defects found in the quenching experiments, had these been present. Referring to the calculation on page 19 of this thesis, the calculated time to diffuse by 10^{-4} cm, which was the probable mean spacing of the dislocations forming the sinks at which the vacancies were absorbed, would have increased from 3 hours, in the case of the defects in the quenched materials, to 48 hours in the experiments of the present author. This last figure would seem to be in reasonable agreement with the time taken for the defects to anneal out of the specimens at room temperature, as can be seen from fig. 3.13. It is interesting to note that at the recent conference held at the Argonne National Laboratories, (report in the press), Federighi reported that he had measured a value of 0.63 \( \pm 0.02 \) eV,
or the migration energy of single vacancies in Aluminium, quenched from high temperatures. The discrepancy between this value and those obtained previously, is probably due to the presence of a large number of di-vacancies in the earlier experiments. Such defects are certainly thought to be produced during quenching. It is probable, therefore, that the defect which was mobile at room temperature in the deformed Aluminium used by the present author, was the single vacancy.

Basinski et al.\textsuperscript{36} (1963) measured the resistivity of dislocations at different temperatures in Copper, Silver, and Gold. No comparable measurements have been made in Aluminium. The present author decided to measure the ratio of the resistances of several specimens at room temperature, liquid air temperature and liquid Helium temperature. From these three measurements, the change in resistivity of dislocations from liquid Helium temperature (4.2\textdegree{}K) to liquid air temperature (approximately 80\textdegree{}K) was deduced. The assumption behind these calculations was that the change in resistivity of dislocations between the above two temperatures, was much greater than the change in resistivity from liquid air temperature to room temperature. This was found to be so by Basinski et al. for Copper, Silver and Gold.
The theory for the derivation of the temperature dependence from the measurements, is given in Appendix 4.

The measurements at room temperature and at liquid Helium temperature, were made exactly as described in Chapter 2. The measurements at liquid air temperature were made inside the dewars during the cooling period, before liquid Helium was transferred. These measurements were made in the second apparatus constructed. In this case convection currents could not circulate round the specimens and so the specimens were probably in good thermal contact. Several measurements were made at different times and the period of cooling increased, in order to let the specimens attain thermal equilibrium with the surroundings. Two sets of measurements of this type were carried out, one of these was carried out during the measurement of the annealing at room temperature and the other was carried out during one of the last three isothermal annealing measurements.

The results of these measurements are shown in fig. 3,17 and as can be seen, there is a considerable scatter in these due presumably, to small temperature differences between the specimens at liquid air temperature. It is clear that in each case the results fall into two categories. In the
first category (marked as column A in the table fig. 3.17) both dislocations and the defects mobile at room temperature were present in the specimens. In the second category, (marked as column B in the same table) the majority of the defects mobile at room temperature had annealed out, so that only the dislocations were left. The eight results of this latter group indicated that the resistivity of dislocations increased from liquid Helium temperature, to liquid air temperature, by a factor of $1.6 \pm 0.2$. The error quoted is the probable error derived from the scatter of the results. The values found by Basinski et al.\textsuperscript{36} for the same factor in Copper, Silver and Gold, were 1.6, 1.8 and 1.3 respectively.

The results of the measurements in column A of fig. 3.17 show that the presence of the defects which were mobile at room temperature increased significantly the temperature dependence of the resistivity of the defects present. Since the single vacancy is little more than the absence of one atom in an otherwise perfect crystal, it is perhaps reasonable to suppose that its resistivity will be affected to a great degree by the vibrations of the atoms immediately surrounding it. By the same token the resistivity of the core of a dislocation ought also to be affected by the thermal vibrations of the atoms. In this latter case, however, the position
and width of a dislocation are likely to be affected much less, since the surrounding atoms do not vibrate in phase. There is moreover, no reason to suppose that these results were merely spurious. The present author is of the opinion therefore, that in the absence of any other evidence, the resistivity of single vacancies is extremely temperature dependent.
Appendix to Chapter 3. The distribution of dislocations found in deformed and partially annealed Aluminium.

It was well known even in the earliest studies of dislocations by thin foil transmission electron microscopy, that the density of dislocations in a deformed metal was not constant throughout the specimens. Regions of extremely high density and regions apparently devoid of these defects were often observed. The first attempt to analyse the nature of the distribution found, was made by Ham (1961) who studied the variation of dislocation density in cold-rolled Aluminium foil. In this study he deformed specimens by three different amounts and took three specimens from each. From each specimen he prepared a thin foil and examined these by a similar method to that of the present author. In each case he examined two grains and took two micrographs from each grain. Using the normal laws of statistics he deduced the following component of variance.

<table>
<thead>
<tr>
<th>Amount of Cold Rolling</th>
<th>Components of Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Between Specimens</td>
</tr>
<tr>
<td>18%</td>
<td>0</td>
</tr>
<tr>
<td>45%</td>
<td>0</td>
</tr>
<tr>
<td>88%</td>
<td>1.07</td>
</tr>
</tbody>
</table>
There is clearly a significant difference between the dislocation distribution he found in the specimens deformed by different amounts.

It was worthwhile, therefore, trying to carry out the same sort of analysis in the case of the experiments conducted by the present author. In the absence of any other information, the present author decided that the foils deformed by tensile strain would approximate more closely to the foils rolled to 18% in the experiments of Ham. In these very little variation was found from foil to foil, but equal variations were found from grain to grain and from micrograph to micrograph. Ham did not state how he attempted to take each individual micrograph, so that this cannot be compared exactly with the technique used by the author of this thesis, who attempted, as far as possible, to photograph complete subgrains. As was explained in Chapter 2, the author of this thesis decided therefore, to photograph at least two subgrains within two grains of two specimens from each deformed foil.

The analysis used by the present author was slightly different to that used by Ham. Three components of variance could be deduced directly from the measured values of the
dislocation density. The first in each case was the variation from subrain to subgrain, which was obtained by normalising the densities found within each grain, by expressing these as a fraction of the average density within each grain. The second component of the variance was obtained by expressing the density of dislocations found within each grain as a fraction of the average density found for the specimens. It is clear that this must also include the component of variance due to the variation of the density of dislocations from subgrain to subgrain. In the case of the deformed high purity Aluminium, two specimens given the same nominal treatment have also been compared. As before, this third component of the variance will also contain the variances due to the variation of dislocation density between subgrains and grains. The results of this analysis are shown in fig. 3.18 in tabular form. Each set of results has been divided into measured variances (A) and derived variances (B).

To deal first with the case of the deformed Aluminium of commercial purity, it is clear that the density varied most markedly from grain to grain: but some variation was observed from subgrain to subgrain. The chosen method of obtaining an average density was therefore probably as good as any other that could have been devised. In the case of
the deformed high purity Aluminium, however, the situation was somewhat different. Here the greatest variation took place from subgrain to subgrain and the degree of variation was approximately the same as that found for the commercial purity material. The variation from grain to grain was clearly much less marked. This was quite different to the behaviour of the commercial Aluminium. It is also interesting to note that the variation from one specimen to another, which had also received nominally the same treatment, was negligible. The specimens in this case were those deformed to approximately 10% in the second experiment described (see section 3.2 for a discussion). The two dislocation densities were respectively \((12.4 \pm 0.6) \times 10^8 /\text{cm}^2\) and \((12.8 \pm 1.0) \times 10^8 /\text{cm}^2\). This gave a mean density of \((12.7 \pm 0.6) \times 10^8 /\text{cm}^2\). A students \(t\) test showed that the difference was not significant, as was intuitively obvious. In retrospect, therefore, it would have been better to have taken more micrographs of subgrains within fewer grains. In the case of the partially annealed foil, which was also taken from the second experiment and was heated to 150°C, the variation from micrograph to micrograph was less than the variation from grain to grain.

The results summarised above are interesting for several reasons. Since the different grains were differently orientated,
the resolved shear stress on the primary slip planes must have differed from grain to grain. If most of the slip were taking place on the primary slip planes, then a marked variation ought to have been observed in the density of dislocations in different grains. It would seem to the author of this thesis that the lack of any marked variation in dislocation density from grain to grain in the high purity Aluminium, must mean that there was a great deal of secondary slip during the process of deformation. The impurity present in the commercial Aluminium had a number of effects on the density of dislocation found. The first effect was clearly that the density of dislocations for a given plastic strain was greater in the commercial grade specimens, as can be seen from figs. 3.2 and 3.7. The second interesting result was that the impurity did not seem to alter the distribution of dislocations within a single grain, but did result in a marked variation of density between different grains. It is also interesting to note that in the recovered specimens, there was a marked variation in dislocation density from one grain to another. The author of this thesis, is therefore of the opinion, that the annealing must have taken place at different rates in the different grains, since, as has been shown, the density of dislocations within the grains before annealing, did not differ greatly from grain to grain.
As was stated earlier, it is possible to explain the nature of variations of dislocation density with foil thickness, as a result of the above analysis. It is well known that the dissolution rate of an electro-polish is affected by the free energy of the surface. Clearly, in the commercial specimens, the variation of impurity known to exist between different grains of a specimen, will have caused a variation of the free energy of the surface from grain to grain. Since also the foils selected for viewing were those that were almost dissolved away, then, on average, the thinnest areas will be those where the impurity content was highest. As has been shown, an increased impurity content would have caused an increased hardening rate and, therefore, an increased dislocation density. Thus the thinnest foils viewed in the commercial Aluminium would have had the greatest dislocation densities. This was, in fact, observed, as can be seen from fig. 3.3. In the case of the high purity Aluminium, no such variation should have been observed, since in this case, the variation of impurity between different grains was small. This too was observed as may be seen from fig. 3.8.

The final interesting feature observed during the thin foil microscopy of the partially annealed foils, was that wavy slip occurred in most cases when viewing thin specimens.
An example of this can be seen in figure 3.19. This must mean that pure screw dislocations were present after the annealing, which were retained during the electropolishing. Figure 3.20 shows a series of micrographs of the distribution of dislocations between different sub-grains for the high purity Aluminium.
Figure 3.1 Stress-strain curve for commercial grade Aluminium.
Figure 3.2 The relation between the dislocation density and the plastic strain for commercial grade Aluminium.
Figure 3.3 Variation of dislocation density with foil thickness for commercial grade Aluminium.
Figure 3.4 Micrographs of typical dislocation arrangements found in commercial grade Aluminium at different stages of deformation.

a) Fully annealed X 30,000
b) Deformed 4% X 30,000
c) Deformed 8% X 30,000
d) Deformed 11% X 30,000
e) Deformed 13% X 30,000
f) Deformed 18% X 30,000
Figure 3.5 Stress-strain curve for high purity Aluminium.
Figure 3.6 The change in residual resistivity due to plastic strain for high purity Aluminium.
Figure 3.7  The relation between the dislocation density and the plastic strain for high purity aluminium.
Figure 3.8 Variation of dislocation density with foil thickness for high purity aluminium.
Figure 3.9 Micrographs of typical dislocation arrangements found in high purity Aluminium at different stages of deformation.

a) Fully annealed X 40,000
b) Previous specimen after slip has occurred X 40,000
c) Selected area diffraction pattern of same region
d) Deformed 4% X 40,000
e) Deformed 7% X 40,000
f) Deformed 9% X 40,000
g) Deformed 13% X 40,000
h) Deformed 13% X 40,000
Figure 3.10 The change in the flow stress and residual resistivity of deformed high purity Aluminium on annealing.
Figure 3.11 Micrographs of typical dislocation arrangements found in high purity Aluminium deformed approximately 10% and subsequently annealed. (Annealing-rate 100°C/hour)

a) & b) As deformed X 40,000

c) & d) Annealed to 100°C X 40,000

e) & f) Annealed to 150°C X 40,000

 g) & h) Annealed to 150°C X 40,000

k) & l) Annealed to 250°C X 40,000

m) & n) Annealed to 350°C X 40,000
Figure 3.12  Variation of the dislocation density with foil thickness for high purity Aluminium.
Figure 3.13 The annealing behaviour of deformed high purity Aluminium at room temperature.
Figure 3.14. The change in the flow stress of deformed high purity Aluminium during isothermal anneals.
Figure 3.15: The change in the residual resistivity of deformed high purity Aluminium during isothermal anneals.
Figure 3.16  Activation energy for migration of point defects generated by tensile deformation at room temperature.
The defects present in specimens shown in column A were defects mobile at room temperature, which the present author considered to be single vacancies and dislocations, both of which were introduced by plastic deformation. The defects present in specimens shown in column B were dislocations.

Figure 3.17 The temperature variation of the electrical resistivity of defects introduced by plastic deformation.
### Deformed commercial grade Aluminium.

<table>
<thead>
<tr>
<th></th>
<th>Subgrain to subgrain / &amp; grain to grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$v_{sg} = 0.057 \pm 0.021$</td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$v_g + v_{sg} = 0.125 \pm 0.035$</td>
</tr>
<tr>
<td>25</td>
<td>Subgrain plus grain to grain</td>
</tr>
</tbody>
</table>

### Deformed high purity Aluminium.

<table>
<thead>
<tr>
<th></th>
<th>Subgrain to subgrain / &amp; grain to grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$v_{sg} = 0.075 \pm 0.017$</td>
</tr>
<tr>
<td>25</td>
<td>Subgrain plus grain to grain</td>
</tr>
<tr>
<td>B</td>
<td>$v_g + v_{sg} = 0.060 \pm 0.017$</td>
</tr>
<tr>
<td>38</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Two different specimens</td>
</tr>
</tbody>
</table>

### Partially annealed high purity Aluminium.

<table>
<thead>
<tr>
<th></th>
<th>Micrograph to micrograph / &amp; grain to grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$v_{sg} = 0.050 \pm 0.017$</td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$v_g + v_{sg} = 0.152 \pm 0.059$</td>
</tr>
<tr>
<td>15</td>
<td>Micrograph plus grain to grain</td>
</tr>
</tbody>
</table>

### Grain to grain / Specimen to specimen

<table>
<thead>
<tr>
<th></th>
<th>Grain to grain / Specimen to specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$v_g = 0.066 \pm 0.040$</td>
</tr>
<tr>
<td>B</td>
<td>$v_g = 0.085 \pm 0.020$</td>
</tr>
<tr>
<td>24</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$v_g = 0.102 \pm 0.076$</td>
</tr>
</tbody>
</table>
Figure 3.19 Examples of wavy slip found in partially annealed Aluminium.
Figure 3.20 The distribution of dislocation found in four subgrains of 4% deformed high purity Aluminium.
Chapter 4. Discussion.

Two types of systematic error may have arisen in the measurements described in the last chapter. Point defects were generated during tensile deformation and contributed to the electrical resistivity of the specimens, and it is therefore possible that these were still present when the measurements of the change in resistivity took place. A second error might also have arisen, due to the loss of dislocations during the preparation of specimens for thin foil microscopy. In all the experiments described, the specimens were thinned from 100 microns thick, to between 0.07 and 1.2 microns thick. If a loss of dislocations took place during these experiments then the measured values of the resistivity of dislocations would have been greater than the true value. For the moment, the loss of dislocations will be expressed as the ratio of the density of dislocations in the bulk material, to the density of dislocations in the thin foils, thus:

\[ Y = \frac{\text{Density of Dislocations in Bulk Material}}{\text{Density of Dislocations in Thin Foils}} \]

Clearly Y may differ from metal to metal and may differ according to the density and arrangement of the dislocations within a particular metal. This last error will be discussed further in section 2 of this chapter.
4.1 The resistivity of dislocations in deformed high purity Aluminium.

The energy of migration of point defects, other than single vacancies, was considered to be small\(^3\) compared to that of the single vacancy, and so it was reasonable to assume that the defects mobile at room temperature were single vacancies. The results of the third experiment on high purity Aluminium, (see section 3.4) indicated that these defects annealed out with a time constant of about 4 days. No other changes in electrical resistivity were observed, without changes in the flow stress of the deformed foils. The present author is of the opinion, therefore, that the only significant contribution due to point defects, was that measured in the experiment referred to above. The results of the first and second experiments on high purity material (section 3.2 and 3.3) have been considered in the light of this experiment, and in the second experiment, where vacancies were present, a correction has been made for this.

The results of the first experiment showed that there was a unique relation between the increase in residual resistivity due to deformation and the degree of plastic strain. The foils in this experiment had been stored for 28 days
and as the results of the third experiment showed (chapter 3 section 4) there was then no systematic change in resistivity with time. Therefore the increase in resistivity due to dislocations was:

$$\frac{\Delta \rho}{\rho_0} = 3.3 \times 10^{-3} \varepsilon_m^2 \pm 0.02$$

where $\varepsilon_m$ = plastic strain%

In the same series of experiments, it was seen that a unique relation also existed between the observed dislocation density ($N_m$) and the plastic strain ($\varepsilon_m$), of the type:

$$N_m = 1.26 \times 10^8 / \text{cm}^2 \times \varepsilon_m$$

where $\varepsilon_m$ = plastic strain%

In the range 0 to 13% plastic deformation, the total density of dislocations varied from $0.2 \times 10^8$ to $12.6 \times 10^8$ /cm$^2$ and the resistivity due to dislocations was:

$$\Delta \rho = \frac{(18 \pm 1) \times 10^{-20} N_1}{Y(1)} \text{ ohm-cm.}$$

In the second experiment described in Chapter 3 section 3 the change in the residual resistivity was measured during annealing (see fig. 3.10). The initial value for the total change in resistivity was due in part to the presence of vacancies. This contribution was allowed for, using the results of fig. 3.13. The magnitude of the increase in
residual resistivity due to dislocations, was

$$\frac{\Delta p}{p} = (3.6 \pm 0.2) \times 10^{-3}$$

This is in agreement with the previous experiment. The corrected change in residual resistivity, is shown as a dotted line in fig. 3.10. The observed dislocation density for the two foils deformed to 10% plastic strain, was:

$$N_m = (12.7 \pm 0.6) \times 10^8 / \text{cm}^2.$$ 

This again is in agreement with the previous experiment.

The measured value for the resistivity of dislocations was, therefore:

$$\Delta p = (18 \pm 1) \times 10^{-20} N_1 \text{ ohm-cm.}$$

for a dislocation density of: $$N_1 = 25.4 \times 10^8 / \text{cm}^2.$$

In the second experiment, a plateau region was observed, in which the dislocation existed in a lower energy state. The residual resistivity of this state was $$(1.65 \pm 0.12)\%$$ greater than the value for the annealed foil. This value was derived as the mean of the value for the foils heated to 150°C, 200°C, 250°C and 300°C. This analysis was probably the best available as the flow stress was constant in this region and also the dislocation arrangement was seen
to be similar. (see figs 3.10 and 3.11). The errors in the individual values for the residual resistivity, were such that all the four points lay on the plateau, within the experimental error. The dislocation density was measured at the one strain 150°C, but there was no reason to regard this as atypical of the results obtainable elsewhere. Certainly for the deformed foils, the present writer has shown that similar treatment gives rise to the same dislocation density to within the experimental error. (See the Appendix to Chapter 3).

The density of dislocations was:

\[ N_m = (6.3 \pm 0.6) \times 10^8 /\text{cm}^2. \]

The resistivity of dislocations in the recovered state was:

\[ \Delta \rho = (17 \pm 2) \times 10^{-20} N_1 \text{ ohm-cm}. \]

with a dislocation density of: \[ N_1 = 12.6 \times 10^8 /\text{cm}^2. \]

It is clear that the three measured values agree, within the experimental error, and that no change in the resistivity of dislocations has been observed in the range of dislocation densities studied. The results of all the experiments, where the observed changes in residual resistivity and measured values of dislocation density were conducted on the
same foils, have been plotted in fig. 4.1. The experimental errors for each specimen have also been plotted on this graph. Clearly the results indicate a one-to-one correlation between the increase in residual resistivity and the observed dislocation density, in the range \( N_1 = 0 \) to \( 40 \times 10^8 \) dislocations /cm\(^2\). The slope of the graph has been measured to give an average value for the resistivity of dislocations of:

\[
p = (17.9 \pm 0.6) \times 10^{-20} N_1 \text{ ohm-cm.}
\]

in the range; \( N_1 = 0 \) to \( 40 \times 10^8 /\text{cm}^2 \).

The value for the dislocations in the partially annealed state, where their strain energy must have been reduced, also agrees with the value found in the deformed state, as can be seen in fig. 4.1.

4.2 The loss of dislocations during the preparation of specimens for thin foil microscopy.

As was stated previously, the author of this thesis hoped to obtain an estimate of the loss of dislocations during electro-polishing, by conducting experiments on both high purity and commercial grade Aluminium. It was felt that the additional impurity present in the latter material would serve as an additional source of pinning, during the preparation
of thin foils. If the deduced values for the resistivity of dislocations had been greater in the commercial grade Aluminium, than in the high purity Aluminium, then it would have been reasonable to have assumed that a greater loss of dislocations had occurred in the high purity Aluminium specimens prepared for transmission electron microscopy.

It was not possible to deduce a value for the resistivity of dislocations in commercial grade Aluminium, as was explained in Chapter 3 section 1. It was possible, however, to measure both the flow stress and the dislocation density in both grades of Aluminium. As was explained in Chapter 1 section 1 of this thesis, various theories have been developed which attempt to relate the flow stress and dislocation density. All gave rise to an equation of the form:

\[ \gamma - \gamma_0 = \alpha \cdot G \cdot b \cdot N^2 \]

where \( \gamma_0 \) is the frictional flow stress
\( G \) is the shear modulus
\( b \) is the Burgers vector of the dislocations
and \( \alpha \) is a constant, dependent only upon the type of dislocation arrangement postulated, but essentially independent of the metal.
The various theories, which have been reviewed recently by Nabarro and Holt\(^5\), as was stated in Chapter 1 section 1, predict differing values of the constant\(\alpha\). If a loss of dislocations occurs during the preparation of thin foils, then the relationship found will be of the form:

\[
\gamma - \gamma_0 = \beta \cdot g.b.N_o^2
\]

where \(N_o\) is the observed dislocation density and \(Y = N/N_o\) is the loss factor, thus

\[
\alpha = \beta / Y^2
\]

The present author measured the flow stress and dislocation density for both grades of Aluminium used, and the results of these measurements can be seen in fig. 4.2. The graphs indicate that a relation such as postulated above, holds for both grades of Aluminium, where for:

Commercial Grade Aluminium: \(\gamma_0 = 1.3 \times 10^5\) gms/cm\(^2\)

\[
\beta = 0.42 \pm 0.04
\]

High Purity Aluminium: \(\gamma_0 = 0.2 \times 10^5\) gms/cm\(^2\)

\[
\beta = 0.35 \pm 0.03
\]

Both lines have been fitted by a least squares regression on the abscissa and the errors quoted are the standard errors. Using the theory from above, we have thus:

\[
\frac{0.42 \pm 0.04}{Y_c^2} = \frac{0.35 \pm 0.03}{Y_H^2}
\]

where \(C\) is commercial grade and \(H\) is High purity.
It was assumed that the shear modulus for both materials was the same. Tables given in Kaye and Laby's book indicated that this was so within a few percent. Thus:

\[ Y_c = F \times Y_h \]

where \( 2 \gg F \gg 1 \)

The impurity present in the commercial Aluminium, however, have rise to a measurable value of the fractional flow stress. Since this was the stress necessary to cause dislocations to move, the loss of dislocations, therefore, would have been inhibited by the impurity present in the commercial grade Aluminium. Thus the loss of dislocations from the commercial grade Aluminium cannot have been greater than that from the high purity material. Thus \( Y_c \ll Y_h \). The two can only have been equal if the dislocations were well pinned in both cases. In that case, the additional impurity present in the commercial grade Aluminium will have had no effect upon the loss factor. This would only have been so when: \( Y_c = Y_h = 1 \). From the slopes of the graphs, we know that: \( Y_c \gg Y_h \). It is clear, therefore, that for the two requirements to be equal, the loss in both materials must have been negligible. Thus: \( Y_c = Y_h = 1 \).

A little more evidence for the validity of this statement may be obtained by considering the results of the same
measurements made on the partially annealed and deformed material. Here the same relationship might be expected to hold between the flow stress and the dislocation density, whereas the loss factor might be expected to be greater in the case of the deformed foil, than in the case of the partially annealed foils. Clearly, the higher strain energy in the deformed foils would provide a greater stress to induce rearrangement and loss of dislocations during thinning. The two loss factors would again only be the same if the loss in both cases was negligible. It can be seen that the relation between flow stress and the dislocation density was the same as that observed for the deformed foils (see fig. 4.2). This clearly indicates that the loss factors were approximately the same and that the loss of dislocations in both cases was negligible.

The present author is of the opinion, therefore, that few dislocations were lost during the preparation of specimens for thin foil transmission electron microscopy. The reason for this will be discussed in the light of experiments conducted by other authors. It is interesting to recall, however, that the dislocation density did not vary with the thickness of the specimens for the high purity Aluminium (see figs 3.8 and 3.12 ). The loss factors in the experiments
of the present author are defined, therefore, as:

$$Y_H = Y_c = Y_p = \gamma^p$$

where $p$ = partially annealed

and $\gamma^p \approx 1$

Almost all the other work carried out on Aluminium, in which the loss of dislocations was discussed, is attributable in part, to one man, namely R.K. Ham. In his first experiment, he considered the apparent density of dislocations in cold-rolled foils, using both the random line technique and also the surface intersection technique. Both of these have been fully discussed in Chapter 2 page 37. As the present author pointed out, any conclusion about a different apparent density, could be attributable in part to the different conditions for dislocation invisibility. (See Chapter 2 page 38 for a discussion).

Faulkner and Ham (1962) measured the dislocation density in the same Aluminium used by Clarebrough et al. to measure the stored energy of dislocations. They were thus able to obtain an experimental value for the stored energy of dislocations and they compared this with the measured value for Silver, due to Bailey and Hirsch. The results indicated that the value of the apparent energy of a dislocation in
Aluminium exceeded that for Silver by a factor of 4.7. Assuming that the loss of dislocations was negligible in Silver, the authors inferred that the observed difference was not attributable to a genuine difference in the energy of dislocations in Aluminium and Silver, but simply to the loss of dislocations from Aluminium during thinning. Thus they estimated the loss factor as:

\[ Y_{C1} = 4.7 \]

where \( C1 \) = Clarebrough et al.

where the dislocation density was \( 80 \times 10^8 \text{cm}^2 \) and a marked subgrain structure of diameter about 1.54 microns, was observed.

Ham64 then took an Aluminium-Silver alloy and deformed this by cold-rolling. Part of the samples were then aged and the Silver present aggregated to form pinning points in the material. Both of the samples were then thinned and the dislocation density determined for each. Ham stated that he observed a highly significant difference in the density of dislocations and attributed this to the greater loss in dislocations in the unaged alloy. In terms of the loss factors for the two alloys, this was:

\[ Y_{\text{unaged}} = Y_{\text{aged}} \times 2.5. \]
The implication was that since $Y_{\text{aged}}$ had a minimum value of 1.0, then $Y_{\text{unaged}}$ was greater than 2.5. Clearly this was concordent with the results of the previous experiment.

Ham and Wright\textsuperscript{65} have also conducted experiments on the loss of dislocations during electro-polishing, by observing the change in the resistance ratios of deformed and annealed specimens during thinning. In these experiments the resistance ratio was from liquid air to room temperature. They invoked Fuchs theorem\textsuperscript{39} for the magnitude of the size effect and showed that for the annealed specimens, the resistance ratio decreased due to this phenomenon, in the predicted manner. They then showed that in the case of deformed foils, the resistance ratio decreased less rapidly than one might have expected from the theoretical model and they attributed this to a loss of dislocations during thinning. The next step in their argument, was to postulate a model for dislocation loss and to do so, they argued that since Ham\textsuperscript{66} found that the density of dislocations was independent of thickness in the range 1500°A to 5000°A in a separate experiment, then the loss must have occurred from a region close to the surface and that the density of dislocations, in this region, must have been constant. Fig. 4.3 shows the type of arrangement that they postulated existed. The thickness
of the regions, they stated were \( \frac{1}{2} \) the subgrain diameter. This they assumed to be true since they felt that all the known causes of dislocation loss were due to a surface intersecting a subgrain. They then compared the expected variation of the ratio of resistivity, with that predicted by Fuchs' theory and invoked the agreement with their own results for annealed specimens to justify this assumption. The difference between the theoretically predicted resistivity and the measured value gave the change in resistivity, which they attributed to the loss of dislocations. It should be stated, that in each case, the same specimens were progressively thinned, so no systematic error arose from this source. This change in resistivity was related to the dislocation density, by the following expression, using the model described:

\[
\Delta \rho = 2.3 \cdot C \left( N_1 - N_2 \right) \left( \frac{1}{t} - \frac{1}{t_0} \right)
\]

where 
- \( C \) was the resistivity of dislocations.
- \( N_1 \) was the density of dislocation in the bulk.
- \( N_2 \) was the density of dislocations in the region S.
- \( t \) was the thickness of the foil.
- \( t_0 \) was the initial thickness of the foil.

The value for the resistivity of a single dislocation, they derived from the results of Faulkner and Ham\textsuperscript{63}, and Clarebrough et al.\textsuperscript{38}. These last named authors found that the change in resistivity due to the annealing out of dislocations
in the same material was measured by Faulkner and Ham and was \(8 \times 10^9/\text{cm}^2\). They then invoked the discrepancy between the expected value of the stored energy of a dislocation, and the measured value, to estimate the true density of dislocations in the manner described in the last paragraph, and hence arrived at a value for the resistivity of a dislocation. Substituting this into the above formulae, they arrived at a loss factor of:

\[ Y_{\text{H\&W}} = 5 \pm 2 \]

where \( Y_{\text{H\&W}} = \text{Ham and Wright} \).

It is apparent that to deduce this loss factor, they had to use this same factor to estimate the value of the resistivity of a dislocation.

The material in this last experiment had been deformed in the same manner as the cold-rolled Aluminium, also found to have a dislocation density of \(8 \times 10^9/\text{cm}^2\), by Faulkner and Ham\(^{63}\). We have thus:

\[ C = \frac{0.013 \times 10^{-6} \frac{N}{8 \times 10^9 Y_{\text{Cl}}}}{\text{ohm-cm}} \]

where \( Y_{\text{Cl}} \) is the loss factor in the material used by Clarebrough et al., which had been compressed by 75%. They could have substituted this, to get:
If, as was assumed implicitly by Ham and Wright, 

\[ Y_{H&W} = Y_{Cl} \]

then for the three foils, we have on average, 

\[ 1 = 0.85(Y - 1) \]

This solves to give \( Y \) approximately equal to \(-6\), which is clearly inadmissable. The attempt to estimate the loss factor in this way, clearly gives nonsensical answers, because the choice of the width of the region \( S \) is wrong. A value of the loss factor cannot be deduced by this analysis of the results of the experiments carried out by Ham and Wright, without either, an independent estimate of resistivity of dislocations in an experiment where the loss factor is known, or an accurate knowledge of the dislocation distribution throughout the foils of different thickness.

It is possible, however, to use the results of the present author, and those of Clarebrough et al.\(^{38}\) and Faulkner and Ham\(^{63}\), to estimate the loss factor during the preparation of the thin foils used by Faulkner and Ham\(^{63}\), from the material prepared by Clarebrough et al.\(^{38}\), which had been compressed by 75%. The change in electrical resistivity due to the
annealing out of dislocations was $0.013 \times 10^{-6}$ ohms, measured at liquid air temperature. The dislocation density measured by Faulkner and Ham was $8 \times 10^9$. Thus the resistivity of dislocations was:

$$ p = \frac{0.013 \times 10^{-6} \times N}{8 \times 10^9} \text{ ohm-cm} $$

If we assume, that the resistivity of dislocations is approximately independent of the dislocation number or arrangement; this was certainly found to be true in the experiments of the present author, then

$$ \Delta p = (1.6 \pm 0.4) \left(\frac{18 \pm 1}{Z}\right) \times 10^{-20} = \frac{163 \times 10^{-20}}{Y_{\text{CL}}} N $$

thus $Y_{\text{CL}} = (5.7 \pm 1.5)Z$

It is clear, therefore, that the loss factor in the experiments of Faulkner and Ham greatly exceeded the same factor in the experiments of the author of this thesis.

The only other direct evidence on the loss of dislocations during the preparation of thin foils for transmission electron microscopy, was provided by Valdre and Hirsch, who conducted a series of electro-polishing experiments on lightly deformed strips of stainless steel, in which the slip traces were visible for periods of several days. They electro-polished the specimens from one side only and were thus able to observe
the slip traces formed in the unpolished surface by dislocations which had moved during the electro-polishing process. In this way, they estimated that not more than 10% of the dislocations were lost and that a further error in estimating the dislocation density arose, due to the shortening of dislocations during thinning. This they estimate to be approximately 10%. The present author would like to draw attention to the fact that, as in his own experiments, a small deformation was used and a marked subgrain structure was not observed.

Some additional information may be gained by comparing the measured values of flow stress and dislocation density in various materials. Experiments were carried out upon polycrystalline Silver by Bailey, polycrystalline Copper by Bailey and Hirsch, and Iron by Charrington et al. All these indicated that there was a relationship between the flow stress and dislocation density of the form found by the present author for Aluminium (see page 191).

\[ \tau - \tau_0 = \beta \cdot G \cdot b \cdot N_0^\frac{1}{2} \]

where \( \beta \) was 0.50 \( \pm \) 0.05

These results have been reviewed by Howie. We may, therefore, use these values to relate the loss factor in the
above experiments, to the loss factor in the case of the present author.

Thus

\[
\left(\frac{0.5 \pm 0.05}{Y_{Cu, Au, & Fe.}}\right)^2 = \left(\frac{0.35 \pm 0.03}{Z^2}\right)
\]

\[
i.e. \quad Y_{Cu, Au & Fe.} = (1.4 \text{ to } 3)Z
\]

where \(Z \approx 1\)

We see again, that the loss factor appears to be greater and the present author would like to draw attention to the fact, that the dislocation densities in these experiments were greater than those of the present author, by a factor of approximately 10 and that, moreover, a more marked substructure was observed in these experiments, than in those of the present author.

There appears, therefore, to have been a trend established in all the experiments conducted on polycrystalline material, which indicated that the loss of dislocations is a function of the observed dislocation density and more particularly, of the observed substructure. A high loss factor is seemingly associated with a small subgrain size. In the experiments of the present author, the substructure was poorly developed and the subgrain size did not decrease to less than 5 - 10 microns, at minimum and was much greater than this during the early stages of deformation. In the experiments of Bailey,
Bailey and Hirsch\textsuperscript{11} and Charrington et al\textsuperscript{13}, however, a marked substructure was observed with most of the dislocations found present in the cell walls. In the measurements of Faulkner and Ham\textsuperscript{63}, both on compressed Aluminium (75\%) and cold-rolled Aluminium (88\%), a very marked substructure was observed with almost no dislocations in the interior of the cells and a subgrain size of approximately 1.54 microns. The present author is of the opinion, therefore, that where the substructure is loosely defined and possibly where the subgrain size is large compared to the specimen dimensions before electro-polishing, the loss of dislocations is small, whereas in a material where the substructure is well defined and therefore small compared to the specimen size before electro-polishing, the loss is much greater. The relative sizes of the specimen and substructure may just be due to the fact that well defined structures are always developed as the subgrain size diminishes. It is probable therefore, that the loss of dislocations is associated with the cutting of the subgrain walls during electro-polishing and that the more developed these walls the greater is the loss of dislocations. This is to some extent borne out by the fact that only a small loss was observed by Valdre and Hirsch\textsuperscript{67} in the case of Stainless Steel, where the dislocations lie in well defined slip bands which extend throughout the specimens.
Several experiments are possible to test this type of theory. It would be interesting to repeat the measurements of the present author on much more heavily deformed material. It would also be of interest to carry out an experiment of the type conducted by Ham and Wright but to thin the specimens progressively to less than one micron, so that the final dislocation density and subgrain size could be observed in the same specimens. A comparison between deformed and annealed specimens of decreasing thickness, could yield the increment of resistivity due to dislocations, using an analysis of the type described in Appendix 4 for foils. Another interesting experiment to carry out would be one in which the dislocations were introduced in a known way (e.g. by bending), but the sensitivity of the resistivity measuring apparatus would have to be better than that used by the present author, by a factor of 10. Such an experiment would also require much purer Aluminium than had hitherto been used. It would also be interesting to make measurements of dislocation density in irradiated and non-irradiated specimens, where the irradiation might be used to generate defects which would effectively pin the dislocations and thus change the loss factor.
4.3 A comparison of the various measured values for the resistivity of dislocations in Aluminium.

The various measured values of the resistivity of dislocations in Chapter 1 section 3 of this thesis and the more reliable values for Aluminium, have been summarised in fig. 4.4. The value measured by the present author, has also been included for comparison. Clearly there is a good agreement between the value found by the author of this thesis and that found by Clarebrough et al., but both of these are lower than the measured values of Cotterill and Yoshida.

The value measured by Cotterill may have been in error for two reasons; firstly, the loss factor for the dislocation loops he observed may well have been higher than that for a random array of dislocations; secondly, small unseen aggregates of vacancies may have been present in the measurements made in his quenched materials. Both of these would have introduced an error, such that the measured value was larger than the true value.

Yoshida et al. conducted a series of experiments similar to that described in Chapter 3 section 2 of this thesis, but in their experiments the specimens used to
determine the change in residual resistivity, were different in shape to those used to measure the change in dislocation density. They assumed that the density of dislocations, due to the same plastic strain of these two differently shaped specimens, would have been the same. Furthermore, they allowed only one day for the contribution due to vacancies to decay. It would seem to the present author that this was insufficient, as he found a decay time of about 4 days for vacancies at room temperature. The first error would almost certainly have been systematic, but might have been such that as to over- or under-estimate the resistivity of dislocations; the second error would certainly have led to an estimate value for the resistivity of dislocations greater than the true value. Yoshida et al. did not publish any stress strain data, so it was impossible to obtain an estimate of the relevant loss factors, in the manner adopted by the present author in the last section.

As was stated in the opening paragraph of this section, the values measured by Clarebrough et al. and the present author, agree within the experimental error. It should be recalled that in the experiments of Clarebrough et al. the dislocation densities were deduced from stored energy measured. If the agreement is not fortuitous, and the author
of this thesis can find no reason to suppose it is, then several conclusions of great importance can be drawn. Firstly it must mean that the loss of dislocations was negligible in the experiments of the present author. Secondly that the theoretical relationship used to derive the dislocation density from the stored energy, was correct to \( \pm 25\% \), in the experiments of Clarebrough et al.\(^3\). Thirdly, that over a wide range of dislocation densities, i.e. from \( 2 \times 10^8 \) to \( 4 \times 10^{10} \), the resistivity of dislocations was constant.

The third conclusion will be discussed further in the next section, but the present author would like to discuss briefly, the second conclusion. As was stated in Chapter 1 section 4 of this thesis, Bailey and Hirsch\(^{11}\) and Bailey\(^7\) made direct experimental comparisons between the stored energy of cold work and the dislocation density in Silver and Copper. They found that the expected dislocation densities exceeded the measured dislocation densities by a factor of about 2 to 3. The present author has attempted to show, however, that the loss factor in the experiments of Bailey and Hirsch\(^{11}\) and Bailey\(^7\), exceeded that found in the experiments of the present author, by a factor of 1.4 to 3. (For a discussion see page 202). Clearly, therefore, the discrepancy found by Bailey and Hirsch\(^{11}\) and Bailey\(^7\) could have been due to a
loss of dislocations in their experiments and if this loss was allowed for, then in Copper and Silver, the measured values of the stored energy of dislocations would have agreed with the theoretically calculated values. A similar conclusion may be drawn with respect to the measurements of Faulkner and Ham in Aluminium, who found a discrepancy of 4.7 in the same sense as before; in this case, the present author has shown the loss factor to be \((5.7 \pm 1.5)\). The author of this thesis is of the opinion, therefore, that the theoretically predicted value for the energy of dislocations in Aluminium is correct to within \(\pm 25\%\) and that the values are also correct in Copper and Silver to within the experimental error.

4.4 A comparison of the theoretically predicted and experimentally measured values of the resistivity of dislocation.

The various theoretically predicted values for the resistivity of dislocations have been summarised in fig. 4.5. These have been discussed in greater detail in Chapter 1 section 3 of this thesis. It is clear that all but the last estimate try to distinguish between the contribution due to the core of a dislocation and that due to the long range strain field. It will be useful, therefore, to look at the
experimental evidence of the present author to see what light
this throws on the relative contributions of these two regions.

It may be assumed that the resistivity of a dislocation
is made up of two parts, thus:

$$\Delta \rho = \Delta \rho_c \cdot \Delta \rho_l$$

where $\Delta \rho$ = the total resistivity
$\Delta \rho_c$ = the resistivity of the core
$\Delta \rho_l$ = the resistivity of the long range strain field

Further, if it is assumed that the contribution of the long
range strain field is a function of the total strain energy
of a dislocation, then the results of Clarebrough et al. \cite{38}
may be used to determine the change in the contribution due
to the long range strain field due to recovery. They found
that in cold-rolled Aluminium, about $\frac{1}{3}$ of the strain energy
was lost during recovery and that therefore, about $\frac{2}{3}$ remained.
We may, therefore, write that the contribution of disloca-
tions in the recovered state would be of the form:

$$\Delta \rho = \Delta \rho_l + \frac{2}{3} \Delta \rho_c$$

It is true that the dislocation arrangements were very
different in the experiments of Clarebrough et al. and the
present author. However, since the dislocations had less
strain energy in the former case, the reduction in strain
energy during annealing in the experiments of the present
author was probably a greater fraction of the overall strain
energy than in the case of Clarebrough et al. We may thus
write:

$$\Delta \rho = \Delta \rho_c + \leq \frac{2}{3} \Delta \rho_L$$

for the contribution due to dislocations in the partially
annealed specimens used by the present author. The resis­
tivity of dislocations in the deformed and partially an­
nealed foils was respectively:

$$p = (18 \pm 1) \times 10^{-20} \text{ N\text{-}cm\text{-}cm}.$$  
$$p = (17 \pm 2) \times 10^{-20} \text{ N\text{-}cm\text{-}cm}.$$  

Thus:

$$\frac{(18 \pm 1)}{(17 \pm 2)} = \frac{\Delta \rho_c + \Delta \rho_L}{\Delta \rho_c + \leq \frac{2}{3} \Delta \rho_L}$$

This reduces to: $$0 \leq p_1 \leq 3 p_c.$$  It is clear, there­
fore, that the contribution of the core is at least 25\% of
the total and not negligible as some authors have supposed,
and it is possible that the only significant contribution
could come from the core region.

Fig. 4.5 shows that the long range strain field cal­
culations of Hunter and Nabarro and Seeger and Stehle are much too small to explain the experimentally determined values.
The long range strain field calculation of Seeger and Bross was about 10 times greater than either of the above two, but there are several experimental and theoretical reasons for believing it to be in error. Firstly, it predicted a dependence upon arrangement which has not been found in the experiments of the present author, secondly the value was too small by a factor of about 4 to explain the measured value of the present author and thirdly, Nabarro and Ziman considered that this was an incorrect use of the higher order terms in the Born approximation.

The effect due to diffraction, calculated by Howie for Aluminium, was somewhat too small and in the case of Copper could not possibly have explained the measured values, albeit that they are subject to a large unknown error, Basinski, Dugdale and Howie on the other hand, do not mention the earlier calculation of Howie in their paper.

These same authors also believe that the core contribution is small compared to that of the long range strain field. Harrison on the other hand, produced a value for the resistivity of the core which was by no means negligible, but which was still somewhat too small to explain the measured value of the present author.
Ziman\textsuperscript{39} in his recent review article showed that by treating a metal as made up of neutral-pseudo-atoms an estimate of the resistivity of dislocations could be obtained. The value he estimated was:

\[ \text{\text{\text{\text{\text{(10 to 20)}} X 10}^{-20} N_1 \text{ ohm cm}}, \text{ which is concordent with the measured value of the present author. Furthermore this calculation does not predict a strong dependence upon the arrangement or number of dislocations.} \]

It is also possible to look upon the dislocation as a row of vacancies at the core of the dislocations. For Aluminium the number of atoms per cubic cm is approximately:

\[ N = 6 \times 10^{22}/\text{cm}^3 \]

Simmons & Balluffi\textsuperscript{52} and Reale\textsuperscript{72} have both found that the resistivity of vacancies is approximately:

\[ = 3 \times 10^{-6} \text{ ohm per atomic \%} \]

Since for a given density of dislocation in Aluminium the equivalent vacancies will be at each atom site in the core, then the number of vacancies will be; \[ N_1 \times 10^8/2.89 \text{ per cm}^3 \]

The equivalent resistivity of dislocation will therefore be:

\[ = 17 \times 10^{-20} N_1 \text{ ohm cm} \]

Clearly both this and the last model are in agreement with the values obtained experimentally by the present author.
Figure 4.1 The change in residual resistivity due to dislocations in high purity Aluminium.
Figure 4.2: Relation between the flow stress and dislocation density in Aluminium.

\[ \text{Flow Stress} \times 10^5 \text{grms/cm}^2 \] vs. \[ (\text{Dislocation Density} N_1)^{1/2} \times 10^4 \text{/cm} \]

- As deformed commercial
- As deformed 99.996%
- Recovered 99.996%
Thus $N_2$ is the observed dislocation density in thin foil electron microscopy and $N_1$ the density in the bulk of the material, i.e. $Y = N_1/N_2$

Figure 4.5 The distribution of dislocations in thin foils during electro-polishing, after Ham & Wright.
<table>
<thead>
<tr>
<th>Units</th>
<th>Clare-brough et al.</th>
<th>Cotterill 50</th>
<th>Yoshida et al.</th>
<th>Present Author</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Compression 75%</td>
<td>Quenching</td>
<td>Tensile strain 3 to 14%</td>
<td>Tensile strain 2 to 13%</td>
</tr>
<tr>
<td></td>
<td>X 10^9 cm^2</td>
<td>X 10^9 cm^2</td>
<td>E.M.</td>
<td>E.M.</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>60 to 110</td>
<td>17 to 50</td>
<td>9 to 36</td>
</tr>
<tr>
<td></td>
<td>S.E.</td>
<td>E.M.</td>
<td>E.M.</td>
<td>E.M.</td>
</tr>
<tr>
<td></td>
<td>33 at 80°K</td>
<td>60 at 80°K</td>
<td>65 at 80°K</td>
<td>18±1 at 4.2°K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40± at 80°K</td>
<td></td>
<td>29±4 at 80°K</td>
</tr>
</tbody>
</table>

Measured by stored energy shown as S.E.
Measured by thin film transmission electron microscopy shown as E.M.
+ after applying estimated correction for dislocation loss.

Experimental measurements of the temperature variation of the resistivity of dislocations.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Metal</th>
<th>( \frac{(\Delta \rho/N)<em>{0K}}{(\Delta \rho/N)</em>{4.2K}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basinski et al</td>
<td>Copper</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Gold</td>
<td>1.3</td>
</tr>
<tr>
<td>Present author</td>
<td>Aluminium</td>
<td>1.6 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 4.4 Summary of Experimental measurements.
Theoretical estimates of the resistivity of dislocations

<table>
<thead>
<tr>
<th>Authors</th>
<th>Value. $10^{-20} \text{ohm cm}^3$</th>
<th>Method and remarks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hunter and Nabarro$^{26}$</td>
<td>0.4</td>
<td>Long range strain field 1st Born approximation.</td>
</tr>
<tr>
<td>Seeger and Stehle$^{33}$</td>
<td>0.6</td>
<td>Long range strain field with large dilatation</td>
</tr>
<tr>
<td>Harrison$^{28}$</td>
<td>5</td>
<td>Core as hollow tube</td>
</tr>
<tr>
<td>Seeger and Bross$^{32}$</td>
<td>$\gamma^4$</td>
<td>Long range strain field 2nd. Born approximation gives a dependance upon arrangement.</td>
</tr>
<tr>
<td>Howie$^{30}$</td>
<td>5</td>
<td>Diffraction effect only significant for Aluminium</td>
</tr>
<tr>
<td>Nabarro and Ziran$^{35}$</td>
<td>--</td>
<td>Considered that 2nd. Born approximation gave value for phase shift of electrons not to resistivity.</td>
</tr>
<tr>
<td>Basinski et al.$^{36}$</td>
<td>--</td>
<td>Considered core to be liquid and thus of little effect on resistivity.</td>
</tr>
<tr>
<td>Ziman$^{39}$</td>
<td>10 to 20</td>
<td>Neutral-psuedo-atoms Resistivity not affected by arrangement.</td>
</tr>
</tbody>
</table>

Figure 4.5 Summary of theoretical estimates of the resistivity of dislocations.
Appendix 1. Method of eliminating the error due to thermal e.m.f.'s, when measuring the resistance of a specimen, using a standard potentiometric technique.

When comparing the electrical resistances of two specimens by a standard potentiometric technique, it was necessary to allow for the presence of thermal e.m.f.'s in the potentiometer, the leads to the specimens, galvanometer and standard resistor and also in the specimens themselves. Since the potentiometer was balanced at zero current flowing between the specimens and the potentiometer, the current flowing through all the specimens was the same. Fig. A.1 shows a simplified schematic diagram of the potentiometer and switching circuit used. The procedure for taking measurements, was in all cases to measure the potential across the standard resistor, that across the dummy, then across each of the specimens and finally the dummy. The currents through both the potentiometer and specimens were then reversed, and the measurements repeated. The sum of the potentials in each direction was related directly to the resistance of a specimen and the sum of the currents flowing through the specimen.

With the current flowing in the forward direction, the potential across specimen A was balanced, as shown in fig. A.1,
when:

\[ E_p + \varepsilon_p - \varepsilon_q - I_1R_s = 0 \]  \( - (1) \)

where \( E_p \) = the potential recorded by the potentiometer
\( \varepsilon_p \) = the thermal e.m.f. within " "
\( \varepsilon_q \) = " " " " the specimen leads
\( R_s \) = " resistance of the specimen.
\( I_1 \) = " current through the specimen.

If both currents are reversed, we have:

\[ - E_p - \varepsilon_p - \varepsilon_q + I_2R_s = 0 \]  \( - (2) \)

(1) - (2), gives:

\[ E_p + E_p - (I_1 + I_2)R_s = 0 \]  \( - (3) \)

Thus the sum of the potentials with the currents in the forward and reverse directions, was related only to the sum of the currents in both directions and the resistance of the specimens.

When comparing a specimen \((s)\) to a dummy \((d)\), we have:

\[ E_p^s + E_p^d - (I_1 + I_2)R_s^s \]  \( - (4) \)

and \[ E_p^d + E_p^d - (I_1 + I_2)R^d \]  \( - (5) \)

thus, \((4)/(5)\) gives:

\[ R_s^s = \frac{E_p^s + E_p^s}{E_p^d + E_p^d} \]  \( - (6) \)
Appendix 2. The effect of varying thermal e.m.f.'s in the resistance ratio of two specimens.

If the thermal e.m.f.'s $e_p$ and $e_q$ defined in the previous section, are no longer regarded as constant, then equation (9) becomes:

$$E_{p1} + E_{p2} - \xi_p + \Delta \xi_q = (I_1 + I_2)R_s$$

where $\xi$ changes to $\xi + \Delta \xi$ between measurements.

Clearly equation (6) becomes:

$$E_{p1} - E_{p2} = \frac{(I_1 + I_2)R_s}{2}$$

From equations (1) and (2), we have:

$$E_{p1} - E_{p2} - (I_1 + I_2)R_s = -2(e_p + e_q)$$

The change in thermal e.m.f. could therefore have been estimated from subsequent readings of the potentials across the specimens. This would have required the recording of the time at which each individual reading was taken. The error was reduced, however, to negligible proportions, by waiting for the thermals to become constant.
Appendix 3. Measurement of the change of electrical resistivity due to deformation by high temperature annealing.

The ratio of the resistances of a deformed specimen (s) and an annealed specimen (d) was observed during the annealing out of the defects caused by deformation, and the change in electrical resistivity was deduced.

\[ R_s = \frac{p_s \cdot l_s}{A_s} \quad \text{and} \quad R_d = \frac{p_d \cdot l_d}{A_d} \quad -(10) \]

where
- \( p \) = the resistivity of the specimen
- \( l \) = the length of each specimen
- \( A \) = the area of each specimen

If the specimens were within an enclosure at temperature \( \Theta \) and differed from this by temperatures \( \Delta \Theta_s \) and \( \Delta \Theta_d \) respectively, then:

\[ \frac{\varepsilon_s}{\varepsilon_d} = \frac{\varepsilon_{20s}}{\varepsilon_{20d}} \left( \frac{1 + \alpha (\Theta + \Delta \Theta_s)}{1 + \alpha (\Theta + \Delta \Theta_d)} \right) \]

\[ = \left( \frac{\varepsilon_s}{\varepsilon_d} \right)_{20^\circ} \left( 1 + \alpha (\Delta \Theta_s - \Delta \Theta_d) + \ldots \right) \]

Similarly

\[ \frac{\varepsilon_s}{\varepsilon_d} = \left( \frac{\varepsilon_s}{\varepsilon_d} \right)_{20^\circ} \left( 1 + 2 \alpha (\Delta \Theta_s - \Delta \Theta_d) + \ldots \right) \]

The assumption being that the expansion coefficients were not greatly affected by deformation.
Then \[ \frac{R_s}{R_d} = \frac{p_s}{p_d} \cdot \frac{S}{S'} \] \[ -(12) \]

where \[ S = \left( \frac{c}{\sigma} \cdot \rho \cdot \frac{a_1}{a_2} \right) \] \[ -(12b) \]

and \[ S' = 1 - \alpha \left( \Delta \sigma_s - \Delta \theta_d \right) \] \[ -(12c) \]

If \( X \) is defined as \( \left( \frac{R_s}{R_d} \right)_o \), then it will change if the resistivity of either specimen changes during annealing.

If we define

\[ p_s = \rho \left( \sigma + \Delta \sigma_s \right) + \rho_0 \] \[ -(13) \]
\[ p_d = \rho \left( \sigma + \Delta \theta_d \right) \]

where \( \rho \) = the resistivity due to thermal vibrations

and \( \rho_0 \) = the resistivity due to defects.

Thus \[ X = \frac{\rho \left( \sigma + \Delta \sigma_s \right)}{\rho \left( \sigma + \Delta \theta_d \right)} \cdot \frac{S}{S'} \] \[ -(13a) \]

and \[ \frac{\rho_0}{\rho \left( \sigma + \Delta \theta_d \right)} = X \cdot \frac{S}{S'} - \frac{\rho \left( \sigma + \Delta \sigma_s \right)}{\rho \left( \sigma + \Delta \theta_d \right)} \] \[ -(13b) \]

Clearly the changes in \( X \) would only reflect the changes in the resistivity \( \rho_0 \), if the second term \( \left( k \right) \) was kept constant. Since to a first approximation, the resistivity of a pure metal was proportional to the absolute temperature, then a small change \( \Delta \sigma \) in the temperature difference caused the
second term K to change by an amount $\Delta G/\Theta$. A change also occurred in $S'$, but of a much smaller magnitude, since

$\alpha \approx 3 \times 10^{-5}/^\circ\text{C}$. The value of $S$ could be derived from the measurement at room temperature to within a few percent, so that the error in such a measurement was limited only by the variations of temperature difference between the specimens. Thus $\Delta G/\Theta$ had to be much less than $p_0/p(\Theta + \Delta \Theta)$ the change to be measured, as was explained in Chapter 2 section 2; this was not so for Aluminium pulled in tension.
Appendix 4. Measurement of the change in residual resistivity of a deformed and undeformed specimen.

If the resistance ratio $X$ as defined in the previous section, was measured at two widely different temperatures, then the resistivity due to defects could be deduced;

Subscripts $o$ - indicate measurements at liquid Helium temperature

$1$ - at liquid air temperature

$2$ - " room temperature.

Thus from equations (12) and (14)

\[
\frac{X^o}{X^2} = \frac{T_{o2}}{T_{s2}} = \left(\frac{\rho_s}{\rho_\infty}\right)^o \cdot \frac{S'^o}{S'^2} \quad \text{(16)}
\]

\[
\frac{S'^o}{S'^2} = \delta_{o2} \quad \text{(17)}
\]

Over the wide temperature range used, the expansion coefficient may have changed, due to deformation and if this was so, then:

\[
\delta_{o2} = 1 + (\alpha_s - \alpha_\infty) \Theta_{o2} \quad \text{(18)}
\]

If the contribution due to impurities was the same in each specimen, then:

\[
\rho_\infty = \rho_\infty^o + \rho_o \quad \text{(19)}
\]

and

\[
\frac{T_{o2}}{T_{s2}} = \frac{1 + \frac{\rho_o}{\rho_\infty^o}}{1 + \frac{\rho_o}{\rho_\infty^o}} \quad \text{(20)}
\]
where \( \rho^2_0 \gg \rho^o \)

\( \phi_{o2} \) was the increase in the resistivity of defects from a temperature 4.2\(^{0}\)K, to room temperature, thus:

\[
\phi_{o2} = \frac{\rho^2_0}{\rho^o} - (21)
\]

thus

\[
\frac{\rho^2_0}{\rho^o} \cdot (1 - \frac{\rho^o}{\rho^0 \phi_{o2} T_{o2}}) = T_{o2} - 1 - (22)
\]

and

\[
\frac{\rho^2_0}{\rho^o} = \frac{R_0^2}{R_0^o} (1 + \alpha \theta_{o2}) - (23)
\]

Since in these experiments \( R_0^2/R_0^o \approx 200 \) and \( T_{o2} \approx 1.05 \)
and from Basinski et al.\(^36\), we know that for Cu, Au, and Ag \( \phi_{o2} \approx 1 \) to 2, then:

\[
\frac{\rho^2_0}{\rho^o} = T_{o2} - 1 - (24)
\]

For the purposes of graphical representation, the change in residual resistivity has been plotted throughout this thesis.

It is also apparent that:

\[
T_{12} = \frac{1 + \frac{\phi_{o1} \rho^2_0}{\rho^o}}{1 + \frac{\phi_{o1} \rho^2_0}{\rho^o}} - (25)
\]

and

\[
\rho_{o2}^2 > \rho_{o1}^2 > \rho^o
\]

Thus

\[
\frac{T_{12} - 1}{T_{o2} - 1} = \phi_{o1} \left( \frac{X_{12}^2 (1 + \alpha \theta_{o2}) - \phi_{o2} T_{o2}}{X_{o2}^o (1 + \alpha \theta_{o2}) - \phi_{o2} T_{o2}} \right) - (26)
\]
It was assumed that $\rho_{az} = \rho_{az} = \rho$, to the first approximation. That is, the temperature variation of the resistivity of defects was greatest in the range, liquid Helium to liquid air temperature. The curves of Basinski et al.\textsuperscript{36} indicate that this was reasonable approximation. The author was able therefore to deduce an approximate value for the increase in resistivity of the defects present in the foils, using the measurements of resistance ratio at the three temperatures; liquid Helium temperature (4.2°K), liquid air temperature (80°K) and room temperature.
Calculation of the 'Size Effect' in Thin Films.

As the temperature of a metal decreases, the scattering of conduction electrons by thermal vibrations of the atoms in a crystalline lattice also decrease. As a result of this, the mean free path of the electrons in an infinite crystal increases. However, if the mean free path of the electrons is large compared with the dimensions of the specimen, then the scattering at the surface of the crystal, effectively limits the mean free path of the electrons. The original theory is due to Fuchs, and this predicts that:

\[
\frac{\sigma}{\sigma_0} = 1 - \frac{3(1 - p)}{8 \lambda} + \ldots
\]

(28)

where \( \sigma_0 \) = the bulk conductivity of the material
\( \sigma \) = the measured conductivity of the material
\( p \) = the fraction of electrons specularly reflected at the surface
\( \lambda \) = film thickness
\( \lambda_0 \) = bulk mean free path

The other terms in equation (28) are negligible for \( t \ll \lambda_0 \) and it is most likely that \( p = 0 \), since the surface is unlikely to be regular on the atomic scale.

Chambers deduced values of \( \frac{\sigma}{\sigma_0} / \lambda_0 \) from measurements of
the anomalous skin effect and found that for Aluminium

\[ T_0 = 2 \times 10^{11} \text{ ohms}^{-1} \text{cms}^{-2} \]

For the specimens used in these experiments, of the present author, there was only one small dimension, so that the equation was valid for this case. The value of \( T_0 \), at \( 4.2^\circ\text{K} \) was \( 200 \text{ ohm}^{-1} \text{ cm}^{-1} \), and for \( t = 10^{-2} \text{ cms} \).

\[ 2.7 \times 10^{-6} \]

thus

\[ l_0 = \frac{2 \times 10^8}{2.7 \times 2 \times 10^{11}} = 3.7 \times 10^{-4} \text{ cms} \]

The effective change in resistivity was therefore:

\[ \frac{\Delta \rho}{\rho_0} = \frac{3 \times 3.7 \times 10^{-4}}{10^{-2}} \]

\[-(32)\]

where \( \rho_0 \) = the residual resistivity of the specimen

\[ \frac{\Delta \rho}{\rho_0} = 1.014 \]

\[-(32a)\]

For a foil deformed by \( \xi \% \) plastic strain, the change in residual resistivity was calculated:

\[ \rho = \rho_0 \left( 1 + \frac{\epsilon}{\epsilon_0} \right) \]

\( \ell \) was the specimen length, initially \( l_0 \).

\( w \) was the specimen width, initially \( w_0 \).

and \( t \) was the specimen thickness, initially \( t_0 \).

Now measurements have shown that the change in thickness is approximately twice the change in the width, for these foils,
thus:

\[
\frac{t}{t_0} = \left(1 + \frac{\varepsilon_m}{\varepsilon_0}\right)^{\frac{3}{2}}
\]

\[
= \frac{3 \times 3.7 \times 10^{-4}}{8 \times 10^{-2} \left(1 + \frac{\varepsilon_m}{\varepsilon_0}\right)^{\frac{3}{2}}}
\]

\[
= 0.1 \times 10^{-3} \varepsilon_m
\]

\[-(33)\]

\[-(34)\]

\[-(35)\]

The author of this thesis found, by experiment, that:

\[
= 0.5 \times 10^{-3}
\]

\[-(26)\]

(See section 2 of Chapter 3 for a discussion.)
Appendix 5. The visibility of dislocation

When this thesis was first drafted no one book covered adequately the subject of diffraction contrast. Since then both Heidenreich and Amelinckx have discussed this subject in great detail and the reader is referred to one of these books for a complete treatment. The present author therefore intends this section to outline some of the assumptions behind the theories of diffraction contrast and to be a reference source for the reader.

The conditions for diffraction may be represented graphically by the Ewald sphere construction. (see fig. A.2) The vector $k_o$ is drawn parallel to the incident beam of length $1/\lambda$. The terminal point of this vector is taken as the origin of the reciprocal lattice. A sphere of radius $1/\lambda$ is drawn about the initial point of the incident vector. The condition for diffraction by the $(hkl)$ planes is that the point $(hkl)$ in the reciprocal lattice ($G$ on $\Lambda$) touches the surface of the sphere. The direction of the diffracted beam is $OG$ and $OG = 1/d$, where $d$ is the interplanar spacing thus: $2d \sin \beta = n \lambda$, which is the condition for Bragg reflection. Since the associated wavelength of the electrons accelerated to 100kVolts is $0.037\,\AA$ and the interplanar spacings are $2\,\AA$, the Ewald sphere will cut an
an almost plane section through the reciprocal lattice.

Some of the electrons penetrating the metal are inelastically scattered and these give rise to the phenomenon known as Kikuchi lines. The electrons scattered inelastically through an angle \( \theta \) may be oriented for Bragg reflection so that a fraction of these will appear at \( P_1 \) (see fig. A.3) scattered through an angle of \( 2\theta \) from their original direction. Electrons scattered inelastically through an angle \( \theta \) will also be oriented for Bragg reflection in the same planes when:

\[
\beta_2 = \beta_1 + 2\theta
\]

where \( \theta \) is the angle for Bragg reflection.

Since the number of inelastically scattered electrons decreases with increasing angle of scattering more electrons will reach \( P_1 \) than \( P_2 \). In terms of the diffraction pattern a pair of almost parallel lines will be seen one of which is brighter than the general background and one of which is darker. When the set of planes is exactly at a Bragg reflecting condition the dark deficient line will pass through the central spot and the bright excess line will pass though the diffraction spot of the planes. The position of the Kikuchi lines is therefore sensitive to small changes in crystal orientation and may be used to determine the direction of the incident radiation to a high degree of accuracy.
The kinematic theory of electron diffraction assumes that one electron beam only has been diffracted through the Bragg angle and that it no longer interacts with the incident electron waves. Hirsch et al. 75 show that this is so for thin crystals where no strong Bragg reflection is operating. It is, however, in thick crystals near to the Bragg condition that most micrographs are obtained.

The dynamical theory attempts to solve the Schrodinger wave equation for electrons in a periodic lattice. 72, 73 The effect of the periodicity of the lattice is to split an incident wave into many possible modes. This also leads to a splitting of the energy states of the electron where there was previously a single degenerate state. The theory as at present developed cannot consider all these possible states but some advance has been made by considering only the incident wave and one other. This is equivalent to stating that only one set of planes is oriented for Bragg reflection. By carefully tilting the specimen it is possible to approximate to this condition. The wave equations that result in this approximation can be integrated by the 1 column approximation and in this way it has been possible to account for such observed phenomena as, the effect of thermal vibrations on the diffraction pattern, the thickness and bend contours in electron images. 74
Diffraction contrast arises when only one beam is allowed to contribute to the final image. Under these conditions the kinematical theory has been used to compute the intensity distributions around, stacking faults\textsuperscript{75}, edge dislocations\textsuperscript{76}, screw dislocations\textsuperscript{75} and mixed dislocations\textsuperscript{77}. The dynamical theory has also been used to calculate the distributions around, stacking faults\textsuperscript{79}, screw and mixed dislocations\textsuperscript{80}. Both theories predict remarkably well the type of contrast that arises but the dynamical theory can also account for such features as the variation in image positions as a dislocation as it nears the surface of the crystal. (see eg. Fig 3.\textsuperscript{9}a) The dynamical theory has also been applied to the problem of the contrast that arises from dislocations that intersect the foil normally.\textsuperscript{81} Due to the buckling of the foil surface at the dislocation contrast arises even when the Burgers vector of the dislocation lies in the reflecting planes. With this sole known exception, contrast does not arise when the Burgers vector lies in the reflecting planes, i.e. when: \[ g \cdot b = 0 \]

where \( g \) is the lattice vector in reciprocal space of the planes giving rise to the contrast, and \( b \) is the Burgers vector of the dislocation. Figures A.\textsuperscript{4} & A.\textsuperscript{5} show the intensity profiles for mixed dislocations as predicted by the kinematic and dynamic theories. They give a qualitatively similar picture.

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P refers to the potentiometer circuit
S refers to the specimen circuit
Sw is the selector switch
Es is the potential given by the instrument
Rs is the resistance of a specimen

Figure A.1 shows a schematic arrangement of potentiometric circuit.
Figure A.2 The Ewald sphere construction.

Figure A.3 The origin of Kikuchi lines.
Intensity line profiles for $n=2$ and $\eta = -2, -\frac{1}{2}, -\frac{5}{4}, -1, -\frac{3}{4}, -\frac{1}{2}, -\frac{1}{4}, 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}, \frac{3}{2}, 2$. 
Figure 12. Bright-field image profiles for dislocations of mixed character shown as a function of $p$ (see text) for the case $n = 1$, $t'/\xi_p = 8$, $y/\xi_p = 4$, $w = 0$, $\xi_p'/\xi_p = 0.1$, $\xi_0 = \xi_p$. In order of increasing width the images are for $p = -0.5$, 0, 0.5 and 1.0. The broken curve is for $p = 1$, $\tan \gamma = 1$ and shows the effect of tilting an edge dislocation. This curve is closely similar to that obtained for $p = 1.5$, $\tan \gamma = 0$. 
References.


5. Nabarro & Holt (1964), Advances in Physics, April.


37. Blewett, Coltman & Redman (1955), Rep. of Bristol
Conf. Defects in Crystalline Solids. Physical Society
40. Livingston (1962), Acta Metallurgica 1, 519.
42. "Direct Observation of Imperfections in Crystals," Inter-
Science.
43. Seeger & Schoeck (1953), Acta Metallurgica 1, 519.
44. Seeger & Kronmuller (1962), Phil. Mag. 7, 897.
45. Clarebrough, Heargreaves & Loretto (1962), Phil. Mag., 7,
115.
48. Silcox & Whelan (1960), Phil. Mag. 5, 1.
50. Cotterill (1963), Phil. Mag. 8, 1937.
51. Yoshida, Wino, Kiritani, Kabemoto, Maeta and Shimomura
53. Feltham (1964), Metallurgia 70, 55.
54. Kovacs, Nagy & Feltham (1964), Phil. Mag. 9, 797.
58. Smith & Guttman (1953), J. Metals, N. Y. 5, 81.
61. Ham & Sharpe (1961), Phil. Mag. 6, 1193.
62. Kaye & Laby "Physical and Chemical Constants," Longmans-
Green.
63. Faulkner & Ham (1962), Phil. Mag. 7, 279.
64. Ham (1962), Phil. Mag. 7, 1177.
65. Ham & Wright (1964), Phil. Mag. 10, 937.
66. Ham (1962), McMaster Univ. Conf. of Metallurgists.
70. Howie & Swann (1964), Phil. Mag. 6, 1215.
72. Heidenreich (1964), "Fundamentals of Transmission
    Electron Microscopy", Inter-Science.
77. Gevers Ibid 7, 651.
    Ibid 267, 206.
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