STUDIES OF DISLOCATIONS IN CADMIUM BY OPTICAL AND X-RAY MICROSCOPY

by

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ABSTRACT

Specimens prepared from melt grown high purity single crystals of cadmium have been examined by optical and X-ray microscopy. The X-ray microscopy examination was carried out using the Lang technique. A correlation, although not a direct one, between etch pits on the (10\(\bar{1}0\)) plane produced using a dilute Nital solution and dislocations has been obtained. The substructure of cadmium in specimens prepared in both basal and (10\(\bar{1}0\)) orientation has been studied.

Large edge type dislocation loops have been observed in basal oriented slices after annealing and slow cooling and provisional Burgers vectors of \{0001\} and \{1\(\bar{2}3\)\} attributed to them. A tentative explanation as to their origin has been arrived at.

The annealing kinetics of \{1\(\bar{2}3\)\} loops at room temperature has been studied.

A marked dependence upon the cooling rate and annealing regime on the room temperature dislocation density and subgrain size for basal oriented specimens has been found.

The alcohol based nitric acid etching and polishing solutions for cadmium have been chemically examined.

A novel temperature programmer developed in conjunction with another person in this department and used for producing high quality single crystals of cadmium for X-ray microscopy examination has been patented by N.R.D.C.
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The deformation modes of metals possessing a hexagonal structure have been somewhat neglected as a subject of research in recent years, despite many interesting features not possessed by cubic metals (such as pronounced elastic anisotropy and non-close-packed slip directions). The reasons for this neglect are mainly technical, inherent in the low melting point and consequent rapid recovery at room temperature and their extreme softness in the pure condition.

1.1. The deformation modes in h.c.p metals

Table 1.1 gives a list of the lattice parameters of some hexagonal close packed metals and table 1.2 a list of the six available types of slip system by which an hexagonal close packed metal may deform. The most recent review of the deformation modes of hexagonal close packed metals has been given by Partridge.

Slip in the \( \langle 11\bar{2}0 \rangle \) direction occurs in all h.c.p metals and such basal slip predominates in magnesium, zinc and cadmium from which the Burgers vector of the slip dislocations, knowing the c/a ratio for these metals can be inferred. Prismatic slip in magnesium single crystals at room temperature is difficult to promote. At elevated temperatures zinc single crystals have been observed to exhibit prismatic slip and at room temperature slip on the \( \{11\bar{2}2\} \langle 11\bar{2}3 \rangle \) system. Single crystals of cadmium exhibit prismatic slip at elevated temperatures: At low temperatures, second order pyramidal slip has been detected.

An important deformation mode for certain orientations of h.c.p crystals in compression is kink boundary formation and this has been observed in magnesium, zinc and cadmium.

H.c.p metals may also deform by twinning which occurs on the \( (10\bar{1}2) \) plane and there is also some experimental evidence for
twinning on a variety of other planes but the mechanism of nucleation and growth is obscure (15).

1.2 Recent deformation studies on bulk single crystals of cadmium

Blasdale et al (12,13,14) have investigated the formation and structure of kinks formed during tensile deformation. The structure of the kinks formed was elucidated by using a dislocation etch for the (10\overline{1}0) plane, which consisted of 1 part by volume of fuming nitric acid in 99 parts by volume of ethanol (1% Nital). Considerable work was carried out by them to establish that this solution was a dislocation etch and in particular Blasdale (16) showed that linear edge dislocation multipoles and symmetrical quadrapole etch pit configurations observed by them were in excellent agreement with such configurations calculated using anisotropic elasticity theory.

More recently Luke (17) has deformed high purity crystals of the same dimensions and orientation as those used by Blasdale et al and studied the deformation of such crystals while suppressing kinking. He evaluated further the dislocation etch of Blasdale et al and his work, added more evidence that the etching solution was a dislocation etch, although he was not able to show conclusively a one to one correspondence between dislocations and etch pits on the (10\overline{1}0) plane. Luke also made an extensive investigation of the damage injected into single crystals of cadmium by a Servomet SMD spark cutting machine. This was the instrument used by him for cutting, and by the author for cutting and sectioning of single crystals and was carried out to enable suitable cutting procedures to be found for preparing damage free thin foils for transmission electron microscopy studies.

In conjunction with the author Luke carried out a chemical
examination of the 1% Nital etch and a chemical and electrochemical polish for cadmium, 20% Nital, and attempted to elucidate the mechanism of etch pit formation on the (10\text{10}) plane.

1.3 Significance of studies of dislocations in undeformed single crystals

The work for this thesis was initially the study of the pre-yield region of deformation in cadmium, using etch pit and X-ray topography techniques. The X-ray topography technique necessitated using foils 75\text{um} thick at most and of low dislocation density $10^5$ lines per cm$^2$. This combined with the extreme softness and marked recovery at room temperature exhibited by cadmium presented technical difficulties which could not be overcome in the time available. Attention was therefore directed towards obtaining information of the substructure and individual dislocation configurations in undeformed single crystals using an etch pit and X-ray topography technique. It was hoped that the correlation between dislocation etch pits on the (10\text{10}) plane and dislocations within the bulk foil could be determined using the techniques referred to earlier. Such a correlation is particularly important in a low melting point metal such as cadmium where considerable recovery takes place at room temperature. It is this excessive recovery which takes place and the extreme softness of the material which necessitates that ideally in all experiments two independent methods should be used estimating the dislocation density and determining the dislocation configuration.

In order to understand the deformation mechanism of a crystalline material it is necessary to have a knowledge of the dislocation arrangement before deformation has occurred, since the manner in which the crystal does deform is dependent upon the
initial dislocation density and configuration. As pointed out by Seeger, Mader, and Krommüller (18) "The low values of the critical resolved shear stress $\tau_c$, which is one of the most striking features of the plastic deformation of single crystals is due to the presence of mobile dislocations even in the virgin crystal". Thus any realistic work hardening theory proposed must take into account the prestrain dislocation arrangement. The study of the dislocation arrangement in undeformed crystals is thus of considerable importance if any great advances are to be made in the understanding of work hardening mechanisms.

This is particularly true in the case of hexagonal close packed metals. As pointed out by Clarebrough and Hargreaves in a review article as late as 1959 (19) "apart from rather indefinite suggestions, there is no clear indication from available experimental evidence of the mechanism of work hardening in hexagonal metals". Later Price (20) wrote "What is needed, clearly, is a detailed knowledge of the substructure which develops in these crystals as a result of mechanical and thermal treatment". Price (his work is discussed in section 1.5) has obtained such information from vapour grown platelets of zinc and cadmium using the electron microscope. The platelets he used were initially dislocation free. Such material is far removed from melt grown single crystals, upon which most deformation studies are carried out. In such material the initial dislocation density alone is of the order of $10^6$ lines per cm$^2$ at least.

The author has attempted in this thesis to obtain detailed information of the substructure of undeformed bulk single crystals of cadmium. The X-ray technique used enabled specimens far more representative of the bulk to be examined than could have been examined by transmission electron microscopy, since the thickness
of the specimens examined were two orders of magnitude greater than could be examined with the latter technique, even though prior to X-ray examination, specimens produced from as grown single crystals had to be subjected to an exacting heat treatment.

Unexpected results were obtained which could not have been predicted from previous work carried out on platelets and this has justified the great deal of time that was spent in overcoming the many technical difficulties presented by the problem.

1.4 Etching of dislocations in Zinc and Cadmium

Luke (17) has recently reviewed the etching methods available for zinc and cadmium; of those reported for zinc, the majority have been of the decorative method. Wernick and Thomas (21) first reported a dislocation etch for high purity cadmium single crystals which was operative on the (10\{\}O) plane, but Blasdale (12) found that the fine detail of the kink structure on his deformed crystals was not clearly shown using this etch. A further etch for the (10\{\}O) plane of cadmium has been reported by Kratochvil and Homala (22), but both Blasdale (12) and Luke (17) have cast doubt on its validity as a dislocation etch.

Of all dislocation etches available for zinc and cadmium, that of Blasdale et al for the (10\{\}O) plane of cadmium has been most fully evaluated. Not only has considerable work been carried out by them to establish that their etch was in fact a dislocation etch, but Luke (17) has added further evidence as to its validity, even though to date a one to one correspondence between etch pits and dislocations has not been shown.

1.5. Electron Microscopy of Zinc and Cadmium

Berghezan et al (23) have prepared thin foils of zinc from heavily deformed cold rolled ingots. They observed the frequent appearance of large edge dislocation rings in the basal plane,
and concluded that these were formed by the condensation of vacancies produced during cold work. In the electron beam the loops were observed to expand and contract. They proposed that the growth of loops was due to the condensation of further point defects, either vacancies resulting from deformation, which had started to migrate as a result of thermal activation by the electron beam, or vacancies originating at the foil surface.

Mader (24) has reported the work of Pfeiffer (25) who has examined deformed zinc single crystals by thinning slices cleaved parallel to the basal plane. He observed a large number of dislocation rings containing stacking faults, lying parallel to the basal plane which he concluded were produced by condensation of point defects created during deformation and were of a prismatic nature. Kratochvil (26) has recently studied basal slices of zinc crystals and observed the loops reported by Berghezan et al in foils from deformed crystals. Kratochvil also prepared foils from slices of deformed crystals and found that the density of loops did not increase.

Price (27) has deformed vapour grown zinc platelets by second order pyramidal glide in the electron microscope and observed the subsequent formation of long narrow dislocation loops in the basal plane. He concluded that these loops were formed from jogs in \( \langle \overline{1}1\overline{2}3 \rangle \) screw dislocations as a result of these dislocations cross gliding to avoid obstacles. He observed that these loops split up into rows of circular loops the Burgers vector of which was the same as that of the parent dislocation or \( \langle 0001 \rangle \) as a result of the dislocation reaction

\[
\frac{1}{3} \langle \overline{1}1\overline{2}3 \rangle \rightarrow \frac{1}{3} \langle \overline{1}1\overline{2}0 \rangle + \langle 0001 \rangle
\]

both types of loop were sessile and shrank and disappeared at room temperature, by he concluded, diffusion of vacancies between the
loop and platelet surface. In a later report (28) he states that he observed in a zinc platelet that the long narrow dislocation loops produced by deformation showed no tendency to break up into smaller loops when the deformation took place at -60°C. However in a later review (29) he states that the narrow loops formed in zinc did break up into smaller loops even at -120°C.

Harris and Masters (30) have studied the annealing of faulted loops in quenched zinc and have reported that all the loops lay in the basal plane. The image contrast was consistent with the hypothesis that the loops were formed from vacancy clusters and had a Burgers vector equal to 1/6<20\bar{2}3>. By various annealing procedures they found they could produce loops which both grew and shrank. In specimens air cooled from 415°C the vacancy concentration at room temperature, estimated from the loop density was of the same order of magnitude as that of the thermal equilibrium value at a temperature just below that of the melting point of zinc. They concluded that quenched in vacancies could not escape from the specimen as the thin foil surfaces were coated with an oxide film. Commenting on the previous observation of loops in deformed zinc specimens by other workers they suggested that loops were formed as a result of quenched in vacancies produced at some time during the specimen's cooling history.

Dobson and Smallman (31) have studied the formation of dislocation loops in quenched zinc specimens. They have rejected the proposals of Harris and Masters and advocated that the growth and shrinkage of loops is due to the formation of an oxide film formed on the specimen surface during electron irradiation. The growth of loops they attributed to the absorption of vacancies emitted during the formation of the oxide film and the shrinkage as a result of vacancies to regions immediately below cracks in
Electron microscopy of cadmium is almost entirely limited to the work carried out by Price (32,33) on vapour grown basal platelets. These he studied by deforming them in the electron microscope over the temperature range +25° to -150°C. During second order pyramidal glide \( _c^a \) screw dislocations were observed to become jogged while cross gliding to avoid an obstacle. These jogs were observed to become pinched off and subsequently split up into rows of circular sessile loops of Burgers vector \( _c^a \), and sometimes \( _c \) by the reaction:

\[
\frac{2}{3}\{\{1120\} - \frac{1}{3}\{1120\} + \{0001\}
\]

in which a \( _c^a \) loop split up into two concentric loops, the outer having a Burgers vector \( _c \) and the inner having a Burgers vector \( _a \). The inner loop subsequently collapsed by glide leaving only a \( _c \) loop. In (10\(\overline{1}0\)) reflections some of the loops had dark centres indicating that they contained a stacking fault. Price suggested that many of the \( _c^a \) loops decomposed into stacking fault loops with Burgers vector \( \frac{1}{2}\{1120\} \), since this would lead to a reduction in the loop energy, provided the loop was not too large. All the loops were stable below -120°C, above this temperature the loops both grew and shrunk, the growth he concluded resulted from the absorption of point defects produced by ion bombardment. Price has summarised his work on cadmium and zinc in a review on electron microscopy of h.c.p. metals (29).

More recently Crump and Mitchell (34) have studied the formation of basal loops in cadmium platelets exposed to the electron beam. They concluded that the formation of loops was due to the aggregation under the influence of the electron beam of small vacancy clusters incorporated in the platelet during growth, and often observed the rapid disappearance of loops and the subsequent
appearance a few seconds later of linear arrays of imperfections. These arrays always lay in the basal plane and grew into an hexagonal network which subsequently shrank and disappeared. Their interpretation of their results contained a number of difficulties which they could not resolve without further work.

Michel and Ogilvie (35) have examined zinc and cadmium platelets by the Lang X-ray technique and electron microscopy. On exposure to air at 20°C these platelets initially dislocation free become less perfect with time. The imperfection structure was found to be similar in both zinc and cadmium. Loops, hexagonal arrays and line defects were observed to appear during the whole observation period, except in the case of zinc where no new loops were nucleated after a period of a few days. In the cadmium specimen examined most of the loops were unfaulted and they concluded that they had Burgers vector equal to \( c \). The rate of growth and final size of the loops formed in cadmium was greater than that in zinc, and in the latter the hexagonal arrays were observed to contract and disappear, as previously observed by Crump and Mitchell. Platelets of cadmium again initially dislocation free when subjected to electron irradiation in the electron microscope showed expanding loops after a few seconds. They were still observed to be nucleated and grow when a carbon film, acting as a barrier to negative ions was interposed between the platelet and electron beam. They explained their results by the oxide film mechanism proposed by Berghezan et al for zinc.

1.6. X-ray Microscopy

1.6.1 In this section a review will be given of various methods of microscopic examination of crystals by X-ray diffraction methods. Micrographs obtained by such means are termed X-ray diffraction topographs. Before however going onto discuss these methods some
limited discussion will be given of the general theory of diffrac-
tion of X-ray by crystals.

When considering X-ray diffraction properties of large nearly
perfect crystals, the situation is far removed from the more fam-
iliar case of X-ray diffraction from small usually imperfect
crystals as are used for instance in X-ray structure analysis.
The diffraction behaviour in large crystals can only be satis-
factorily described in terms of a dynamical theory which deals
with the wavefield in the crystal as a whole. The Darwin model
gives a useful picture of the behaviour in perfect crystals.
Consideration in this model is given to the interchange of energy
between the direct and diffracted beams as a result of multiple
reflection from planes under conditions where extended lattice
periodicity enables phase relations to be maintained between all
rays. As a result of the maintainence of coherence the direct
beam is especially rapidly attenuated when Bragg reflection occurs
and the same destructive interference greatly limits the strength
of the integrated reflections. It is found that the integrated
reflection from an "ideally perfect" crystal is one to two orders
of magnitude smaller than that from an "ideally imperfect" one;
Moreover the angular range of reflection from perfect crystals is
limited to a few seconds of arc. Thus any imperfection in the
crystal which disturbs the regular lattice periodicity upon which
the maintainence of coherence depends will manifest itself by an
increase in the diffracted intensity in the vicinity of the im-
perfection. Coherence can be lost at a variety of imperfections:
low angle boundaries, stacking faults, distortions around inclu-
sions and particularly at dislocations.

In the transmission X-ray diffraction methods there is a def-
ine distinction made between "thin" and "thick" crystals. If
is the mass absorption coefficient for X-rays, \( \mu \) equals the true linear absorption coefficient, \( p \) equals the density of the crystalline material and \( t \) equals the thickness of the crystal measured along the diffracting planes, then \( \mu t \leq 1 \) defines a "thin" crystal and \( \mu t > 1 \) defines a "thick" crystal. If \( \mu t > 1 \), only a small fraction of the incident beam will normally be transmitted, and the intensity of the emergent beams will only be appreciable if anomalous transmission (see below) can be induced. The absorption coefficient varies with wavelength and atomic properties of the crystal and the transition between the two cases may vary between 1\( \mu \)m and 1cm.

1.6.2 The X-ray microscopy methods which allow one to measure point by point on the surface or in the interior of a crystal the local crystal perfection are

(a) The Berg-Barrett (Back diffraction Bragg case)

(b) The Borrmann Anomalous transmission (Thick crystal transmission Laue case \( \mu t > 1 \))

(c) Lang, scanning transmission (Thin crystal transmission Laue case \( \mu t \leq 1 \)).

A feature common to all three methods is that they use a characteristic X-ray wavelength, normally the K\( \alpha \) line. This line is chosen principally because of its high intensity. The K\( \beta \) lines are filtered out to avoid confusion during orienting the crystal for a particular Bragg reflection, by a material in the form of a foil of suitable thickness whose K absorption edge lies between the K\( \alpha \) and K\( \beta \) lines emitted by the target element.

Berg-Barrett Method

This method originated with Berg (36, 37) who around 1930 reported two methods for studying the fine structure of diffraction spots. From these studies it was possible in principle to map local imperfections in crystals. Barrett (38) in 1945 improved
upon the technique with the following critical conditions (for
the experimental arrangement see Fig. 1.7) (i) Minimum distance
between the crystal and photographic emulsion.
(ii) Large distance between X-ray source and crystal.
(iii) Fine grained emulsions protected from the direct beam
(iv) X-ray target element of low atomic number. The first two
conditions were instituted to obtain the maximum geometrical
resolution and the fourth to produce characteristic radiation
relatively free of "white radiation" which tends to contribute to
an increased overall background radiation, so reducing the clarity
of the diffracted image.

With this technique only surface layers up to a thickness of
5μm can be examined and this represents only a small volume of
material. Moreover since a line focus is used, the horizontal
width of the X-ray source leads to both components of the Kα-line
i.e. the Kα₁ and Kα₂ contributing to the diffracted image leading
to two images on the recording emulsion and this limits the reso­

Borrmann Anomalous transmission Method

The phenomenon was first reported by Borrmann (39) (see Fig.
1.8 for the experimental arrangement). It arises as a result of
interference between the incident and reflected waves, which set
up a stationary wave system inside the crystal. The nodes of the
stationary waves for the transmitted and diffracted beams are
situated at atomic sites, if the crystal is highly perfect and
oriented exactly for Bragg reflection. Absorption is thus nearly
eliminated because the wave amplitude is minimum at atomic sites.
The standing waves lie along the diffracting plane. Anomalous
absorption properties are lost at imperfections such as dislocations
and they give a weaker image than the perfect matrix. The
diffracted and transmitted beams leave the crystal at the same point and experimentally either beam maybe used to reveal information regarding the defects in the crystal since they have comparable intensities.

Lang scanning Method

Lang first reported this method in 1959 (40). The experimental arrangement is shown in Fig. 1.9. In this method a point X-ray focus is used so that the crystal is effectively uniformly bathed in radiation. The angular divergence of the beam is thus sufficiently small to allow only one component of the characteristic radiation i.e. the $K_{\alpha}$ to be diffracted.

The emulsion plate and the crystal are synchronously scanned to and fro through the X-ray beam. A stationary opaque screen allows only the diffracted beam to reach the emulsion. A large area and hence volume can be examined, a distinct advantage over the Berg-Barrett method. Further advantages of the method are that a lower background intensity is recorded and less trouble is encountered with simultaneous reflections, since the incident beam is well collimated. A marked advantage over the Borrmann method is that less highly perfect crystals maybe examined. This follows from the fact that for defects to be individually resolvable, the following relationship must be satisfied $P \ll W \cdot t$, where $P$ is the defect density $/cm^3$, $W$ the defect image width, $t$ the thickness of the crystal measured along the diffracting planes.

1.7 Further consideration of the Lang Method

It is evident from the outline of the method given in the previous section that a two dimensional picture is obtained on the emulsion plate, and that this picture is the projection of the crystal slab and its imperfection content, and hence is termed a "projection topograph". Additional information e.g. the spatial
distribution of the imperfection content maybe obtained from stereo projection topographs, composed of a pair of projection topographs of the reflections hkl and \( \overline{h}k\overline{l} \).

Since the Lang scanning method was the X-ray technique which was used for observing the substructure and dislocations in bulk grown single crystals of cadmium for this thesis some consideration will be given to outlining the resolution attainable and the factors governing it.

Hart (41) has given a detailed account of these and the summary given here is that resulting from detailed discussions between him and Lang and reported by the former.

1.7.1 Geometrical factors

(i) The geometrical resolution in the vertical direction is determined solely by the projected size of the focus in that direction. He and the author used in all experiments a Hilger and Watts micro-focus generator the focal dimensions of which are 1.4mm x 0.1mm. The focus is viewed end on with a takeoff angle of 5° and the ratio of distance of focus to crystal to crystal to emulsion is approximately 45. Thus the effective shape is a square of sides approximately 100\( \mu \)m. Using this value Hart estimates the geometric resolution in the vertical direction as 1.5\( \mu \)m.

(ii) The geometric resolution in the horizontal plane is determined by the angular width of the diffracted beam. This is dependent upon the reflection curve, due to the finite wavelength spread in the characteristic wavelength peak and upon the width of the convolution of the intrinsic perfect crystal reflection. Hart has estimated these to be 0.6\( \mu \)m and 2.6\( \mu \)m respectively, which is commensurate with the resolution in the vertical plane.

1.7.2 Geometric topographic distortion

In all reflections the emulsion plate is placed so that it
is perpendicular to the diffracted beam. Under this condition the topographic distortion is as given below.

(i) The amount of distortion in the vertical direction is given by \((1 + b/a)\) where \(a\) is the focus to crystal distance and \(b\) is the crystal to emulsion distance. This is always greater than unity by a few percent and varies from point to point on the topograph unless the emulsion is parallel to the crystal.

(ii) The distortion in the horizontal direction is equal to \(\sin(\alpha - \theta)\), where \(\alpha\) is the angle between the operative reflecting planes and the surface of the crystal exposed to the X-ray beam, \(\theta\) is the Bragg angle for the operative reflecting planes and X-ray wavelength.

1.7.3 Recording emulsions

Nuclear emulsion plates are used to record the diffracted beam. Two types since 1959 have become commercially available, Ilford G5 and L4. Their chief qualities for use in X-ray work are their small grain size 0.27\(\mu\)m and 0.14\(\mu\)m respectively, well below the limits set by the geometrical factors of the technique and the availability of a range of thicknesses 25\(\mu\)m to 100\(\mu\)m, sufficient to ensure high absorption efficiencies even for the most penetrating radiations. Their disadvantage is their long and complicated processing times.

Hart (41) reports that the amount of shrinkage on drying of these emulsions is 38\% in the direction of the thickness of the emulsion but that he has detected no contraction in the plane of the emulsion provided the image is not too close to the edge of the plate.

Lang (42) has considered in detail the physical processes accompanying the absorption of radiation by nuclear emulsion plates and its effect on the quality and resolution attainable with
varying radiation wavelength. Taking into account the contributions to the limitation of resolution from all sources i.e. geometrical and those associated with radiation absorption by the emulsions he concludes that highly penetrating radiations i.e. AgKα, MoKα set the limit of resolution at 2μm with useful magnifications up to X300. Softer radiations i.e. CuKα, CoKα set the limit at 1μm, with useful magnifications up to X800.

1.8 Transmission X-ray Microscopy of Single Phase Metals

Studies of the substructure and defects in metals by the transmission electron microscopy technique are far more common than the examination of such materials by X-ray microscopy. This is because the examination of a metal by X-ray microscopy necessitates that the specimen be in the form of a highly perfect single crystal, whereas with the electron microscopy technique this is not so. The difficulty in obtaining highly perfect metal single crystals is the cause of the lack of a more widespread examination of metals by X-ray microscopy to date and there is at present no standard method for producing such crystals, as is exemplified in this section. Table 1.3. gives a list of the necessary thickness values for varying radiation wavelength, calculated from the transition case ut=1 for single phase metals which have recently been examined by X-ray microscopy.

Lang and Meyrick (43) first obtained low dislocation density single crystals of zone refined aluminium around 1959, by the strain anneal technique. Elbaum and Howe (44) observed that zone refined aluminium single crystals grown from the melt were dislocation free if the diameter of the crystals did not exceed 0.03cm. More recently Nøst (45) has shown that large strain anneal grown crystals of zone refined aluminium with dislocation densities of $10^2$ lines/cm² are realisable.
The method of producing aluminium single crystals of high perfection by Lang and Meyrick was to cold roll aluminium sheet down to 1 to 2 mm's thick, cut strips from these, clean the specimen and anneal it at 500°C for fifteen hours. During the anneal the specimen was placed on a slab of aluminium so that on cooling no strain would be introduced into the specimen as a result of differential thermal expansion between it and the bedplate. After the specimen had been cooled down to room temperature it was usually strained between 1% and 8% and then reannealed usually under the same conditions as the previous anneal. Before X-ray examination the specimen was electropolished. The highest quality specimens were found to be those which were strained and given second anneal. With crystals produced in this manner Burgers vectors of dislocations were determined and dislocation movement on low deformation was observed.

Nøst (45) obtained his specimens by the so called critical strain anneal method. In this method a 1mm thick strip of aluminium was initially strained 3%, heated to 500°C, held at this temperature for one hour and then cooled at 4°C/hr. Later Nes and Nøst (46) carried out annealing experiments in order to determine whether there was any systematic change in dislocation density versus cooling rate. The specimens prior to cooling were prepared in the manner previously reported by Nøst. Three supplies of aluminium were used; annealing was carried out in air and after cooling and electropolishing the crystals were examined by the Lang method. The dislocation density at room temperature of crystals from two of the aluminium supplies was found to be approximately linear with cooling rate and was $2 \times 10^2$ lines/cm² for the slowest cooling rate, 2°C/hr. Three crystals were reannealed with maximum temperature of 510°C and cooled at 4°C/hr.
Topographs subsequently revealed both increases and decreases in dislocation density.

At about the same time Nøst and Sørensen (47), began annealing experiments in which crystals were examined by X-ray microscopy in situ on a Lang X-ray apparatus at elevated temperatures. Dislocations were first observed when the temperature was 400° C. Topographs were taken at 340° C and 370° C at certain time intervals.

Following this work Nøst, Sørensen and Nes (48), carried out further X-ray microscopy studies of aluminium single crystals in situ on a Lang X-ray apparatus. Heating and cooling of the crystals at different rates, 2°C/hr to 20°C/hr was carried out between 270° and 370° C. They observed that new dislocations were formed as co-axial prismatic loops in rows on both heating and cooling.

Elbaum and McFarlane (49) have observed dislocations in gallium single crystals 0.5mm thick by the Borrmann anomalous transmission method. They obtained crystals with large regions free of dislocations by firstly solidifying gallium on an acrylic plastic mould and then secondly removing the crystal and placing it on a Teflon block one end of which was set on a hotplate. The crystal was then melted from one end and then resolidified by removing the heat source before the melting was complete. In this way they eliminated the stress normally imparted to melt grown crystals on cooling, since the only mechanical constraint on the crystal during resolidification was the adherence of the crystal to the Teflon block.

Young and Sherill (50) have obtained copper single crystals with dislocation densities $10^3$ lines/cm$^2$ and with no subgrain boundaries. Their method was to acid saw parallelepipeds 1mm thick from a 2.5cm diameter high purity single crystal with a $[111]$
growth direction grown by the method described by Young and Savage (51). One of the faces of the parallelepipeds was (111) and the long axis was either [110] or [211]. These specimens were acid polished and annealed at a temperature of 1075°C for fourteen days, after which they were slowly cooled down to room temperature. With these specimens they studied the pre-yield deformation region by the Borrmann method.

Lang and Polcarova (52) have examined iron + 3.5% silicon single crystals. The specimens were spark machined from a bulk single crystal grown over a period of twenty four hours (53) by the Bridgman method and had the form of platelets 1.5cm² and 0.5cm thick. These were ground down with emery paper and annealed for about ten hours in dry hydrogen at 1000°C and then slowly cooled down to room temperature. Finally they were electrolytically polished to a thickness value suitable for X-ray examination by the Lang method. They made Burgers vector determinations and demonstrated for this material a one to one correspondence between dislocations and dislocation etch pits produced by an etch developed by Sestak (54).

Michel and Olgivie (35) have examined zinc and cadmium vapour grown platelets by the Lang method. Their specimens were prepared by a method due to Coleman and Sears (55). Reference to their work has been made in section 1.5 and further reference to it will be made in chapter 7.

In the light of the work carried out by Sørensen, Nøst and Nes it would appear that with specimens which are prepared by annealing and subsequent cooling down to room temperature, that the cooling rate is an important parameter in determining whether or not the dislocation density at room temperature is low. Yet the details in the literature concerning this aspect of specimen
preparation are sadly lacking and expressions such as "slowly cooled" are usually the only mention of the manner in which specimens are retrieved from the elevated anneal temperature.

1.9 Comparison between Transmission X-ray Microscopy and Electron Microscopy

X-ray microscopy allows dislocations to be observed if the bulk dislocation density does not normally exceed $10^6$ lines/cm$^2$. The minimum image width of a dislocation is of the order of $\mu$m and this places a restriction on the fine detail which can be observed. No significant magnification occurs on the topograph but subsequent lightoptical microscopy can be used to obtain magnifications up to X800 if the softest X-radiations are used. Specimens up to 1cm thick can be examined if anomalous transmission can be induced, in this case however the dislocation density must not normally exceed $10^4$ lines/cm$^2$. Thinner though larger crystals maybe examined by the Lang method. The most successful applications have been with semi-conducting and non-metallic single crystals. The disadvantages of the technique are the long exposure times and the long nuclear emulsion plate processing times.

By comparison, thin film electron microscopy is capable of much higher resolution since the minimum width of the defect image is of the order of $10^2\mu$m and useful magnifications up to X100,000 are realiseable, allowing observation of individual dislocations when the dislocation density is far in excess of $10^6$ lines/cm$^2$. The disadvantages of this technique however are that only thin specimens of the order of $10^3\mu$m maybe used, which may not be representative of the bulk specimen from which they were prepared and that only small areas and hence volumes maybe examined. Moreover the technique is inherently a destructive one.
Table 1.4. from a review article by Kato (56) illustrates the differences between X-ray and electron waves. Two important differences between them should be noted. First the ratio of angular range of illumination to angular range of reflection is very different. The angular range of reflection of 100kv electrons by a perfect crystal is about $10^{-2}$ radians for strong reflections, but the range of illumination of the specimen does not usually exceed $10^{-4}$ radians. Thus the incident electron beam effectively acts as a plane wave; if the illuminated region of the specimen is oriented as a whole for Bragg reflection, then a locally distorted part of the illuminated region will no longer be able to satisfy the Bragg condition fully. On the other hand in the X-ray case the angular range of reflection is of the order of $10^{-5}$ radians and the angular range of illumination is of the order of $10^{-3}$ to $10^{-4}$ radians; the angular range of illumination is thus more than adequate to generate the full integrated reflection both from the perfect matrix and from an incoherently reflecting slightly misoriented region within it. It is this ratio of angular range of illumination to angular range of reflection that in the X-ray case permits such intense contrast of dislocation images to be generated when absorption is low. Second there are large differences in Bragg angle typically $1^\circ$ for the electron case and $10^\circ$ for the X-ray case. This difference coupled with the fact that specimens are thicker in the X-ray case leads consideration to be given in determining the image contrast at the X-ray exit surface to a triangular fan shaped region in the crystal, in contrast to the "narrow column" approximation technique used in transmission electron microscopy, notably by Hirsch, Howie and Whelan (57), (cf Figs. 1.10, 1.11).

In specimens whose thickness ranges upwards from a few
extinction distances a variety of diffraction phenomena can occur which are not observed in thin film electron microscopy and these bear witness to the fact that there are complexities in the X-ray diffraction situation from which electron-microscopy is free; Such complexities are in part responsible for the less developed state of X-ray diffraction contrast theory compared with that worked out for electrons. A notable simplification with the X-ray technique however is that a single Bragg reflection can be arranged and that only one is responsible for producing the topograph.
some of the hexagonal close packed metals

<table>
<thead>
<tr>
<th>METAL</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a (Room Temp)</th>
<th>Melting Point °C</th>
<th>T_{RT}/T_{MP}</th>
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</thead>
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<tr>
<td>Cd</td>
<td>2.972</td>
<td>5.605</td>
<td>1.886</td>
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<tr>
<td>Zn</td>
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<td>1.856</td>
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<tr>
<td>Ideal</td>
<td>-</td>
<td>-</td>
<td>1.633</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>2.502</td>
<td>4.061</td>
<td>1.623</td>
<td>1478</td>
<td>0.17</td>
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<td>5.200</td>
<td>1.625</td>
<td>650</td>
<td>0.31</td>
</tr>
<tr>
<td>Re</td>
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<td>1.615</td>
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<td>0.08</td>
</tr>
<tr>
<td>α-Zr</td>
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<td>5.147</td>
<td>1.593</td>
<td>1860</td>
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<tr>
<td>β-Ti</td>
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<td>4.683</td>
<td>1.587</td>
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</tr>
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<td>α-Hf</td>
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<td>5.051</td>
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<td>2220</td>
<td>0.12</td>
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<tr>
<td>Be</td>
<td>2.281</td>
<td>3.576</td>
<td>1.568</td>
<td>1300</td>
<td>0.18</td>
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Table 1.3 Values of t(μm). For ut=1. Values of Atomic number and melting point are also given.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>Z</th>
<th>AgKα, =0.5604</th>
<th>RhKα, =0.6149</th>
<th>MoKα, =0.7097</th>
<th>CuKα, =1.539</th>
<th>NiKα, =1.6565</th>
<th>MP °C</th>
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<tr>
<td>Al</td>
<td>13</td>
<td>1850</td>
<td>1030</td>
<td>700</td>
<td>76</td>
<td>63.5</td>
<td>660.1</td>
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<td>Fe</td>
<td>26</td>
<td>64</td>
<td>45</td>
<td>33</td>
<td>4</td>
<td>3</td>
<td>1537</td>
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<td>29</td>
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<td>21</td>
<td>17</td>
<td>1083</td>
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<tr>
<td>Zn</td>
<td>30</td>
<td>50</td>
<td>35</td>
<td>26</td>
<td>24</td>
<td>20</td>
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<tr>
<td>Ga</td>
<td>31</td>
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<td>43</td>
<td>29</td>
<td>27</td>
<td>22</td>
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<tr>
<td>Cd</td>
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<td>75</td>
<td>58</td>
<td>39</td>
<td>5</td>
<td>4</td>
<td>321</td>
</tr>
</tbody>
</table>

-23-
Table 1.2. The slip systems available in h.c.p metals

<table>
<thead>
<tr>
<th>SLIP SYSTEM</th>
<th>SLIP PLANE</th>
<th>SLIP DIRECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal</td>
<td>{0001}</td>
<td>{11\bar{2}0}</td>
</tr>
<tr>
<td>Prism Type 1</td>
<td>{10\bar{1}0}</td>
<td>{11\bar{2}0}</td>
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<tr>
<td>1st Order Pyramidal type I</td>
<td>{10\bar{1}1}</td>
<td>{11\bar{2}0}</td>
</tr>
<tr>
<td>2nd Order Pyramidal type II</td>
<td>{11\bar{2}2}</td>
<td>{11\bar{2}3}</td>
</tr>
<tr>
<td>Prism type I</td>
<td>{10\bar{1}0}</td>
<td>{0001}</td>
</tr>
<tr>
<td>Prism type II</td>
<td>{11\bar{2}0}</td>
<td>{0001}</td>
</tr>
</tbody>
</table>

Fig. 1.1. Basal slip system {0001} \{11\bar{2}0\}
Fig. 1.2. Prismatic slip system {10\bar{1}0} \{11\bar{2}0\}
Fig. 1.3. Pyramidal slip system {10\bar{1}1} \{11\bar{2}0\}
Fig. 1.4. Pyramidal slip system {11\bar{2}2} \{11\bar{2}3\}
Fig. 1.5. Prismatic slip system {10\bar{1}0} \{0001\}
Fig. 1.6. Prismatic slip system {11\bar{2}0} \{0001\}
**TABLE 1.4. COMPARISON BETWEEN X-RAY AND ELECTRON WAVES.**

<table>
<thead>
<tr>
<th>Incident Wave</th>
<th>Crystal</th>
<th>Diffraeted Wave</th>
<th>Resolving Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>ω</td>
<td>θB</td>
<td>Δφ</td>
<td>t</td>
</tr>
<tr>
<td>X-rays</td>
<td></td>
<td>Δλ/λ</td>
<td>θB</td>
</tr>
<tr>
<td>10⁻³, 10⁻⁴</td>
<td>±1⁰</td>
<td>10⁻⁵</td>
<td>0.4mm</td>
</tr>
<tr>
<td>5µm</td>
<td>50µm-10⁹</td>
<td>10⁻²</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>

ω = Angular width, Δλ = Spread in wavelength, H = effective width of wavefront on entrance surface

H₀ = effective width of wavefront on exit surface (Lower limit in electron case is determined by specimen dimensions), θB = Bragg angle, Δφ = Angular width of Bragg reflection.
Fig. 1.10 X-RAY CASE

Fig. 1.11 ELECTRON CASE
The growth of bulk single crystals of cadmium and the final method used for the production, from these crystals, of specimens suitable in thickness and in shape for X-ray topographic examination.

The orientation of the bulk crystals grown is shown in Fig. 2.1 and is the same as the crystals used by Blasdale (12) and Luke (17); they were grown vertically by a modified Bridgman method (17). Suitable seeds in which the (1010) plane was misoriented from the exposed face of the crystal by not more than \( \pm 1^\circ \) were available, only crystals misoriented by no more than this amount could be etched in 1% Nital to bring up etch pits on this plane. The method to be described allowed many such crystals of this orientation to be grown from a single seed.

2.1 Bulk crystal growth

The starting material comprised 99.999% pure cast cadmium rod, purchased from Johnson and Matthey and these were cut into 6.5cm lengths, polished in 20% Nital and placed in the integral funnel of a square cross-section, three piece graphite ingot casting mould. The mould was placed in a Pyrex tube which was pumped out to 1.0um pressure and flushed out with commercial argon three times. A small amount of argon was finally bled into the tube. The tube was then placed vertically in a furnace so that the bottom of the mould was positioned in the centre of it and the tube was heated in this position for 15 mins. after which the furnace was raised by an electric motor at a rate of 40cm/hr for 30 mins. The furnace system was automated using process times and square cross-section ingots 0.187" square were obtained free from holes in their interior. After cooling the ingot was removed from the mould and cut to a length of 13cm by a spark erosion machine.
The single crystals were obtained using a similar three piece split graphite mould of square cross-section and channel dimension of 0.190+001". A polished 5cm long single crystal seed was accurately located in the assembled two piece base of the mould with its (1010) face parallel to the side of the channel and a spark machined ingot which had been polished in 20% Nital butted up gently against it. The lid was fitted to the base of the mould and the complete mould placed in another Pyrex tube which was evacuated and finally partially filled with argon in the manner previously described for producing an ingot. The tube was then placed in a furnace identical to that in which ingots were produced and the bottom of the mould in the Pyrex tube was positioned 3.5cm below the bottom of the furnace. 130 volts a.c. (stabilised) via a transformer was dropped across the furnace and the furnace left in this position for 1hr. to ensure that the melt back into the seed had reached its terminal position. By making small variations to the furnace voltage the extent of melt back into the seed could be controlled to ± 1mm. After this period the furnace was raised by an electric motor, at a rate of 6.6cm/hr. for 2.5 hrs. and then switched off. On cooling the lid of the mould was removed and using a 3cm Back-reflection X-ray camera the orientation of the crystal at points along its length determined and compared with the orientation of the unmelted region of the seed, using a Greninger chart. Crystals could be oriented to ± 1.0°. The two piece base of the mould was finally unbolted, after it had been placed on the bed plate of the spark erosion machine, so releasing the crystal without damaging it. Finally the crystal was cut into three 5cm lengths, one of which comprised the original seed and which could be used again to produce another crystal.
During the whole sequence of crystal growth stringent precautions were taken to ensure that no contaminants were injected into the final crystal. After the ingot and crystal growing moulds had been manufactured, they were baked out at 500°C while under a vacuum of 1.0μm for 3hrs. and cooled under this pressure. Before the insertion of cadmium into these moulds, the cadmium whether in the form of a cast ingot, square cross-section ingot or single crystal seed, was polished in 20% Nital and thoroughly quenched off in ethanol before being dried so that no drying stains adhered to it; the moulds themselves were washed before being charged with cadmium, in ethanol and benzene and the Pyrex tubes were cleaned in chromium trioxide and rinsed in ethanol and distilled water after each use.

2.2 The sectioning and slicing of crystals

Single crystal slices of a desired orientation were obtained by spark machining from the bulk crystals grown as described in the previous section.

Since cadmium is an extremely soft material, a detailed investigation of the damage injected into single crystals of this material by spark erosion, using an etch pit technique had been made (17). This was a consequence of electron-microscope studies of cadmium which are being carried out at the present time. The spark machine used was a Servomet SMD model, manufactured by Metals Research Ltd. In the instrument supplied by the manufacturers, a moving wire is used as the cutting tool, but it had been found (17) that a fixed taut wire injected less damage into the crystals for a given cutting range of the instrument and moreover that the gauge of the wire also influenced the depth of damage imparted to the crystal. From the investigation it was concluded that the narrower the wire diameter and the
finer the cutting range the less was the depth of damage.

In the sectioning and slicing of crystals, to be described, great attention was given to obtaining slices which had the minimum amount of damage injected into them during machining and subsequent handling, particularly due to bending in the case of the latter. For the finest cutting range of the spark machine, the smallest gauge wire was found that would enable one complete cut of the crystal to be made without the wire breaking as a consequence of erosion. Range 7 of the spark machine was used and a 0.003" tungsten wire as the cutting tool. The depth of damage injected was 0.2mm under these conditions.

The 5cm x 5mm x 5mm, bulk crystals had been cut from the original crystal taken from the mould on range 6 of the spark machine using a fixed 0.005" tungsten wire. The damage injected into the crystal by such cutting was of the order of a millimetre directly away from the cut edge, and an increased dislocation density above background was detected along the whole length of the trace of the slip plane from this cut edge to the side of the crystal i.e. the 5cm long crystals were effectively damaged to a distance of 10mm from each cut end. Thus before any sectioning or slicing was carried out these damaged ends of the crystal were cut away on range 7 of the instrument using the fixed 0.003" tungsten wire where the damage was only confined to a strip 0.2mm wide and not propagated beyond this distance along the slip plane.

Slices were obtained parallel to the basal plane and parallel to the (10\bar{1}0) plane. The thickness of the slices was 1mm. Figs. 2.2, 2.3 show the manner in which the cutting was carried out "Fortolac" was used to affix the crystals to the goniometer head of the spark machine and the slices to be obtained were supported with this lacquer to prevent them folding in towards
the parent crystal during the final stage of the cut. The final dimensions of the basal and (10\(\overline{1}0\)) slices was 10mmx5mmx1mm. It is pointed out that in the case of the (10\(\overline{1}0\)) slices, specimens could be obtained with only one damaged face and this enabled subsequent thinning to be carried out in one direction only and furthermore enabled the profile of one etchable face to be retained. Finally after a slice had been cut the goniometer head was removed from the spark machine and the slice released from its lacquer support by soaking in a bath of acetone; the slice itself was removed from the goniometer head by gently sliding it off it using a fine camel hair brush and placing it on a glass microscope slide.

2.3 The thinning of the basal and (10\(\overline{1}0\)) slices

Inspection of table 1.3 shows that the maximum value of thickness for cadmium single crystals which allows their examination by the thin crystal X-ray transmission method is 75\(\mu\)m. The thinning technique to be described produced uniformly thin foils between 50-75\(\mu\)m thick, and which were adequately supported for subsequent handling. Such foils were free of damage due to spark machining, since the original slices had been cut under conditions which imparted only 0.2mm of damage per cut face of the slice.

Each slice obtained in the manner described in the previous section after its removal from the goniometer head of the spark machine and transference to a microscope slide was placed in a Petrie dish containing a 20\% Nital polishing solution. In this solution it was thoroughly polished on both sides for 10mins to remove spark machining debris and produce bright polished surfaces. After quenching off the polishing reaction in ethanol, the slice was transferred under this liquid from the microscope slide to a
thin stainless steel plate 2.5cmx2.5cm square having a rectangular aperture 9mmx4mm at its centre. The transference was carried out using a fine camel hair brush and the slice was positioned over the aperture in the plate. Both the plate and slice were then removed from the dish containing ethanol and dried by bringing the corners of lens tissues into contact with them. A 1.5mm wide frame of "Fortolac" was applied to the slice and the undersurface of the slice exposed to the aperture in the plate coated with this lacquer. A second coating was applied after 15 minutes. When the second coating had completely dried the slice and plate, to which the slice was now affixed were placed horizontally in a Petrie dish containing 20% Nital. After a period of approximately 4 hours the uncoated area of the cadmium slice had been polished uniformly away to a depth of approximately 0.5mm. At this stage the slice and plate were removed from the 20% Nital solution, quenched off in ethanol and placed in a further dish containing acetone, which dissolved away the "Fortolac" masking material. Using the camel hair brush again the slice was turned over, repositioned over the aperture of the stainless steel plate and both were then quenched in ethanol and dried as previously described. A 1.5mm wide frame of "Fortolac" was applied to the unthinned surface and the thinned surface now exposed to the aperture was likewise masked. As before a second coating was applied after 15 mins. The slice and plate were then placed again in a Petrie dish containing 20% Nital. After approximately 3 hours thickness measurements of the foil contained within the frame were made. The thickness measuring device used (74) comprised a low energy X-ray source, a detector and a particle counter (IDL Scalar 1805 model). The count rate versus thickness had been determined previously for a range of polycrystalline
foils whose thicknesses ranged from .001" to .01" in steps of .0005", as measured by a feeler gauge and micrometer.

The thinned specimen, supported on the stainless steel plate after quenching in ethanol and dried was positioned vertically between the source and detector and count rates measured over a period of 5 minutes. The specimen and plate were moved slightly between successive count rate measurements to ensure that a true thickness measurement was being made, especially if small holes were present in the foil, a frequent occurrence during the final thinning process. At this stage if the foil was not thin enough it was put back into 20% Nital solution for some minutes, after which it was removed, quenched, dried and a further thickness measurement made. This procedure was repeated until the foil thickness was estimated to be 50-75um, which corresponded to a count rate of approximately 350 c.p.m.

The above thinning technique produced foils surrounded by a stout frame slightly less than 1mm thick and approximately 1mm wide, adequate, as subsequently shown to support the foil region during subsequent handling.

No appreciable difference was found in the thinning rates for basal and (10\Bar{1}0) slices. (10\Bar{1}0) slices one side of which had been exposed to the virgin side of the original bulk crystal were thinned in from the cut side only, the etchable face being protected during the thinning process by the "Fortolac" masking material.
FIG 2.1 Orientation of bulk crystals

\[ x_0 = \lambda_0 \pm 28^\circ \]

Growth Axis

FIG 2.2. Basal Sectioning

Direction of cutting tool

damaged

"Fortolac"

FIG 2.3. (10\overline{1}0) Sectioning

(10\overline{1}0)

(10\overline{1}0)
Crystal growing unit

Ingot casting mould showing cadmium billet in funnel

Crystal growing mould showing seed and ingot
The Chemical Examination Of The 1% and 20% Nital Solutions

The examination set out to identify which species of ions or molecules are present in 1% (etching solution) and 20% (chemical and electro-chemical polishing solution) Nital. No such chemical examination for any etching or polishing solution has been reported in the literature; this coupled with the fact that initially both the etch and polish were considered to be a fairly simple two component system namely ethanol and nitric acid prompted the present investigation. Further interest in these solutions was stimulated by the observation that the 20% solution appeared to age markedly after a period of a few days, whereas the 1% solution maintained its etching ability over a period of at least several months.

With a knowledge of the composition of the 1% solution it was hoped to elucidate the mechanism of dislocation etch pit formation on the (10\(\bar{1}0\)) plane of cadmium by making well informed systematic changes to the solution and observing the effects such modified solutions had on the (10\(\bar{1}0\)) plane.

From a purely chemical viewpoint the composition of Nital solutions is of considerable interest since little is known of nitric acid alcohol based solutions generally (67). In fact Daniels (68) has written "Although the study of non-aqueous solutions has been quite limited in comparison with the extensive studies of aqueous solutions there is much of theoretical significance and practical importance to be obtained from investigation of non-aqueous solutions". He has further pointed out the fact that water is an abnormal solvent and a broader knowledge of electrical behaviour in other solvents is more pertinent in contributing knowledge to the theory of solvents generally.
The solutions were examined by three electrical methods; by electrolysis, pH meter and by specific conductance measurements. Towards the end of the period of examination by the electrical methods the solutions were further investigated by Ultra-violet spectroscopy.

3.1 Reported examinations of dislocation etches

Those examinations which have been reported have been concerned only with the variation of the internal structure and size of etch pits with changes or modifications to the etching solution.

Gilman and Johnston (58) have reported two etches for the (100) plane of Lithium fluoride, so called "A" and "W" etchants. The former attacked all dislocations piercing the (100) plane equally well, whereas the latter distinguished between aged and fresh dislocations. The first reported etch (59) "A" was termed reagent cp-4. This solution they found, only acted as a dislocation etch, if, prior to use after being freshly prepared, they dipped the steel forceps with which they handled their crystals into it i.e. they introduced some iron into the solution. The second reported etchant, the "W" etch was of a far simpler composition than the "A" etchant and comprised a dilute aqueous solution of ferric fluoride FeF$_3$. With this etchant Gilman et al (60) elucidated the manner in which this etchant operated. This was accomplished by observing the change in shape of the etch pits on varying both the FeF$_3$ and LiF concentrations, changing the anion and cation of the salt and adding to the etch anions which formed complexes with the Fe$_3^+$ cation. From their observations, they proposed that the formation of etch pits at dislocation sites was due to preferential nucleation of unit pits one molecule deep at the dislocation site and the inhibition of the dissolution of the edges of the pit by absorption of ferric ions. In this way lateral growth of the unit pit was retarded, while the vertical growth was
not and hence steep visible pits were observed. They further proposed that the surface generally free of dislocations was protected from dissolution by further ferric ions complexing with fluoride ions.

Lovell and Wernick (61) have reported that the shape of etch pits produced by their dislocation etch for the (111) plane of copper depended to a marked extent on the amount of bromine, one of the constituents of their etchant present. If this constituent was absent no pits were produced at all and if replaced by iodine, another of the halogens, the etchant still appeared ineffective. They concluded that the greater oxidising power of bromine had an important effect on the etching ability of their solution.

Young (62) and Livingston (63) have reported dislocation etchants for the same plane in copper, both contain bromine as a constituent. Young (62) has divided the chemical reactions of the dissolution of copper into "fast" and "slow" reactions, "slow" reactions being oxidising reactions promoted by oxygen dissolved in the solution and "fast" reactions being those promoted by oxidising agents contained within the solution. Young investigated fast reactions by etching a copper sphere with a variety of solutions containing iron halides and subsequently studying the poles of the sphere. His results indicated that the dissolution of copper involved the formation of complex ions and he suggested that bromine and chlorine acted as "poisons" in retarding lateral pit growth. "Slow" reactions have been studied by Jenkins (64) using copper single crystals placed in a continuously stirred aqueous solution of $10^{-2}$ M ethylenediamine. He found that the nucleation of reaction sites appeared at random on the (100), (110) and (111) planes and could offer no explanation of the lack of correlation between crystal imperfections and chemical
reactivity produced by this type of reaction.

3.2 Preparation of the 20% and 1% Nital solutions

(a) 20% Nital

All 20% Nital solutions which were examined were made up in batches of 100ml. 80ml of Analar absolute ethyl alcohol was poured into a 250ml glass beaker and the beaker was placed in a glass trough containing cold water. 20ml of nitric acid was added to the 80ml of alcohol in small amounts, with a time lapse of several minutes between each addition. This procedure was adopted to prevent overheating of the solution. Irrespective of the colour of the nitric acid which was added to the ethyl alcohol the resultant solution was always colourless.

(b) 1% Nital

1% Nital solutions were always made up by dilution of freshly prepared 20% Nital solution. 5ml of 20% Nital was added to 95ml of Analar ethyl alcohol. The mixing of these constituents did not appear to warm the ensuing solution, and the solution remained colourless.

3.3 The electrolysis of 1% and 20% Nital Solutions

The acid constituent of the 1% and 20% Nital solutions used for electrolysis experiments was Analar fuming nitric acid.

Bright platinum electrodes were used and currents not exceeding 20mA, to prevent heating and thermal decomposition of the solution were passed through a cell containing the solutions.

Possible ionic equilibria in both the 1% and 20% solutions are according to Lee (67):

\[
\begin{align*}
2\text{HNO}_3 & \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O} \quad (69) \quad \text{la.} \\
2\text{NO}_2 & \rightleftharpoons \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^- \quad (70) \\
\text{HNO}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{NO}_3^- + \text{H}_3\text{O}^+ \quad \text{lb.}
\end{align*}
\]
The NO$_3^-$ ion can, during electrolysis, discharge at the anode according to one of two possible reactions

\[ \text{NO}_3^- \rightarrow \text{NO}_2 + \frac{1}{2}\text{O}_2 + e \] .......................... 2

or  \[ \text{NO}_3^- \rightarrow \text{NO}_2^+ + \frac{1}{2}\text{O}_2 + 2e \] (71) .......................... 3

The NO$_2$ molecule has a brown colour, whereas the NO$_2^+$ ion is colourless. If the HNO$_3$ molecule is dissociated into the dissociation products given by 1a, 1b, then the course of dissociation can be observed qualitatively by the discharge products of the NO$_2^+$, NO$_3^-$, H$_3$O$^+$ and C$_2$H$_5$OH$_2^+$ ions at the electrodes during electrolysis.

If the reaction given by 2 is operative then during electrolysis the NO$_2$ molecule would be liberated at the anode and produce a brown colouration around it and oxygen gas would be evolved. However it does not necessarily follow that if a brown colouration is not detected in the vicinity at the anode this reaction is not operative since whereas the original nitric acid which was used to prepare the 1% and 20% solutions had a brown colouration, indicating the presence of the NO$_2$ molecule, the resulting Nital solutions were colourless and Lee (67) has proposed that in ethyl alcohol the following equilibria have been pushed towards the right.

\[ 2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^- \]

brown  colourless  colourless

The NO$_2^+$ ion would be liberated at the anode and oxygen gas would be evolved if reaction 3 were operative. There would be no colour change in the vicinity of this electrode since the NO$_2^+$ ion is colourless.

Experimentally it was observed that no gas was evolved at the anode and no colouration changes were observed in its vicinity. Slight evolution of gas was observed at the cathode in the 20%
solution and a more rapid evolution at the cathode in the 1% solution. Observation of the anode was carried out during the course of electrolysis, which lasted several hours, using a hand lens.

Both reactions given by 2 and 3 would involve the liberation of oxygen at the anode. No gas evolution was observed at this electrode. Lee (67) has suggested that if such oxygen were evolved it would probably not be liberated from solution but react with the ethyl alcohol in solution according to the following molecular reaction

\[ \text{C}_2\text{H}_5\text{OH} + \frac{1}{2}(\text{O}_2) \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \]

nascent acetaldehyde

Reaction 3 being operative would involve the formation of the \( \text{NO}_2^+ \) which would subsequently discharge at the cathode to \( \text{NO}_2 \) which would normally impart a brown colouration to the solution in the vicinity of this electrode. But it has been previously proposed that the \( \text{NO}_2 \) molecule in ethyl alcohol dimerises into \( \text{N}_2\text{O}_4 \) in equilibrium with the ions \( \text{NO}^+ \) and \( \text{NO}_2^- \), since nital solutions are colourless. The discharge of the \( \text{NO}_2^+ \) ion in any case would not result in the evolution of any gases. A gas was however observed to be evolved at the cathode and this could have resulted only from the discharge of ions carrying an excess of hydrogen i.e. the ions \( \text{C}_2\text{H}_5\text{OH}_2^+ \) or \( \text{H}_3\text{O}^+ \).

From these observations of the electrolysis of 1% and 20% nital one can infer the presence of the \( \text{NO}_2^- \) ion (this is the only negative ion in solution) and either the \( \text{H}_3\text{O}^+ \) or \( \text{C}_2\text{H}_5\text{OH}_2^+ \) ions. Which of the latter two ions is preferentially discharged cannot be deduced since their discharge potentials in aqueous ethyl alcohol are not known. It can be tentatively argued however that as a greater evolution of gas was observed at the cathode with the
1% solution for a given current the ion discharged at this electrode was the \( \text{C}_2\text{H}_5\text{OH}^+ \) ion since in 1% solution there is a greater amount of ethyl alcohol per unit volume than in the 20% solution. This argument leads to the conclusion that the following equilibrium is present in the nital solutions

\[
\text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}^+ + \text{NO}_3^-
\]

3.4. pH determinations of 1% and 20% Nital Solutions using a pH meter

This instrument is basically a valve voltmeter, which measures the e.m.f produced between the electrodes of a cell in which the solution upon which measurements are being made acts as the electrolyte. If one electrode is reversible to hydrogen ions and the other a reference electrode of constant potential, this e.m.f maybe interpreted as a measure of the hydrogen ion concentration in the solution, the pH value being defined as \(-\log_{10}\) of this concentration. The pH meter used was a Vibron model 39A and measurements were made at 25°C. This type of meter is commonly used for determining the hydrogen ion concentration in aqueous solutions. For pure water it is known that the hydroxyl ion concentration is \(10^{-14}\) at 25°C hence for aqueous solutions the pH value may range from zero for a solution of strong acid of unit activity, through 7 for a neutral solution to 14 for a solution of unit alkali activity.

The 1% and 20% Nital solutions were prepared using Analar fuming nitric acid. Values registered on the meter were negative and this indicated that the pH electrode which was in the instrument and available for these measurements, though suitable for aqueous solutions was not suitable for alcoholic solutions. Lee (67) suggested, and this was borne out by later work that the predominant positive ion in solution was \( \text{C}_2\text{H}_5\text{OH}^+ \) and that this
ion being much larger than the $H^+$ ion, could not penetrate the membrane of the pH electrode. He suggested further that this could be resolved by attempting to measure the pH value of these solutions using the basic hydrogen electrode i.e. platinum black in contact with molecular hydrogen at a known partial pressure over the solution.

3.5 The Conductivity of the Nital solutions

An A.C. wheatstone bridge circuit was used to measure the value of specific conductance of the Nital solutions. The solutions were contained in a cell comprising a glass stoppered vessel containing platinum foil electrodes, and this cell made up one of the four resistive arms of the bridge circuit. The determination of the resistance of the solution in the cell enabled its specific conductance $K$ to be found using the relation $R = c/K$ where $c$ = the cell constant. The cell constant was determined by loading it with a solution of known specific conductance and measuring the resistance of this solution. Two cells were used, one with a cell constant of 0.1 and the other with a cell constant of 9.3. The former was used with 1% solutions and the latter with 20% solutions. In use the cells were immersed in a constant temperature oil bath, which kept the solution temperature at $25^\circ C \pm 0.1^\circ C$.

A knowledge of the value of the specific conductance of an electrolyte at a given concentration enables the degree of dissociation i.e. the fraction of molecules dissociated into ions to be estimated and the dissociation constant for the dissociation equilibrium to be found. The fraction of molecules dissociated into ions is equal to $\frac{\Lambda}{\Lambda^\infty}$, where $\Lambda$ is the equivalent conductance of a solution at a given concentration $c$ and $\Lambda^\infty$ the equivalent conductance of the solution at infinite dilution. The latter
quantity is normally available from the literature. The specific conductance $K$ and the equivalent conductance are linked by the relation $\Lambda_e = \frac{1000K}{c}$, where $c$ is the number of gram equivalents of the solute per litre. The dissociation constant $k$ can be determined knowing $c$ and $\alpha$, from Ostwald's dilution law i.e. $k = \frac{c\alpha^2}{(1-\alpha)}$.

Molecular reactions which may occur over periods of time in electrolytes can be investigated by noting at set time intervals any changes in the value of the specific conductance, such changes indicate a change in the ionic content of the solution.

3.6. Measurement of the specific conductance of the Nital solutions

The specific conductance of four Nital solutions was determined over an extended period of time. They consisted of two 20% solutions and the 1% solutions, all four solutions being prepared using absolute ethyl alcohol.

(a) 1% Solutions: Acid constituents.

(i) Analar fuming Nitric acid (comprising 95% Nitric Acid, 5% water) Colouration brown. Plot 3.2.A.

(ii) 100% Nitric Acid. Produced by distillation of a mixture of concentrated sulphuric acid and concentrated Nitric acid. This acid was stored at $-40^\circ C$ as the solid and only warmed up to room temperature just before use and in this manner the self-decomposition of this acid was prevented. Colourless. Plot 3.2.A.

(b) 20% Solutions.

(i) Analar fuming Nitric acid (95% Nitric acid, 5% water) Colouration brown. Plot 3.1.A.

(ii) Colourless commercial water white Nitric acid (approximately 96% Nitric acid, 5% water). Colourless. Plot 3.1.B.
3.7. Interpretation of the characteristics of the specific conductance versus time plots of the Nital solutions

3.7.1. 20% solutions

Plots 3.1.A and 3.1.B show the change in specific conductance with time of these solutions prepared from variants of nitric as given in sec. 3.6. It is proposed for both these solutions that initially the following ionic equilibrium is present

\[ C_2H_5OH + HNO_3 \rightleftharpoons C_2H_5O^+ + NO_3^- \]

These plots show that immediately the specific conductance begins to decrease, indicating that ions generated by the above equilibrium are being removed from solution. Observation of the colour of the solution after this period of time showed that it had changed from colourless to straw yellow and the solution had taken on a sweet apple smell. These are the ageing properties exhibited by 20% Nital solutions. The colour of the solution indicated the presence of the NO₂ molecule and the smell the presence of acetaldehyde. Over a period of a few days the following molecular reaction is proposed to have occurred.

\[ 2HNO_3 + C_2H_5OH \rightarrow 2NO_2 + 2H_2O + CH_3CHO \]

with the subsequent removal of ions from solution.

3.7.2. 1% Solutions

Plot 3.2.B corresponds to the Nital solution prepared from nitric acid as given by a(ii) sec. 3.6.

It is proposed that the initial ionic dissociation operative in this solution is

\[ C_2H_5OH + HNO_3 \rightleftharpoons C_2H_5O^+ + NO_3^- \]

It is observed that in this solution for a period of six days after preparation there is a gradual reduction in the specific conductance. Subsequently this value rises and levels off. It is proposed that the lowering of the specific conductance
value is due to the reduction in the ionic content of the solution as a consequence of the molecular reaction

\[ \text{C}_2\text{H}_5\text{OH} + 2\text{HNO}_3 \rightarrow 2\text{NO}_2 + \text{CH}_3\text{CHO} + 2\text{H}_2\text{O} \]

The subsequent increase is attributed to the increased mobility of \( \text{H}_3\text{O}^+ \) as compared with \( \text{C}_2\text{H}_5\text{OH}_2^+ \); the protonation of water is a result of the above molecular reaction.

The experimental evidence supporting this proposal was obtained from a subsidiary experiment in which known incremental volumes of distilled water were added to a freshly prepared 1% Nital solution, Plot 3.3.B. Observation of this plot shows that the specific conductance markedly increases on addition of water. Lee (67) using this plot has deduced that the relative basicity of water to ethyl alcohol in 1% Nital solution is 40:1 i.e. the ionic equilibrium

\[ \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}_2^+ \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_5\text{OH} \]

is pushed towards the right.

Plot 3.2.A refers to the 1% Nital solution prepared from the acid constituent as recorded under a(i) sec. 3.6.

The increase in specific conductance is proposed to be operative as a result of the protonation of water referred to above. The immediate onset of this increase compared to a delay of six days in the case of the other 1% Nital solution is a consequence of the presence of water in Analar fuming nitric acid and the initial absence of water in 100% nitric acid.

3.8 Determination of the Ionic dissociation in 1% and 20% Nital

In dilute solution i.e. 1%, the only equilibrium proposed is

\[ \text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}_2^+ + \text{NO}_3^- \]  \( \text{(i)} \)

The equivalent conductance of freshly prepared 1% solutions is
given by \( \Lambda_{\infty} \approx \frac{0.80}{0.239} \times 10^{-3} \), where 0.80 is the approximate average of the value of K for the two 1% solutions examined and 0.239 is the concentration of nitric acid at 1% dilution. Fortunately \( \Lambda_{\infty} \) for protonated ethyl alcohol is known (73) to be 83.35 ohm\(^{-1}\) cm\(^{-1}\) l g-equiv\(^{-1}\). Hence \( \Lambda_{\infty} \approx \frac{3.2}{83.35} = 0.039 \) (\( \Lambda_{\infty} = 83.35 \)). The percentage dissociation of nitric acid in 1% Nital is thus 3.9 and the classical dissociation constant k is approximately 3.6x10\(^{-4}\).

In 20% solution it was initially proposed that two equilibria were present in the freshly prepared solutions, namely

\[
\text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}^+ + \text{NO}_3^- \\
3\text{HNO}_3 \rightleftharpoons \text{NO}_2^+ + 2\text{NO}_3^- + \text{H}_3\text{O}^+ \quad \text{......... (ii)}
\]

The second equilibrium was proposed to be operative to account for the approximately 40 fold increase in the initial value of specific conductance in going from a 1% to a 20% solution (cf plots 3.1, 3.2). Inspection of these two equilibria shows that the \( \text{NO}_3^- \) ion is generated by both of them and therefore the extent of dissociation according to (ii) will be dependent upon the amount of \( \text{NO}_3^- \) present in solution from the dissociation according to (i) and vice versa. The concentration of \( \text{NO}_3^- \) present from the equilibrium given by (i) was determined by Lee (67) using the same approximate dissociation constant as determined for equilibrium (i) in the 1% solution, namely 3.6x10\(^{-4}\). The concentration of the \( \text{NO}_3^- \) ion present as a result of equilibria (ii) was then determined taking into account that generated by equilibria (i). Plots 3.1.A, 3.1.B were used for determining the value of K.

Lee's calculations showed that the degree of dissociation for the 20% solution was 0.22 i.e. 22% dissociation of \( \text{HNO}_3 \) occurred and since the concentration of nitric acid at 20% dilution is 4.8 moles/litre there are 0.6 moles per litre of \( \text{NO}_3^- \), 0.3 moles per
litre of $\text{NO}_2^+$ and 0.3 moles/litre of $\text{H}_3\text{O}^+$.

At the time the author was examining the Nital solutions Luke and Buist (17,72) were examining them also by means of ultraviolet spectroscopy. They had found that 1% Nital comprised undisassociated nitric acid in ethyl alcohol. This was compatible with the degree of dissociation of nitric acid in 1% Nital as deduced from specific conductance measurements; namely 4%, since the sensitivity of the technique used by them was not capable of detecting this small amount of dissociation in such a dilute solution. Moreover they had reached the same conclusion for the 20% solution namely that 20% Nital comprised undisassociated nitric acid in ethyl alcohol. Lee's calculations based on specific conductance measurements indicated that for 22% dissociation the $\text{NO}_3^-$ absorption peak in the U.V region should have been detected, indicating to Luke and Buist that dissociation had occurred.

In the light of this Buist determined the position of the $\text{NO}_3^-$ absorption peak in the U.V region from a 0.2 moles per litre solution of ammonium nitrate in ethyl alcohol 96% by volume, plot 3.4, using a 10mm path length cell for containing the solution. The author and Buist prepared 1% and 20% Nital solutions from 100% nitric acid and absolute ethyl alcohol; from which U.V spectra plots 3.5, 3.6 were obtained; 10mm and 0.5mm path length cells were used with the 1% and 20% solutions respectively. It was observed from these plots that there was noshouldering on either plot at a wavelength of 302 milli-microns, the position of the $\text{NO}_3^-$ peak in the U.V region. However if one assumes that the concentration of $\text{NO}_3^-$ in 1% solution is small compared with the concentration of $\text{NO}_3^-$ in 20% solution and that the absorption of $\text{HNO}_3$ is confined solely to a wavelength of 270 milli-microns in this region, one can take the difference between the absorbances of the 1% and 20%
U.V spectra of plots 3.5, 3.6 and plot these differences as a function of wavelength. If there is no other absorption peak within the trace of the 20% U.V plot then the differences should be constant. These differences were found and drawn on plot 3.7. This plot shows that there is a definite peak at a wavelength of approximately 302 milli-microns, which can only be attributed to the NO$_3^-$ ion. From this plot Buist estimated the molar concentration of the NO$_3^-$ ion in 20% solution to be 0.27 moles per litre.

Since the specific conductance of a sample of 20% Nital prepared from 100% nitric acid had not been determined previously, the author made such a measurement and this was found to be .0396 (ohm cm)$^{-1}$. The degree of dissociation using the relationship $\alpha = \frac{1000K}{\Lambda_{\infty}c}$ was determined assuming that the only equilibrium operative was

$$
C_2H_5OH + HNO_3 \rightleftharpoons C_2H_5OH^+ + NO_3^-
$$

A value of 0.475 moles/litre for the molar concentration of the NO$_3^-$ ion was obtained. This value is nearly twice that obtained from U.V spectra considerations. It would however be larger i.e. approximately 0.6 moles/litre if equilibria (ii) were operative also.

Following this work the author and Buist obtained further U.V spectra of 20% Nital prepared in the same manner as previously mentioned but diluted 5% and 10% with Analar distilled water Plot 3.8.A, 3.8.B. This experiment was performed in the light of information obtained from specific conductance measurements made on water-diluted 1% and 20% solutions (see sec. 3.7 and plots 3.3A, 3.3.B). These measurements had shown that there was a marked increase in the specific conductance of these solutions on addition of water. Observation of Plots 3.8A, 3.8B shows that
on dilution of 20% Nital the HNO₃ absorption peak is reduced and the peak is shifted to the longer wavelengths, indicating a reduction of HNO₃ in solution and an increase of the concentration of the NO₃⁻ ion. This is supporting evidence for the proposed equilibrium.

\[
\text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}^+ + \text{NO}_3^-
\]

Finally all the U.V spectra data were plotted on the same graph plot 3.9 in an attempt to infer the presence of the NO₂⁺ ion which has an absorption peak in the U.V region which rises sharply at 290 milli-microns. This would indicate that equilibria (ii) was operative. Buist has pointed out that if only one equilibrium, namely that given in (i), is operative, then all the U.V spectra obtained by the author and him should have one common point of intersection; the so-called isobestic point the plot 3.9 shows that the NO₃⁻ peak is removed from the point of intersection of the other curves. This shift would seem to indicate that another species of ion, having an absorption peak in this region, is present in 20% solution. This cannot however be definitely concluded since such a shift could be attributed to small inaccuracies in volume measurement accrued during the preparing of the solutions as set out in sec. 3.2.

The evidence obtained tends to indicate that in 20% solution there is only one ionic equilibrium reaction operative i.e.

\[
\text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}^+ + \text{NO}_3^-
\]

From the specific conductance value obtained using 100% nitric acid in preparing the 20% solution a value of 4x10⁻² is obtained for the dissociation constant compared with the value of 4x10⁻⁴ for the 1% solution. The percentage dissociation of nitric acid in 20% solution is approximately 10%, compared to 4% in 1% solution. Thus the general effect upon the classical equilibrium

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constant of change in composition of the medium is very pronounced. The disparity between the molar concentration of the NO$_3^-$ ion as deduced from U.V spectroscopy and specific conductance measurements has not been resolved.

3.9 An attempt to determine the mechanism of dislocation etching on the (1010) plane of Cadmium using a 1% Nital etch.

Dislocation etching is thought to be initiated by the formation of unit pits one molecule in depth at sites where a dislocation line pierces the exposed crystallographic plane; the preferential nucleation of unit pits at dislocation emergence points is due to the localised excess energy which is associated with each dislocation. This excess energy is thought to comprise the dislocation core energy and the total elastic energy of the dislocation (60, 62, 65).

Steps within the unit pits are considered to move rapidly away from the dislocation site as molecules at kinks on the steps are removed by the etchant. The dislocation emergent point on the crystal surface is thus re-exposed to the etchant and a further unit pit is initiated. This process is considered to repeat itself many times with the resultant formation of an etch pit.

The visibility of an etch pit is dependent upon the number of unit pits nucleated per unit time and upon the rate at which steps associated with each unit pit move in the direction parallel to the crystal surface. For an etch pit to be visible it is thought that many unit pits at a given dislocation site must be formed per unit time and that the etchant must contain a "poison", whose time dependent absorption at kinks on the steps within the unit pit inhibits the movement of steps by preferentially retarding the leading step (66).

It was with this mechanism of etch pit formation in mind that
Luke and Buist (17,72) using spectroscopic data obtained by them of the 1% Nital solution and the results of the observations and data presented in the previous sections on the composition of 1% and 20% Nital attempted to elucidate the etching mechanism on the (1010) plane of cadmium.

It was initially conjectured that the dissolution of cadmium in 1% and 20% Nital took place according to one of the following reactions:

\[
\text{Cd} + \text{HNO}_3 \rightarrow \text{Cd(NO}_3\text{)}_2 \text{H}_2\text{NO}, \text{N}_2\text{O} \text{ etc.}
\]

or

\[
\text{Cd} + 2\text{C}_2\text{H}_5\text{OH}^+ \rightarrow 2\text{C}_2\text{H}_5\text{OH + H}_2 + \text{Cd}^{2+}
\]

To identify which reaction was operative it was decided to collect the gaseous product and determine whether or not it was combustible. The type of reaction

\[
\text{Cd} + \text{HNO}_3 \rightarrow \text{Cd(NO}_3\text{)}_2 \text{NO}_2, \text{N}_2\text{O}, \text{NO} \text{ etc.}
\]

in which the only gaseous products produced are those indicated and not hydrogen as known to occur with varying concentrations of nitric acid in both zinc and cadmium; besides other properties none of these gases is combustible. On the other hand hydrogen is known to burn and this would be produced by the reaction

\[
\text{Cd} + 2\text{C}_2\text{H}_5\text{OH}^+ \rightarrow \text{Cd}^{2+} + 2\text{C}_2\text{H}_5\text{OH} + \text{H}_2
\]

A polished single crystal of cadmium was placed in a stoppered vessel containing fresh 20% Nital and the gaseous product evolved collected over water in the usual way. A lighted taper was applied to the mouth of the test tube containing the product and a blue flame was observed around the neck of the tube. This could only be hydrogen. The possibility of either CO or CH\text{_}4 being produced and which also burn with a blue flame has been ruled out by Lee (67) since these gases would by necessity be produced only by disruption of the ethanol molecule which in turn would involve breaking carbon carbon bonds and such breaking would require far
higher temperatures than that produced in the cadmium Nital system. Hence this test indicated that the cadmium Nital reaction is

\[ \text{Cd} + 2\text{C}_2\text{H}_5\text{OH}^+ \rightarrow 2\text{C}_2\text{H}_5\text{OH}_2 + \text{Cd}^{2+} + \text{H}_2 \]

Contaminants in the nitric acid acting as step poisons could not be ruled out and to investigate this possibility solutions of 1% Nital using Analar absolute ethyl alcohol were prepared from Analar fuming nitric acid, 96% commercial nitric acid and 100% Nitric acid respectively. Crystals with a maximum misorientation of \( \pm \frac{1}{2}^\circ \) of the (10\overline{1}0) plane relative to the crystal surface were used and the etching time was standardised to 30 minutes per solution. All three Nital solutions produced etch pits of the same size and shape. This showed that any contaminants present in the Analar and commercial acids were not responsible in acting as a "poison", since the 1% solution prepared from 100% nitric acid also produced etch pits and this acid contained no contaminants, since it was produced by distillation. In particular the NO\(_2\) of "fuming" nitric acid is unimportant.

Since the type of the nitric acid constituent did not appear to be important, attention was turned to the importance of the alcohol base of the solution. The ethanol base C\(_2\)H\(_5\)OH was replaced in 1% solution by preparing 1% solutions, using Analar nitric acid, with Analar propyl alcohol C\(_3\)H\(_7\)OH and Analar methyl alcohol CH\(_3\)OH. Etch pits were formed just as effectively on the (10\overline{1}0) plane of crystals etched in both these solutions. This indicated that the size of the positive ion produced by the equilibria

\[ \text{C}_n\text{H}_{2n+1}^+ \text{OH} + \text{HNO}_3 \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH}_2^+ + \text{NO}_3^- \]

did not play an important role in etching.

Since nitrites are known to act as corrosion inhibitors, the possibility of the nitrite ion acting as a step poison was next considered. The observations and results given in sec. 3.8 indicated
that the nitrite ion \( \text{NO}_2^- \) was not present in 1% solution. However it was considered possible that the Nital-cadmium dissolution reactions were more complicated than at first conjectured and that it was possible that the nitrite ion could be produced in situ during the dissolution reaction and be absorbed at a kink, thus acting as a poison.

To investigate this possibility two Nital-like solutions were prepared. One comprised 1ml of Analar fuming nitric acid in 99 ml of ethanol containing 0.005M urea, \( \text{NH}_2\text{CO.NH}_2 \), the other 1ml of Analar nitric acid in 99ml of ethanol containing 0.01M of sodium nitrite \( \text{NaNO}_2 \). In order not to alter the character of the 1% solution, it was decided that the molar concentration of the additives to the 1% solutions should not exceed 10% of the molar concentration of nitric acid in 1% Nital. This is 0.23M, since 4% dissociation occurs in this solution sec. 3.8. In any case the amount of additive that could be dissolved in the 1% solutions was limited by the low solubility of these additives in ethanol.

The urea additive to the 1% solution was used to remove any traces of nitrous acid which may have been initially present in the 1% solution and the sodium nitrite to produce or increase the nitrite ion content in solution. Both these solutions produced etch pits. From this it was deduced that the nitrite ion did not act as a step poison.

Consideration was next turned to the only other possible ion in solution, namely the nitrate ion \( \text{NO}_3^- \). A 0.2M solution of sodium nitrate in 99ml of ethanol was prepared on the assumption that the extent of dissociation was comparable to that of Analar nitric acid in ethanol. With this solution no etch pits were formed and the conclusion was drawn that the \( \text{NO}_3^- \) ion alone was not responsible for etch pit formation. It was concluded that both
the nitrate ion and molecular nitric acid were necessary for etch pit formation and in order to determine whether the $\text{NO}_3^-$ ion was responsible in acting as a step poison an attempt was made to isolate the $\text{NO}_3^-$ from the $\text{HNO}_3$ molecule while both were to some extent in solution.

Two Nital-like solutions were prepared. One comprised .04ml of Analar fuming nitric acid in 99ml of Analar water and the other 1ml of Analar fuming nitric acid in 99ml of dioxan $\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$. In the former solution practically complete dissociation occurs according to the reaction

$$\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + \text{H}_3\text{O}^+$$

This solution was prepared however so that it contained the same concentration of $\text{NO}_3^-$ as did 1% Nital. Ill-defined pits were obtained using this solution, which contained little nitric acid, which indicated that it had little "poison" in it, from which it was deduced that $\text{NO}_3^-$ alone was not acting as a satisfactory poison. The fact that etch pits were formed, however, appeared to invalidate the Nital-cadmium dissolution reaction, previously conjectured, since this aqueous solution contained little molecular $\text{HNO}_3$. The dioxan solution was used since nitric acid in this solution does not dissociate and consists primarily of molecular nitric acid. Well-defined pits were obtained using this solution. Crystals placed for 2 hours in Analar water and dioxan alone produced no pits. The formation of pits using nitric acid in dioxan indicated that not only was nitric acid capable of dissolving cadmium but also in some manner of producing the step poison.

3.10 Conclusions

The ions and molecules comprising 1% and 20% Nital solutions have with reasonable certainty been determined; in both solutions, protonated ethyl alcohol, the nitrate ion, molecular nitric acid
and ethyl alcohol are present. The extent of dissociation of nitric acid in ethyl alcohol in both 1% and 20% solutions has been estimated and the classical dissociation constants for these solutions deduced. The large difference in this constant for the two solutions was a surprising result. The ageing of 20% Nital has been elucidated.

The discrepancy referred to in the text between the extent of dissociation of 20% Nital as deduced from U.V spectra data and specific conductance measurements has not been resolved. This discrepancy could be investigated by repeating the measurements made on the Nital solutions using solutions made up from 100% Nitric acid produced by distillation and making the solutions up by weight in a cold bath so preventing decomposition on mixing. From a chemical viewpoint, such solutions would be more reproducibly prepared.

The mechanism of etching on the (10\overline{1}0) plane of cadmium has not been elucidated. This however is not surprising since what occurs at the molecular level of a crystalline surface in contact with a reactive solution is known to be very complicated.
3.1 Specific Conductance v Time, 20% Nital Solutions

Graph showing the relationship between specific conductance and time for 20% Nital Solutions.
3.2 Specific Conductance v Time. 1% Nital Solutions
3.3 Specific Conductance of 1% and 20% Nital on addition of water
Addition of $\text{H}_2\text{O}$ to 20% Nital

Absorbance

Wavelength (millimicrons)

Curves A and B represent different concentrations of $\text{H}_2\text{O}$.
CHAPTER FOUR

Early attempts at obtaining projection topographs of cadmium crystals

Etch pit studies on as grown bulk grown single crystals grown by the method described in Chapter two have shown (12,17) that their dislocation density is of the order $10^5-10^6$ lines/cm$^2$. The Lang method has enabled dislocations to be observed in some materials e.g. Fe-Si (52) with this level of dislocation density and when the work for this thesis was commenced it was considered that the as-grown crystals were perfect enough for the Lang method to be applied to them, provided a suitable thinning technique could be found.

4.1. Initial lining up procedure for the Lang apparatus and general procedure for obtaining projection topographs.

Figure 4.1 shows the main features of the apparatus used for obtaining topographs of single crystals by the Lang technique. The X-ray source used was a Hilger and Watts micro-focus tube and the Lang apparatus which was positioned on top of the X-ray generator was a Jarrell-Ash model of Langs equipment. The resolution attainable using this apparatus is dependent upon the projected size of the focus as viewed through the 150μm wide slits and before any studies of cadmium were attempted some considerable time was spent in successively re-positioning the slits relative to the focus until good visibility of dislocations on topographs taken of high quality single crystals of silicon were obtained. These crystals were given to us by Mr. A.E. Jenkinson of Mullards Research Laboratories and topographs taken of his crystals were shown to him; he has worked extensively on this material using the Lang method.

The silicon crystals used were approximately 2cm diameter 1mm thick platelets and each was mounted on a lead ring by a small blob of beeswax. A small spigot mounted on the lead ring allowed
the crystal to be mounted vertically on a two circle goniometer (which fitted accurately into a circular machined recess in the bed plate of the traversing stage), so that the desired set of diffracting planes could be oriented approximately parallel to the slits. The X-ray target material used with these specimens as with all subsequent cadmium specimens to be described was silver. A scintillation counter was used as the X-ray detector and this mounted on a rotatable turntable was set at the 2θ angle for a Bragg reflection. For silicon for example for a (220) reflection and the crystal was rotated into the beam until the Bragg reflection was picked up. Initially the angular readings of the scintillation counter had been "zeroed" by placing narrow slits across the window of the counter and rotating it into the direct beam (the slits at the end of the collimator tube were also narrowed for this lining up).

The peak intensity value of the Bragg reflection was found by rotating the crystal on the goniometer in both directions in increments of 1 second of arc using a small key and observing the subsequent changes in reflected intensity using a Panax Ratemeter. Between successive adjustments using the key the crystal was rotated in the horizontal plane by rotating a vernier drum which could be rotated in 1 second of arc increments. To ensure that the peak value was obtained the crystal was always rotated through the peak value and then brought back to it by reverse rotation of the goniometer and vernier drum.

After this alignment procedure the crystal was scanned through the X-ray beam on the fastest of the two speeds of the traversing mechanism to enable the extent of crystal scanned to be set. Observation of the value of reflected intensity on the ratemeter enabled this to be accomplished.
The tantalum slits which prevented the direct beam reaching the plate were positioned and narrowed as much as possible to limit scattered radiation and the cassette containing the plate (only Ilford L4 100μm thick emulsions were used) positioned on the bedplate of the traversing stage perpendicular to the direction of the diffracted beam; the gearing of the traverse control unit was set for the exposure speed i.e. 2.5cm/hour and the specimen scanned through the beam approximately twenty times. Running voltage and current values for the X-ray generator were 50KV and 2.5mA.

After exposure the plate was removed from the cassette under safety lights and processed according to the routine set out in table 4.2.

4.2. The examination of regions of bulk crystal thinned by Jet thinning

Initially the as grown 5cmx5mmx5mm crystals were thinned at their centre region in the <1010> using a jet thinning method which was being developed at the time for obtaining thin foils for electron microscopy. The electro-polish used comprised an orthophosphoric acid plus water mixture and the bulk crystals were thinned from both the (1010) faces simultaneously until the thickness in the foil region was 75μm or less, as determined using the thickness monitoring gauge referred to in sec. 2.3. The circular shaped thinned region produced, only extended 1mm to 2mm at most parallel to the (1010) face and was not of uniform thickness.

After thinning, each bulk crystal was mounted on a lead ring to which was attached a small spigot by applying "Durofix" adhesive to one end of it. The direction of thinning allowed Bragg reflections from the (0002) and \{1120\},((0001) reflections are not realiseable since the structure factor for this reflection is
zero) planes in the symmetrical Laue transmission case (see table 4.1 for a list of Bragg angles for given diffracting planes corresponding to silver radiation).

Specimens prepared in the above fashion exhibited very low integrated reflected intensities ($10^2$ c.p.s for (0002) reflections) and indicated that the as grown crystals were highly imperfect from the X-ray topographic viewpoint. In an attempt to improve the crystal perfection, the crystals after thinning were annealed in air in a high thermal capacity oven at 250°C for 60 hrs. During anneal the specimens rested horizontally on a glass slide with the (1010) face facing upwards. After anneal the specimens were furnace cooled over a period of 8hrs. On X-ray examination the reflected intensity was found to be greater than that of an unannealed thinned crystal ($10^3$ c.p.s for (0002) reflections), but although topographs were obtained they showed no substructure detail and only small scans of the specimen could be made. The latter was attributed to the profile produced by the jet thinning technique.

Since only small regions of the crystals could be examined as a consequence of the jet thinning method, such means of thinning were abandoned and attention directed towards the sectioning and thinning of slices obtained from bulk crystals.

4.3 The examination of thinned slices of bulk crystal

Sectioning was achieved using an acid saw; 1mm thick, 1cm long slices parallel to the (0001) and (1010) planes were obtained. The depth of cutting damage was estimated at 0.3mm, by etching experiments. A .020" diameter tungsten wire was used as the cutting tool and a 20gm weight as the load. This was the minimum diameter wire that could be used to obtain a clean cut of the specimen and weights less than 20gm weight would not produce cuts at all but
merely allow the cutting wire to move across the surface of the crystal. Concentrated hydrochloric acid was used as the etch.

Subsequent work (17) on estimating spark-erosion machine damage showed that far less damage could be introduced into cadmium single crystals using this method of cutting and slicing. Acid sawing produced non parallel sided slices and this feature prevented large uniformly thinned areas from being obtained. After the slices had been obtained they were annealed in air at $250^\circ\text{C}$ for periods up to 60 hrs and furnace cooled over a period of 10 hrs; they were then thinned in the manner set out in sec. 2.3.

The handling and mounting of specimens prepared in this manner, presented a problem which had not been present in specimens produced from bulk crystals since in the latter case the crystal itself had to a large extent supported the thinned region and could be handled by carefully holding the end of the bulk crystal.

The manner in which specimens were mounted after annealing and thinning is shown in Fig. 4.2. The glass slide on which was situated the specimen was positioned in the slot of the metal plate and a lead mounting ring with a spigot already fitted to it placed over the metal plate as shown. The thickness of the plate was such that the lead ring lying on it was situated about 1mm above the specimen. A blob of "Durofix" was then applied to the corner of the specimen and the ring. After the adhesive had set the lead ring was lifted vertically from the metal plate. This manner of mounting reduced the handling of the specimen after thinning to a minimum.

Such specimens produced poor quality topographs showing no substructure detail and of only small regions of the crystal i.e. a few tenths of a millimetre. The latter was attributed to the profile produced as a result of the cutting method. At this stage
the possibility of damaging the annealed specimens during subsequent thinning was considered and subsequently specimens were thinned prior to annealing in air so that the only handling prior to X-ray examination was in the mounting on the lead rings and this was minimal. Such specimens again produced poor quality topographs and as a further improvement upon the technique annealing in air was abandoned and specimens, previously thinned were subsequently annealed in an atmosphere of commercial argon. Pyrex tubes 15cm long and 2.5cm in diameter fitted with glass stopcocks were used for containing the argon atmosphere. The specimen to be annealed was placed on a strip of glass which itself was positioned on a glass shovel which could be slipped into a Pyrex tube. These tubes were in turn placed horizontally in a tubular furnace and the specimen temperature read from a thermometer the bulb of which was positioned directly above the crystal and the stem supported by the column of the stopcock. The voltage applied to the furnace windings was stabilised and specimens were annealed at temperatures up to $310^\circ C \pm 2^\circ C$ with a temperature stability of $\pm 2^\circ C$ for periods of 5 days and subsequently cooled over periods up to 12 hours by manually lowering the voltage across the furnace. The quality of topographs obtained from specimens subjected to this heat treatment was not improved.

4.4 Determination of etch pit density of a heat treated single crystal

In an attempt to elucidate the reason for the consistent failure to produce good quality crystal by heat treating thinned slices annealed under argon a bulk crystal 2cm long was annealed under argon at $310^\circ C \pm 2^\circ C$ with a temperature stability of $\pm 2^\circ C$ for periods of 18 hrs and furnace cooled over a period of 12 hours in a high thermal capacity horizontal tubular furnace.
each heating and cooling cycle the crystal was etched in 1% Nital for 30 mins and etch pit density measurements made along the gauge length of the (1010) face (200 random measurements were made each time the crystal was etched).

Plot 4.1 shows the etch pit density of this crystal versus number of heating and cooling cycles and the histograms shown in plots 4.2 and 4.3 show the change in etch pit distribution between the unannealed crystal and the crystal after 10 cycles, respectively. The final etch pit density was $4 \times 10^4 / \text{cm}^2$ with a standard error of the mean of $0.5 \times 10^4$ and did not change appreciably from the etch pit density obtained after the third cycle. The histograms show that the etch pit distribution on annealing was more uniform.

The results of these etching and annealing experiments on a bulk crystal indicated that the bulk crystal was far more perfect after such an annealing procedure and led the author to subject, thinned specimens, to the same cycling treatment. Discouragingly topographs taken of these crystals showed no clear substructure detail.

4.5. Conclusions drawn from this early work

It was evident from this early work that the production of high quality crystal suitable for X-ray topographic examination was more difficult to produce than had first been envisaged. Expertise was not entirely lacking since topographs of high quality silicon crystals had been obtained with relative ease. The experience gained through this early work however was not wasted and certain features of the techniques developed during this period were retained; namely the procedure of thinning slices of single crystal prior to anneal, annealing under argon and mounting specimens after anneal prior to X-ray examination in the manner related. The sectioning of slices from bulk crystals was improved by going over
to spark machining, by which cutting method accurately parallel smooth sided slices could be obtained which subsequently allowed large uniformly thinned areas of crystal to be produced (chap. 2).

This early work had also shown that quite exacting heat treatments of specimens were necessary to produce good crystal and the consideration given to this problem is laid out in chap. 5.
<table>
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</thead>
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</tr>
<tr>
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<td>100</td>
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</tr>
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</tr>
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<tr>
<td>213</td>
<td>213</td>
<td>18.0 53'</td>
</tr>
</tbody>
</table>

Table 4.1: Ten strongest X-ray diffracting planes for Cadmium and Bragg angles for AgKα1 radiation.
Table 4.2. Processing procedure for Ilford L4 100um Nuclear emulsion plates

1. Water soak for 20 mins.

2. Develop in Kodak D19 for 30 mins at 0°C.

3. Stop for 10 mins in 1% Glacial acetic acid at 0°C and lightly abraid plate with lens tissue to remove all scores and abrasions developed upon plate.

4. Fix in a solution comprising equal volumes of solutions consisting of 500gms/litre of sodium hyposulphate and 30gms/litre of sodium bisulphite for 2-3 hours at room temperature.

5. Wash in tap water for 4 hours.

6. Flush plate with distilled water

7. Air dry plate (of the order 6-8 hours).

---

Fig. 4.2. Specimen mounting technique
The development of an annealing technique for producing high quality single crystals of Cadmium

As a result of the poor quality of diffraction topographs which were obtained from crystals subjected to the heat treatment described in chapter 4 the problem of annealing was re-assessed. It was considered that failure to produce high quality crystals suitable for X-ray topography, was due to (i) lack of temperature stability at the anneal temperature (ii) Too fast a cooling rate (iii) lack of temperature stability on cooling.

The lack of temperature stability at the anneal temperature was overcome by purchasing a high stability temperature control unit from Ether Ltd which was capable of controlling the temperature to $\pm 0.1^\circ$C and by designing a suitable furnace the physical structure of which was commensurate with the temperature stability of the control unit.

Slow cooling, while maintaining a temperature stability equal to that operative at the temperature of anneal presented a more difficult problem. Commercially available temperature programmers which permit cooling rates down to $1^\circ$C/hr (this was the slowest cooling rate that was envisaged would be necessary in order to produce "good" crystal) are not obtainable. Attention was therefore directed towards the design of such an instrument or system which would enable this rate to be achieved.

5.1. Initial considerations

Initially, consideration was given to the configuration shown in Fig. 5.1. with this configuration the temperature control unit permitted temperature control at the anneal temperature and it was envisaged that after anneal slow cooling could be achieved by switching out the controller and simultaneously switching in a motorised variac the voltage across the output terminals of the
variac being previously set to the voltage that was across the heaters when the control unit was in circuit. Slow rotation of the variac, reducing the voltage across the heaters would consequently reduce the temperature. The disadvantages of this arrangement are that the A.C. voltage across the heaters cannot be accurately matched i.e. on switching out the control unit and switching in the motorised variac the temperature can consequently rise or fall several degrees, the reduction in voltage across the heaters, for a uniform rotation of the variac does not result in a linear change in temperature, since the fall in temperature is proportional to $V^2$, where $V$ is the applied voltage; the rate of rotation of the variac would have to be extremely slow e.g. 1 rev/14 days for 1°C/hr cooling rate and this associated with fact that the contacts of the variac sweep over the windings of a coil would result in a non-smooth cooling curve indicating that during cooling that there was not a continuous fall in temperature but large rises and falls with an overall reduction in temperature.

Consideration, after the rejection of the system outlined above, was next given to the configuration shown in Fig. 5.2. This configuration is the basis of commercial electro-mechanical temperature programming systems. In this system as in the one previously described, the sensing element of the control unit is a thermo-couple. The desired temperature of the "furnace" is set on a front panel and when the unit is switched on pre-set voltages for the given temperature setting are developed in it and mains voltage is supplied to the heaters. As the thermo-couple warms up, the emf generated by it is compared with the pre-set voltage for the given temperature setting and when these voltages are nearly equal the voltage across the heaters is reduced from mains voltage. The voltage is further reduced across the heaters until
that voltage generated by the thermo-couple equals the pre-set voltage and the voltage which is then across the heaters is maintained i.e. the unit at this stage is controlling the temperature.

The "furnace" is cooled at a given rate by impressing upon the output voltage of the thermo-couple an additional voltage across the fixed resistor shown in Fig. 5.2, which is in series with the thermo-couple. The control unit regards such an increased input voltage as an increase in the "furnace" temperature beyond that which was pre-set and lowers the voltage applied to the heaters in order to bring the total output voltage from the thermo-couple to a value equal to the pre-set voltage. In the system shown in Fig. 5.2, the voltage addition with time is achieved by a motorised heli-potentiometer which increases the voltage developed across the fixed resistor as the wipers of the potentiometer are rotated. By way of example with a chromel-alumel thermo-couple system an additional voltage of 0.1mV impressed upon the thermo-couple output voltage would lead to a temperature reduction of approximately 2°C. The disadvantages of this system however are the very slow rotation rates of the heli-potentiometer required for slow cooling and the lack of resolution of the additional voltages that can be impressed on the thermo-couple output voltage.

Neither of the electro-mechanical systems described thus appeared adequate for what was required i.e. slow cooling, while maintaining high stability of temperature and high resolution (small temperature drops per unit time), attention was therefore directed towards the development of an electronic system which would replace the motorised heli-potentiometer of Fig. 5.2 and apply voltage additions across the fixed resistor by purely electronic means.

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5.2. The construction of an all-electronic temperature programmer

The basic system that was adopted is shown in Fig. 5.3. Here the motorised heli-potentiometer system of Fig. 5.2. is replaced by a variable pulse generator in series with a staircase waveform generator, a constant current source and current regulator. The staircase waveform generator Fig. 5.4 comprised bi-stable multivibrators (flip-flops) connected to trigger in sequence giving a binary coded output which was read by passing a constant current through resistors which were switched in and out on the reception of a pulse from the pulse generator. When the voltage across the resistors was read the result was a staircase voltage waveform which moved up one step each time a pulse was applied. If the rate at which the input pulses were applied was varied the rate of increase of output voltage was also varied. The number of steps to the total staircase voltage waveform is $2^n$, where $n=\text{number of bi-stables and hence the total time to build up maximum output voltage is } 2^n t$, where $t$ is the time duration between the application of each pulse. The output voltage of the staircase generator was used as the reference potential for a current regulator Fig. 5.5, so that the output current was proportional to the input voltage. The variable $1\Omega$ resistor shown in Fig. 5.5. allowed a max. value of current to be passed through a $1 \Omega$ resistor in series with the thermocouple i.e. set a maximum value of voltage that would appear across this resistor for the maximum voltage developed by the staircase generator and in practise this was set equal to the thermo-couple output voltage at a given anneal temperature. Twelve bi-stables were used in the staircase generator so that the total output voltage appearing across the fixed $1\Omega$ resistor in series with the thermo-couple was applied in $2^{12}$ steps i.e. 4096. By re-setting the pulse rate from the pulse generator at set times
any cooling law could be obtained since in the temperature range 20°C-320°C the thermocouple (chromel-alumel) characteristic i.e. e.m.f VS temperature is linear and for a given pulse rate setting the output voltage from this electronic device was linear with time.

Fig. 5.6 shows the circuit diagram of the pulse generator used. Pulse rates varying linearly with $R_{v1}$ from 1 every 4 seconds to 1 every 4.5 minutes were obtained using this circuit. The pulse rates for a given $R_{v1}$ value were found using an oscilloscope and hence the cooling times could be accurately determined since they equalled $2^n t$. In the device with $n=12$, and $t_{max}=45$ minutes and $t_{min}=4.0s$ the maximum cooling time was $2^{12} \times 4.5/60 \times 24 = 12.8$ days and the minimum was $2^{12} \times 4/60 \times 60 \times 24 = 4.5$ hrs with any number of intermediate cooling times, depending upon the resolution of $R_{v1}$ (a ten turn helipotentiometer was used). The cooling rate is given by $T_A - T_{RM} \times t / 2^{12}$, where $T_A$ = anneal temperature, $T_{RM}$ = room temperature and the stability of this device was better than that of the Ether control unit which was capable of controlling a temperature to 0.1°C and the maximum temperature drop per pulse was 300/2^{12} i.e. less than 0.1°C.

The device described above has been patented by the National Research and Development Corporation (Provisional Patent No. 23966/68) in the names of A.S.T. Bagrick and B. Selway (Chief technician electrical Workshop University of Surrey) with a view to commercial exploitation (see appendix II).

5.3. Furnace Construction

In order that the inherent temperature stability of the controller and programmer previously described were imparted to the specimen being annealed considerable attention was directed towards
the construction of a furnace and the positioning of the thermo-
couple unit.

Figs. 5.7, 5.8 show the furnace that was used. The box
surrounding the heating element was made from Sandanyo and the
heater comprised a cylindrical copper tube around which was
wrapped asbestos paper over the asbestos the heater windings were
wound 0.1" apart and from 32 gauge Nicro-Alloy wire. Over the
wire was wrapped asbestos rope. The junction of the thermo-couple
(chromel-alumel) was positioned in the centre of the table and
its ends were taken out through a small hole in the box. A
polystyrene cap covered the entrance of the furnace and in this
way draughts were prevented from causing excessive temperature
instability at the position of the thermo-couple junction. With
this furnace in operation temperature stability at the thermo-
couple junction better than ±0.2°C was achieved.

5.4. The Annealing Procedure

Specimens were prepared in the manner described in Chap. 2
and not more than two were placed on a glass spoon and located in
the annealing tubes described in Chap IV. In order to prevent
oxidation during anneal the tubes were pumped out using a diffusion
pump to a pressure of .005μm and flushed out with commercial argon
three times. Finally argon was bled into the tube till a pressure
of 0.5 atmos was registered on a pressure gauge connected in
series to the pumping unit, so that at the anneal temperatures
used the pressure over the specimens was about 1 atmosphere. Such
a pressure also prevented excessive vapourisation, which could
not be tolerated using specimens .003" thick.

The tube containing the specimens was then slipped into the
furnace tube to a distance such that the specimens were situated
immediately above the thermo-couple junction and the polystyrene
cap was butted against the furnace so surrounding the stop-cock of the tube and preventing draught's.

The temperature setting on the front panel of the controller was set at a temperature 5°C below the desired anneal temperature, so that the overshoot on warming up would not exceed it. After stabilising the controller at this temperature, the temperature was incrementally raised to the desired anneal temperature and the specimen left at this temperature for the required anneal time. After anneal the thermo-couple output voltage at this temperature and the maximum output voltage to be dropped across the 1 ohm resistor in series with it were matched using a Solartron Digital Voltmeter capable of reading to .01mv, the pulse rate was set and the programmer switched in to produce a given cooling rate.

At room temperature after cooling the specimens were removed from the annealing tubes and mounted on lead rings in the manner described in Chap 4, after which they were ready for X-ray microscopy examination.
Fig. 5.1.

Temperature control unit

Thermo-couple

Heaters and furnace

Motorised variac

Voltage stabiliser

Fig. 5.2.

Millivolt D.C. source from motorised helipotentiometer

Fixed resistor

Temperature control unit

Heaters and furnace
Fig. 5.7.

Polystyrene cap

Heater

Thermo-couple (chromel-Alumel)

15.0"

Fig. 5.8.

15.0"
PRESENTATION OF RESULTS

In this chapter will be presented Lang X-ray topographs of cadmium specimens prepared from slices cut parallel to the basal and (10\(\overline{1}0\)) planes as set out in chapter two, and micrographs of etch pit formations on the (10\(\overline{1}0\)) plane after various annealing procedures.

The original topographs were photomicrographed using a Zeiss transmission optical microscope and Addox KB14 35mm film. Micrographs of etch pits were obtained using a Reichart reflection optical microscope and standard 3"x2½" Ilford plates.

All the topographs were obtained using AgK\(\lambda_1\) radiation and recorded on Ilford L4 (100\(\mu\)m) thick nuclear emulsion plates.

Reflections from \{10\(\overline{1}0\)\}, \{11\(\overline{2}0\)\}, (10\(\overline{1}1\)) were obtained from specimens prepared from slices cut parallel to the basal plane and from (0002) and \{11\(\overline{2}0\)\} in specimens prepared from slices cut parallel to (10\(\overline{1}0\)). The horizontal topographic magnification in the reflections used is shown in table 6.2. Topographs obtained of specimens oriented parallel to the basal plane are prefixed by the letter "A" and those oriented parallel to the (10\(\overline{1}0\)) by the letter "B".

Table 6.1 shows the temperature at which specimens, which will be considered, were annealed and the approximate total cooling time in days, while plot 6.1 shows the details of the annealing history of each specimen.

6.1 Specimens prepared from slices cut parallel to the basal plane; Anneal temperatures in excess of 220\(^\circ\)C

6.1.1. Crystal Al(1)

Topographs obtained from this specimen are shown in prints 6.1a page 104 and 6.1b page 105. The visibility of dislocations is not good in either (\(\overline{1}010\)) or (\(\overline{1}2\overline{1}0\)) reflections. On print 6.1a
some dislocations are visible in the subgrain to the right of the topograph and there is a suspicion of dislocation loops within it. The subgrain boundaries taken in (1210) reflection 6.1b show a splitting indicating that reflection has occurred from both the K components i.e. $\text{AgK}_1$ and $\text{AgK}_2$. Such a splitting of the image of the subgrain boundary, further indicates that the quality of the crystal is not "good". It is pointed out however that the quality of this crystal was the highest obtained to that date.

6.1.2. Crystal Al(2)

This crystal was the same as Al(1) but had been re-annealed at the same temperature and cooled over a period of approximately four days compared to two days for Al(1). The topographs obtained from this specimen are shown in prints 6.2a page 104, 6.2b page 105. It is observed that the subgrain size on re-anneal has increased by at least a factor of 2 and that the visibility of dislocations has considerably improved. In (1210) reflection, print 6.2b, no splitting of the images of the subgrain boundaries is observable, a further indication that the quality of the crystal has been enhanced on re-anneal and slower cooling. The dislocation density is of the order $10^5$ lines/cm$^2$. Print 6.2a shows that there is considerable warpage between adjacent subgrains, evidenced by the lack of uniform reflectivity from such grains. Close examination shows within some of the subgrains small black dots, indicating the possibility of unresolved dislocation loops.

6.1.3. Crystal A2 (2)

This crystal was initially annealed at 250°C and cooled over a period of approximately two days (A2(1)). No topographs could be obtained from this crystal since the extent of traverse was limited by the apparent small grain size. It was subsequently re-annealed at 275°C and cooled over a period of three days. The topographs
obtained from this specimen are shown in prints 6.3a and 6.3b page 166. Individual dislocations are not visible and print 6.3a shows a splitting of the images of the subgrain boundaries, indicating that the quality of the specimen could be improved. An interesting feature is the reversal of contrast of one of the subgrain boundaries when taken in (1011) reflection. The size of the subgrains are comparable to those in specimen Al(2) and a comparable degree of warpage between subgrains is observed.

6.1.4. Crystal A4

Prints obtained from topographs of this crystal are shown in 6.4a and 6.4b page 167. In (1010) reflection the shape of the subgrains appears to be less regular than those shown of topographs of other crystals previously presented. The subgrain size however is comparable to that in crystals Al(2), and A2(2); both these specimens however had been subjected to two consecutive anneals in order to bring the subgrain size up to the observed magnitude, whereas crystal A4 had only been annealed once at 500°C but cooled over a period of three days. The dislocation density of this specimen as estimated from the (1210) reflection is of the order $10^5$ lines/cm$^2$.

6.1.5. Crystal A5

The substructure of this crystal is revealed in print 6.5 page 169. The subgrain size is observed to be larger than in any of the specimens previously considered. Dislocations appear to be narrower in one subgrain than in another; warpage between adjacent subgrains is less considerable. Close examination indicates the possibility of unresolved dislocation loops within the subgrains, as evidenced by small black dots. The dislocation density is estimated at between $10^4$-$10^5$ lines/cm$^2$. 

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6.2.1. Specimen prepared from slice cut parallel to (10\overline{1}0)

Anneal temperature 275°C: Crystal B3

Specimens of "good crystal" in this orientation were difficult to obtain even after annealing and slow cooling. Only one "good crystal" in the annealing regime \( T \geq 220°C \) has been obtained and examined.

The substructure of this crystal is shown in prints 6.6a and 6.6b pages 108, 109 taken in (0002) and (12\overline{1}0) reflection respectively. The three photographs shown in 6.6a are from the same topograph and the central clear region is not due to diffraction effects but depicts the region of a hole in the original crystal, produced during final thinning. Fewer subgrain boundaries are visible than in specimens prepared from slices parallel to the basal plane and annealed and slowly cooled. Bands of varying intensity are observed running across the topograph (the so-called Pendellosung fringes see sec. 7.1). Running towards the holed region are observed dark streaks (generally parallel to (0001)).

Print 6.6b again shows a variation in intensity across the topograph. There is also the appearance of large relatively intense dots in the centre of the topograph these could be dislocation loops viewed end on: bend contours are also visible. As has been pointed out by Lang (87) these topographs exhibit complicated X-ray diffraction effects not easily amenable to interpretation.

Crystal B3 was annealed with crystal A5.

6.2.2. Etch distribution on 1mm thick slice cut parallel to (10\overline{1}0) and annealed with crystals A5 and B3

Prints 6.7 to 6.10 show the etch pit distribution on the uncut face of the crystal after annealing with crystals A5 and B3. The crystal was etched in 1% Nital for 30mins. and in order to avoid damage due to handling, the etching reaction was quenched off.
using ethanol and under this liquid without removing it from the
etching vessel the crystal was photographed. It is observed that
the etch pit distribution is far from uniform even after the
exacting heat treatment to which it had been subjected. The mean
etch pit density has been estimated at 25x10^5/cm^2.

Sec. 6.3. Specimen prepared from a slice cut parallel to
basal plane. Anneal temperature 220°C: Crystal A6

Detailed consideration in this section will be given to the
topographs obtained from this crystal (prints 6.11 to 6.34). Mere
inspection of these topographs shows that the substructure detail
and dislocation nature and configuration is significantly different
from topographs previously presented which were obtained from
specimens cut in this orientation, but annealed at higher tempera­
tures and cooled at faster cooling rates.

6.3.1. Features on time lapse topographs taken in (1210) reflection

Attention is drawn to prints 6.11, 6.12, 6.13 page 111 which
were taken on day 1, day 6 and day 11 respectively. On these
topographs is observed a large number of dislocation loops, which
are thought to lie in the basal plane and which have diameters
approximately 50-70µm. Comparison of the time sequence topographs
reveals.

(i) A decrease in size and density of loops of regions 6.11a,
6.12a, 6.13a, (particularly 6.12a and 6.13a). Also, the dislocation
line length of dislocations emanating from the subgrain boundary
has increased between taking topographs shown in prints 6.12, 6.13
and this is associated with a decrease in the loop density in the
region 6.13a.

(ii) The appearance and disappearance of "straight disloca-
tions". They are evident on print 6.11 at position marked b
(see also high magnification of the same region print 6.15 position
a) and absent on print 6.12 at the corresponding position b. On print 6.13 however they are again apparent at position $b_1$ and in the area marked $b_2$. The new "straight dislocations" however which have appeared are noticeably narrower than those shown at position 6.11a.

(iii) An "S" shaped dislocation on day 1 joining two adjacent loops. See print 6.14 position a which is a high magnification of the relevant part of print 6.11.

(iv) The contrast of the loops observed are not the same. Initially the majority of the loops have lines of minimum contrast approximately perpendicular to the $g$-vector or lines of zero contrast perpendicular to the $g$-vector. See for example print 6.14 and compare regions designated by $b$ and $c$.

(v) The appearance on print 6.13 at $c$ of a double loop with double contrast in outer ring all the way around.

(vi) The appearance of a double (treble?) loop, print 6.13 position $d$ with loss of contrast in the direction perpendicular to the $g$-vector.

(vii) The termination of a subgrain boundary within the subgrain. See print 6.13 for example position $e$.

6.3.2. Features on time lapse topographs taken in (1210) reflection and comparison with those taken in (1210)

Prints 6.16, 6.17 page contribute a stereo pair taken in (1210) and (1210) reflection, in an attempt to obtain information of the spatial relationship within the crystal of the loops observed. Inspection of these reveals

(i) Considerable warpage of the subgrain evidenced by the fact that only approximately one half of the subgrain has been picked up in (1210). However a further subgrain has been picked up in this reflection which was not detected in (1210), where the
main subgrain exhibited uniform reflectivity. See print 6.19 which shows approximately half the subgrain picked up in (1210) and the further smaller subgrain surrounded by a background network of dislocations. The dark band running vertically from top to bottom of the print is a consequence of a technical failure in the traversing mechanism of the Lang X-ray equipment towards the end of the exposure and should be ignored. The misorientation of the two subgrains shown in 6.18 about the vertical axis of the goniometer was estimated at 6 minutes of arc.

(ii) That contrast of the loops in regions 6.16a and 6.17a are different in stereo reflection. The line of minimum contrast shown in 6.16 has disappeared in 6.17.

(iii) A linear feature with striation substructure in (1210) only 6.17b.

(iv) That tangled dislocation arrays surrounding the further small subgrain visible in (1210) reflection prints 6.18, 6.19, 6.20 page114 significantly exhibits no loops. However the dislocation density in these arrays is high of the order $10^5-10^6$ lines/cm$^2$. The nature of this background network appears to be changing with time.

(v) That the two adjacent loops shown in the time lapse topographs in prints 6.21, 6.22, 6.23 page115 and designated by a have shrunk with time.

(vi) The two adjacent loops referred to above appear to be slightly thicker and have less pronounced lines of minimum contrast perpendicular to the g-vector as compared with loops showing minimum contrast in (1210).

(vii) An increase in the line length of dislocations emanating from the subgrain boundary into the subgrain with time which is coupled with the fact that the two adjacent loops referred to in
have shrunk. See prints 6.22, 6.23 areas designated by $b$.

Reflection

Prints 6.24, 6.25 page 66 show with a time lapse the dislocation arrangement in a subgrain in stereo reflections i.e. (1010) and (1010). The subgrain shown is different to that observed in (1210) and (1210) reflections. Inspection of this stereo pair reveals

(i) Differences in loop size and contrast (a) with time (b) at the same time within the same grain.

Prints 6.26, 6.27 page 67 are high magnification photographs of particular regions of prints 6.24 and 6.25. On print 6.27 at $a$ is observed a large "double C" loop and two "double D" loops at $b$ and $d$. The lines of zero contrast of the loops at $b$ and $d$ are misoriented relative to each other. The line of zero contrast of loop $b$ is perpendicular to the $g$-vector while that of $d$ is misoriented from it by approximately 10°

(ii) Comparison of loop $d$ in the time sequence topographs prints 6.26, 6.27 shows that this loop has grown with time and that its contrast appears to have become enhanced.

(iii) The feature designated $c$, print 6.27 has grown into a loop showing treble contrast and having a polygonal nature, $c$ 6.26.

(iv) On print 6.28, which is another high magnification photograph of print 6.24, region $b$ groups of loops exhibiting complicated contrast effects, not easily amenable to interpretation.

(v) That dislocations have been ejected into the subgrain (cf prints 6.22, 6.23 where the line length of dislocations emanating from the subgrain boundary has increased over a comparable period of time, and not been injected into the subgrain).
(vi) Loops exhibiting full contrast around their periphery and with interior detail b and c print 6.25, double loops a, 6.25 which suggest that they are loops stacked one upon the other.

(vii) That there is evidence at a, print 6.29 of a mobile dislocation being held up by a "double D" loop.

6.3.4. Detail obtained in (1011) reflection

Print 6.30 shows the detail obtained in (1011) reflection. Multiple loops of a complicated nature are observed. Diffraction effects are noticeably increased in their complexity in this type reflection, as a consequence of increased absorption arising from an increase in the specimen thickness as measured along the diffracting planes.

6.3.5. Further ageing effects

Prints 6.32, 6.34 are extensions of the topograph shown in prints 6.24, 6.25. Prints 6.31, 6.33 are the same regions of the crystal examined on day 18. It is immediately evident on comparison that the crystal quality has deteriorated markedly in a short space of time i.e. 4 days: features which were at one time well resolveable have taken on a "streaked" appearance. This was the final characteristic of the crystal in all reflections and within all subgrains, and topographs taken two months later still showed these aged characteristics.

The high degree of subgrain warpage in this crystal which prevented the same subgrain from being easily examined in different reflections and the marked degree of recovery occurring at room temperature between all exposures prevented Burgers vector determinations of individual dislocations being made.

The limited "lifetime" of the crystal was also another contributory factor in not permitting more detailed observation of particular features to be carried out.
Fig. 6.3 shows in schematic form the different types of loop contrast observed in this crystal before it took on the final static aged character. (Loop contrast in A6 is summarised in Fig. 6.3) Specimen prepared from slice cut parallel to basal plane
Anneal temperature 220°C. Crystal A7

(Topograph 6.36 and 6.38 have been reversed inadvertently on printing). Inspection of prints 6.35 to 6.38 reveals

(i) Dislocation loops in the low dislocation density subgrain to the left (cf print 6.11 page 111 crystal A6 for example in which the initial size of the loops in this crystal are larger).

(ii) Within the same subgrain long basal dislocations (cf again print 6.11 page 111 where the initial predominance was towards "short" dislocations).

(iii) In the region designated a print 6.35 are seen hexagonal arrays of dislocations. These are also apparent at the corresponding position on prints 6.35, 6.37.

(iv) At the position marked b print 6.35 there is some evidence for an extended node configuration. See also print 6.37 at the corresponding position.

(v) The two lines designated by c print 6.35 trace the position of lines of enhanced contrast running across the subgrain. These are the Pendellosung fringes (see sec. 7.1) and give a qualitative indication that the crystal is "good".

(vi) As the crystal has aged the Pendellosung fringes remain visible, indicating that although changes in loop size had occurred the crystal perfection has not deteriorated as a consequence.

(vii) Over the net period of 4 days shown the diameter of the loops has approximately doubled but that loop density has remained sensibly the same. (cf crystal A6 prints 6.11, 6.12 page 111, which show that over a period of six days the diameter of the loop and
their density has remained relatively constant): however the
dislocation arrangement has remained static.

(viii) The dislocation density of the tangles of dislocations
within the other subgrains seen is of the order \(10^5\) lines per cm\(^2\).
Significantly there are no loops observable within these regions
of the crystal. (cf the tangled dislocation arrangements surrounding
the subgrain containing loops in prints 6.18-6.20 page 114 where
again within such regions loops are not visible).

(ii) The dislocation density within the subgrain containing
loops is estimated to be of the order \(10^4\) lines per cm\(^2\).

(iii) That the region designated in print 6.38 is devoid of
substructure detail as is the corresponding region in print 6.37.
Print 6.36 however which represents the result of a slight re-
orientation of the crystal before exposure has brought this region
into a diffracting position. The significant point is that in
so doing the visibility of dislocations within the subgrain con-
taining loops has deteriorated, indicating that not only is there
warpage between subgrains but also warpage within individual
subgrains. Moreover the hexagonal dislocation arrays referred
to in (iii) have become clearer.

(iv) Print 6.38 taken in (1010) reflection after seven days
shows again, as in crystal A6, the ageing effects associated with
crystals annealed at 220°C and slowly cooled. In this print is
noticed the "streaky" nature of the dislocations and the "blurring"
of the detail of the loop images. Pendellosung fringes are not
clearly visible, indicating that the crystal quality of this time
has deteriorated.

On the right hand side of the subgrain observed are seen
pronounced bend contours which are not visible on prints 6.35-6.37.

After day 7 no detail was observable in this crystal (cf crystal
A6 in which although changes in dislocation arrangement occurred continually with time, the crystal did not deteriorate in quality appreciably until day 18 of its examination and the aged character remained constant, as evidenced by topographs taken six weeks later.

6.5. Specimen prepared from slice cut parallel to the (1010) plane. Anneal temperature 220°C. Crystal B7.

This crystal was annealed with crystal A7 the substructure features of which were considered in section 6.4. Crystal B7 was prepared from a slice one side of which was spark machine damage free and hence had allowed the profile and texture of the etchable face to be retained during thinning, since the thinning was carried out on the damage face of the slice only.

Before X-ray topographic examination this crystal was etched for 20 mins in 1% Nital (on annealing, the crystal had been positioned in the annealing tube with its etchable (1010) face upwards, so that after anneal, the handling of the crystal prior to etching would not necessitate turning the crystal over and hence possibly bending it). After etching for this period (the normal 30 min etching time could not be tolerated since the crystal began to hole in the thinner region of the foil), the reaction was quenched off using ethanol and under this liquid the etch pit configuration on the (1010) face was photographed. See prints 6.42 to 6.45 page 124.

After being photographed, the crystal was removed from the etching vessel (though still on the glass microscope bedplate on which it had been annealed) and the ethanol drained from it. The crystal was finally dried using a cold-air blower and mounted for X-ray topographic examination.

Prints 6.39 to 6.41 show the substructure detail obtained
from this crystal after annealing and etching.

No fine detail is observed in reflection from (0002), print 6.39. Print 6.41 taken in (1210) reflection shows pronounced bend contours, but print 6.40 again from a (1210) reflection does show some dislocation detail.

The possibility of obtaining a correlation, though not a one to one, between etch pits on the surface of the specimen and dislocations within the bulk is realizable from this crystal.

The mean etch pit density as estimated from prints 6.42 to 6.45 in $3.0 \times 10^5$ per cm$^2$, and the mean dislocation density as estimated from the topograph region a in print 6.40 is estimated at $1.0 \times 10^5$ lines per cm$^2$. Since the number of counts of etch pits was greater than the number of counts from the topograph, the standard error of the individual counts is the error that must be attached to the above estimates if comparison between them is to be made. These are $2 \times 10^5$ per cm$^2$ for the etch pits and $0.8 \times 10^5$ lines per cm$^2$ for the dislocations on the topograph.
Anneal Temperature 314°C Approximate Cooling Time 2 days

6.1a Al(1) \[ 700\mu m \rightarrow [1010] \]

Anneal Temperature 314°C Approximate Cooling Time 4 days

6.2a Al(2) \[ 700\mu m \rightarrow [1010] \]
Anneal Temperature 314°C Approximate Cooling Time 2 days

Anneal Temperature 314°C Approximate Cooling Time 4 days
Etch pit distribution on (1010) face of single crystal, thickness 50-75μm × 12.8
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Anneal Temperature °C</th>
<th>Approximate total Cooling time (days)</th>
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</thead>
<tbody>
<tr>
<td>A1(1)</td>
<td>314</td>
<td>2</td>
</tr>
<tr>
<td>A1(2)</td>
<td>314</td>
<td>4</td>
</tr>
<tr>
<td>A2(1)</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>A2(2)</td>
<td>275</td>
<td>3</td>
</tr>
<tr>
<td>A4</td>
<td>300</td>
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<td>6</td>
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</tr>
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<td>220</td>
<td>7</td>
</tr>
<tr>
<td>A7</td>
<td>220</td>
<td>12</td>
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</table>

Table 6.2. Horizontal Topographic magnification for AgKα₁

<table>
<thead>
<tr>
<th>Section</th>
<th>Reflection</th>
<th>Transmission Mode</th>
<th>Magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel to basal plane</td>
<td>(1010)</td>
<td>Symmetrical Laue</td>
<td>0.994</td>
</tr>
<tr>
<td>Parallel to basal and (1010) plane</td>
<td>(1120)</td>
<td>&quot;</td>
<td>0.984</td>
</tr>
<tr>
<td>Parallel to (1010)</td>
<td>(0002)</td>
<td>&quot;</td>
<td>0.994</td>
</tr>
<tr>
<td>Parallel to basal plane</td>
<td>(1011)</td>
<td>Asymmetric Laue</td>
<td>0.851</td>
</tr>
</tbody>
</table>
6.1. Cooling curves of (10\(\bar{1}0\)) and (0001) oriented annealed foils
6.3. LOOP CONTRAST OBSERVED

Reflection (11\overline{2}0)

( ) 6.14a

( ) 6.14b

Line of minimum contrast

( ) 6.22a

( ) 6.13d

( ) 6.13c

(11\overline{2}0)

(10\overline{1}0)

( ) 6.27a (Double "C")

( ) 6.27d (Double "D")

( ) 6.25a

( ) 6.25b

( ) 6.25c

( ) 6.26c

(10\overline{1}0)
7.1. X-ray Diffraction Phenomena in Perfect Crystals

7.1.1. Pendellosung Interference

When a plane wave of monochromatic X-rays falls upon a perfect crystal at an angle that exactly satisfies the Bragg condition for certain lattice planes that are steeply inclined to the crystal surface, both the reflected waves and incident waves are directed into the crystal. As a consequence of the definition of a "perfect" crystal i.e. one in which ideal periodicity of its lattice is maintained through its volume, the coherent addition of the contributions of reflections from individual Bragg reflecting planes to the resulting amplitude of the Bragg reflected wave can build up this amplitude to a value comparable to that of the incident X-ray beam; and that such a build up may occur within a short distance from the X-ray entrance surface. Below some depth from the X-ray entrance surface the energy flow in a crystal exactly satisfying the Bragg condition is equally divided between the directions of the incident and diffracted waves. The depth below the surface at which this occurs is the depth interval \( g \); the extinction distance: within one extinction distance the energy flow direction makes one extreme of flowing purely along the incident beam direction and the other of flowing purely along the diffracted beam direction.

When Bragg reflection occurs in a perfect crystal, waves travelling in the incident and diffracted beam directions are split into two component waves with slightly different phase velocities, one being greater and the other slightly less than the phase velocity given by the expression for the refractive index: the incident and diffracted waves in the crystal each contain two slightly different wavelengths. It is the subsequent interference between the waves of slightly different wavelengths
that causes the energy flow to oscillate between the incident and
diffracted beam directions: it is analogous to the transference
of kinetic energy back and forth between two coupled pendulums.
The solution of the dynamical diffraction problem obtained by
Ewald in 1917 which displayed this oscillation was termed by him
the "Pendellosung" - the pendulum solution.

The extinction distance $\delta g$ in the symmetrical Laue case is
given by $\delta g = \left( \frac{mc^2}{\epsilon^2} \right) \frac{V \cos \theta}{F \lambda}$, where $\theta$ is the Bragg angle and $V$
the volume of the unit cell and $F$ the structure factor for the
reflection operating (in reality a complication arises due to
the two states of polarisation of the X-rays, the $\sigma$ state in
which the direction of the electric vector is perpendicular to
the plane of incidence and the $\pi$ state in which the electric vector
is parallel to the plane of incidence). The above expression for
$\delta g$ applies to the $\sigma$ state.

X-ray Pendellosung phenomena were first studied by Kato
and Lang (75). They took topographs of wedge shaped specimens
of perfect crystals. On the topographs obtained fringes appeared
parallel to the wedge axis. The fringes corresponded to the
intersections of the X-ray exit surface of the wedge with the depth
contours given by the Pendellosung oscillation of energy flow
between the direct and diffracted beam directions. A recognisable
manifestation of Pendellosung phenomena in any part of a crystal is
taken as a criterion of crystal perfection: it can only occur when
direct and diffracted beams have comparable amplitudes, and a good
measure of coherence between the diffracted rays is maintained over
a distance of the order of an extinction distance. Conversely
when any imperfection occurs in a perfect matrix so that phase
relations are abruptly disturbed, the intensity diffracted into
the diffracted beam will depend upon the phase of the Pendellosung
oscillation. Hence a depth dependent periodic intensification of blackening will occur in topograph images of the imperfection: it is a familiar feature in images of low angle boundaries and dislocations. The effect of polarisation of the X-ray beam on the visibility of Pendellosung fringes has been discussed in detail by Hart and Lang (76).

7.2. Diffraction Contrast from imperfections in nearly Perfect Crystals

Zachariasen (77) has given the expression \( R = \frac{2}{\pi D} \int_0^{\pi D} J_0(x)dx \), for the variation with crystal thickness of the integrated reflection produced by a perfect non-absorbing crystal in the symmetrical Laue case where \( D \) equals \( \frac{1}{\varepsilon g} \), \( J_0(x) \) is the Bessel function of zero order. No need has to be taken of contributions from the \( \sigma \) and \( \pi \) states of polarisation. Lang (42) gives the intensities (normalised) of the maxima and minima and the specimen thicknesses at which they occur (expressed as multiples of the extinction distance), calculated by Lang (42) from the above expression. The initial linear rise in intensity corresponds to the situation when the amplitude of the diffracted wave is much less than that of the incident wave and multiple reflection within the crystal maybe ignored as in the calculation of intensity from an ideally mosaic crystal. Thus up to a certain thickness, the ideally perfect and ideally mosaic crystal cannot be distinguished on the basis of a difference in integrated reflection. The transition from "thin crystal" diffraction behaviour to that of the thicker crystal has been investigated in very thin tapering wedges of moderately perfect crystal (42). The topograph image is found to be completely featureless until a thickness of about \( \frac{\varepsilon}{\varepsilon g} \) the extinction distance is reached, (42) fair diffraction contrast from imperfections appears at the first Pendellosung maxima and at the first Pendellosung.
minimum stronger diffraction contrast is manifested than at any other depth.

In discussing X-ray topographic images of dislocations it is useful to distinguish between the "direct" and "dynamical" image (42). The former is produced by the distorted regions close to the dislocation where the Bragg reflected rays have lost their coherence with those in the surrounding more perfect matrix. The dynamical image arises from the weaker distortions more remote from the dislocation. Such weaker distortions act mainly to produce a redistribution of the coherently reflected rays on the crystal exit surface. The dynamical image is diffuse; the direct image is intense and well localised provided it does not much exceed unity. The direct intense images have no counterpart in electron microscopy and arise because the angular range of Bragg reflection by the crystal is only a small fraction of the angular divergence of the incident beam.

The dynamical image of a dislocation has enabled the sense of the Burgers vector of dislocations to be determined (78). Within the last few years adequate theories have been developed for calculating the trajectories of X-rays undergoing Bragg reflection in distorted crystals (79, 80, 81). It is found that when the Bragg planes are curved so that the angle they make with the incident beam direction varies smoothly and not too rapidly with depth within the crystal, then the X-ray energy itself flows along a curved path. The ray curvature is sharpest for those X-rays locally fulfilling the Bragg condition exactly. However waves belonging to different branches of the dispersion surface are curved in opposite directions in simple structured materials, waves belonging to one branch of the dispersion surface (so-called branch 1 waves) i.e. that branch of the dispersion surface whose
wave vectors are closer in magnitude to the X-ray wave vector in vacuo, suffer less than average absorption, whereas those belonging to the other branch of the dispersion surface (so-called branch 2 waves), suffer more than average absorption in the vicinity of the Bragg reflection. This difference is the cause of the Borrmann effect referred to in Chap. 1 and is most marked for rays fulfilling the Bragg condition exactly. For such rays branch 1 rays are several times as strong as branch 2 waves in the absorption region $\mu t=1$, and completely dominant in coherent reflection in the range $\mu t>1$. According to Lang (42) rays whose sense of curvature is in the same sense as the curvature of the Bragg planes are composed of dominant branch 1 waves: the consequence of this geometrical situation is that a topograph of hkl reflection which occurs off the convex side of the Bragg planes will exhibit less intensity than normal whereas a topograph taken in $\overline{h}k\overline{l}$ in which the Bragg plane normal is directed towards the centre of curvature of the Bragg plane will exhibit an extra diffracted intensity. It follows that the dynamical images of dislocations having an edge component will show different contrast in hkl and $\overline{h}k\overline{l}$ reflections, as a result of opposite contributions from their dynamical images to the total image intensity.

The direct image visibility and width is highly dependent upon the local lattice tilt. In the strain fields of dislocations, which give rise to lattice plane curvatures which increase rapidly as the dislocation is approached it appears that (42) it is the magnitude of the tilt away from the matrix orientation reached at a point near the dislocation that can be taken as the criterion for the commencement of a sharp rise in diffracted intensity. If the critical value of tilt is reached a relatively long way from
the dislocation core there will be a relatively large volume of crystal which can give rise to the direct image and the integrated excess intensity from the dislocation will be high. On the other hand if the critical tilt is not reached at all along the X-ray trajectory or at a point so close to the dislocation core that scattering can only occur within a small volume e.g. a micron in diameter then the dislocation will be invisible. Lang (42) has reported that the critical value of tilt is approximately equal to the angular width, \(2\theta_{1/2}\), at half maximum intensity of the perfect crystal reflection curve. In the symmetrical Laue case and negligible absorption, the simple relation applies

\[
2\theta_{1/2} = 2d,
\]

where \(d\) is the interplanar spacing.

7.3. Extinction Distances in h.c.p Metals and fractions of dislocations visible in given reflections

In section 7.1 an expression was given for the extinction distance in terms of the structure factor \(F\), the volume of the unit cell and the Bragg angle. A knowledge of the magnitude of the extinction distance in X-ray topography is useful for several reasons: in good crystal of varying thickness a determination of the specimen thickness can be estimated by counting Pendellosung fringes and using the data given by Lang (42). Thickness measurements can be made of specimens to within a few micron (42) without resorting to mechanical means, such as feeler gauges or micrometers. Furthermore a knowledge of the extinction distance for a given reflection is necessary if accurate determinations of dislocation density are being made. As was pointed out in section 7.2, by studying thin tapering wedges of moderately good crystal, it has been found (42), that the topograph obtained is completely featureless until a depth of about \(d/3\) an extinction is reached within the crystal. Hence this region of invisibility must be taken into
account in making accurate dislocation density estimates. This also sets a limit on the volume of material that can be investigated. It is pointed out however that defects within the specimen right up to the exit surface beyond the distance \( \frac{4\xi}{3} \) are visible and that this does not inhibit surface defects to be observed in crystals by X-ray topography, since the "invisible" region can be investigated by rotating the crystal through 180° in the horizontal plane so reversing the surfaces relative to the X-ray beam.

The shorter the wavelength of X-rays used the longer is the extinction distance. Table 7.3.1 shows the magnitude of the extinction distance for a variety of diffracting planes for cadmium using AgKα₁ radiation. Also shown are the values of the structure factor for the operating reflection. Now the extinction distance for (10\( \overline{1} \)0) reflection is observed to be about twice that for any other reflection shown. Thus for a basal plane foil 75\( \mu \)m thick its thickness in terms of extinction distances is 6\( \xi \) for (11\( \overline{2} \)0) and 3\( \xi \) for (1\( \overline{0} \)10) reflection. Hence in the former the region of invisibility as measured from the X-ray entrance surface is about 4\( \mu \)m and in the latter about 7\( \mu \)m i.e. in the latter reflection about \( \frac{1}{10} \) of the foil thickness is invisible in this reflection. The differences in the extinction distance values arise as a direct consequence in the difference in the structure factor value (which is not compensated for by the difference in Bragg angle).

If CuKα₁ radiation is used then the extinction distances for reflections from (11\( \overline{2} \)0) and (10\( \overline{1} \)0) in symmetrical Laue transmission are approximately 4.5 and 8\( \mu \)m respectively, however for good defect visibility i.e. low absorption the critical value of thickness calculated from the transition case \( \mu t=1 \) for CuKα₁ is about 5\( \mu \)m. Thus we see that the region of invisibility goes up as softer radiations are used. In (10\( \overline{1} \)0) reflection using CuKα₁
only about a half of the crystal will be open to examination. We see that although the absolute depth of invisibility goes up as the radiation used becomes "harder" the proportions of crystal which cannot be investigated decreases.

Table 7.3.2 shows the fraction of dislocations visible in an h.c.p. metal, assuming that all Burgers vectors are equally represented. It is seen that in (11\overline{2}0) reflection all basal dislocations should be visible. In (10\overline{1}0) reflection one third of the basal dislocations will be observed. In a slice cut parallel to the (10\overline{1}0) plane reflections in symmetrical Laue transmission from (0002) and (11\overline{2}0) reflection can be obtained. Topographs obtained from the latter reflection should allow observation of \langle11\overline{2}3\rangle and \langle11\overline{2}0\rangle dislocations i.e. non-basal. Topographs obtained from specimens cut in this orientation and from (11\overline{2}0) reflection should show all basal dislocations and if the (10\overline{1}0) plane of the foil is etched to bring up etch pits the possibility arises for an attempt to be made at correlating the dislocation density in the bulk metal with etch pits on the crystal surface.

7.4. Interpreation of Topographs obtained using (0002) and (11\overline{2}0) reflections from specimens cut parallel to the (10\overline{1}0) plane

As was pointed out in sec. 6.2.1 specimens in this orientation which exhibited dislocation detail were difficult to obtain. Only two such specimens i.e. crystal B3, annealed at 275°C and crystal B7 annealed at 220°C were examined. Crystal B7 however was etched before X-ray topographic examination and its etch pit distribution recorded (see prints 6.42-6.45 page 124).

7.4.1 Crystal B3

We shall first consider crystal B3 (prints 6.6a, 6.6b pages 108, 109). As was pointed out in sec. 6.2.1 in (0002) reflection dark bands are observed running generally parallel to the basal plane. Now Higashi et al (82) have examined by X-ray topography
ice crystals cut in the foil orientation under consideration and 
obtained from the Mendenhall Glacier in Alaska, in (0002) reflection 
and have observed a similar substructure; this they have 
contributed to be due to dislocations having Burgers vector 0001.
The possibility of this being true for the substructure shown in 
prints 6.6a cannot be ruled out. The crystal is fairly perfect as 
evidenced by the large area seen and by the variation in contrast 
across the photographs. In (1210) reflection print 6.6b no 
obvious dislocation detail is visible but again the variation in 
intensity across the print (a consequence of Pendello sung interfer­ 
ence) is evident. The dark spots seen could be dislocations or 
loops seen end on.

7.4.2 Crystal B7

Turning attention to the topographs of crystal B7 prints 
6.39-6.41 page 123, we see that in (0002) reflection no dislocation 
detail is observable. Two regions of the topograph obtained in 
(1210) reflection are shown. In print 6.41 pronounced bend 
contours are observed and in this region of the topograph no dis­ 
location detail is observable. It is instructive to compare prints 
of crystal B7 with those of crystal B3, by which it becomes evident 
(by comparing extent of bend contours in both crystals and 
dislocation detail in (0002)) that crystal B3 is more perfect than 
B7. Print 6.40 shows another region of the topograph obtained in 
(1210). Some dislocation detail is visible. The mean dislocation 
density within the region marked a showing uniform dislocation 
density has been estimated at $1.0 \times 10^5$ lines per $\text{cm}^2$.

7.4.3 Comparison of etch pit density of crystal B7, and interior dislocation density

From prints 6.42 to 6.46 page 124, which show the distribution 
of etch pits on the (1010) surface of crystal B7, prior to X-ray
topographic examination, it has been estimated that the etch pit density is \(3.0 \times 10^5\) per cm\(^2\). In sec. 7.4.2 it was reported that the dislocation density within the crystal was \(1.0 \times 10^5\) lines per cm\(^2\). In order to compare these two estimates one requires the standard errors of the individual counts not the standard error of the mean of the counts. The standard error for the individual etch pit counts was \(2.0 \times 10^5\) and for the topograph counts \(0.8 \times 10^5\). We therefore see that the two estimates overlap, when the standard errors in the individual counts are taken into account. The correlation would be even better if the regions of higher dislocation density from the topograph were taken into account. This is the first time that a correlation between the etch pit density on the \((10\bar{1}0)\) plane of cadmium and the dislocation density within the bulk has been made. This estimated etch pit density also compares favourably with dislocation density estimates made on basal specimens and reported in chapter 6.

Other features are observed on the prints of topographs obtained from crystals B3 and B7. Such features are not easily amenable to interpretation and as such no further attention will be drawn to them.

7.5. **Comparison of etch pit density of cyclically annealed furnace cooled bulk crystal with etch pit density of crystal B7**

In section 4.4 was related the manner in which a 2cm long bulk crystal was cyclically heat treated and that after three heat treatments its mean etch pit density as estimated from its etch pit distribution along the whole 2cm gauge length was \(4.0 \times 10^4\) per cm\(^2\) with a standard error from the mean of \(0.5 \times 10^4\). Yet specimens prepared for X-ray topographic examination and subjected to this heat treatment showed no substructure detail on X-ray examination. In section 7.4.3 it was related that crystal B7 had an estimated
mean etch pit density of $3.0 \times 10^5$ per cm$^2$ and also showed substructure detail upon X-ray topographic examination. This result would appear contrary to the idea of crystal perfection.

In an attempt to resolve this anomaly, resort was made to testing the differences in the two etch pit means statistically i.e. to test whether or not the two sampling means came from two populations of equal unknown means.

Suppose $\bar{x}_1$ and $\bar{x}_2$ are the means of two independent random samples of sizes $n_1$ and $n_2$ from populations with unknown means $u_1$ and $u_2$ and known variances $\sigma_1^2, \sigma_2^2$ respectively. $\bar{x}_1 - \bar{x}_2$ is distributed approximately normally with a population mean $u_1 - u_2$ and variance $\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}$. Thus to test the hypothesis about the value of the difference $u_1 - u_2$ we form the standardized variable $Z = \frac{\bar{x}_1 - \bar{x}_2 - (u_1 - u_2)}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}}$ and test against a value from a normal table.

To test whether the means of the population $u_1$ and $u_2$ from the two random etch samples which were made are the same, we set $u_1 = u_2$ and compare the value of $Z$ at a given level of significance.

The value of $Z$ estimated from the above standardized variable with $u_1 - u_2 = 0$ was 2.9. Now $Z_{0.05}$ (i.e. the value of $Z$ at the 5% level of significance) is 1.96 and $Z_{0.01}$ is 2.58. The evidence is thus against equal population means at both the 5% and 1% levels of significance.

Since statistically the evidence is against equal population means we must conclude that direct comparisons between etch pit counts on bulk specimens (2cmx5mmx5mm) and foils (8mmx3mmx75um at most) cannot be made. It would appear reasonable to assume that the annealing kinetics for these two types of specimen will be different and hence not permit a direct comparison to be made of the dislocation configurations formed on heat treatment.
7.6. Loop Contrast observed by Other workers

In this section will be discussed the contrast of loops observed by other investigators by electron-microscopy and X-ray topography. Such a discussion at this stage is useful, since in the following section space will be given to discussing the loop contrast shown in the prints in chap. 6 and the Burgers vectors which can be determined from it.

Berghezan et al. (23) first observed sessile dislocation loops in a zinc foil, by transmission electron microscopy, and prepared by cold rolling. The interior of the loops observed exhibited contrast. The contrast took the form of either a difference in shade from the surrounding regions or a set of interference fringes parallel to the foil surface. The first appearance was more frequent since normally the basal plane was parallel to the specimen surface, which was also the plane of the loop. They reported that contrast also depended upon the inclination of the foil relative to the electron beam. If the loop happened to be in the vicinity of a plane of maximum diffracted amplitude from the electron beam entrance surface i.e. at a distance $(n+\frac{1}{2})t$, where $n$ is an integer and $t$ the extinction distance, it would exhibit no contrast.

Changing the inclination of the foil not only changed the operating Bragg plane that was active in producing the contrast but at the same time changed the extinction distance $t$ and hence the position of maxima and minima diffracted amplitude. The result was that a loop which did not produce contrast previously could now exhibit contrast and vice versa. In regions where rings overlapped the contrast in general was different from the individual loop contrast.

Apart from regions within the rings the rings themselves presented contrast effects. For some inclinations of the foil the ring contrast was uniform for others non-uniform.
They concluded that the loops were faulted but could not unambiguously determine the Burgers vector and reported that according to the diffracting planes used four types of contrast were possible (always assuming that the loop lay at a suitable depth within the foil).

(i) Only the dislocation ring is visible. This happens if 11\(\bar{2}0\) planes are used, except for the \(\{11\bar{2}0\}\) plane passing through the Burgers vector.

(ii) Neither the dislocation ring or the stacking fault is visible. This happens for a particular \(\{11\bar{2}0\}\) plane passing through the Burgers vector.

(iii) Dislocation and stacking fault are visible. This happens for all planes for which \(g.b/o\) and not an integer.

(iv) Using iblique planes e.g. (1011) passing through the Burgers vector one could make visible the stacking fault only and not the dislocation ring.

In some of their micrographs, some loops in the same region showed much more pronounced contrast than others. This they attributed to either a difference in Burgers vector or to a difference in depth within the foil or to both reasons operating together.

Prior to this electron microscopy study on cold rolled zinc foils, Fourdeaux et al (83) had studied individual dislocation configuration in vapour grown zinc platelets by transmission electron microscopy and X-ray topography. The significant point was that X-ray topographic examination (Lang method), revealed large circular black discs in all \(\{10\bar{1}0\}\) reflections which were absent in all \(\{11\bar{2}0\}\) reflections. Now Paterson (84) has shown that a stacking fault on the basal plane of an hexagonal crystal does not produce a perturbation on the phase of diffraction in \(\{11\bar{2}0\}\).
reflections but does in {10\bar{1}0} reflection. Fourdeux et al thus concluded that the large circular discs observed by them were stacking fault loops. It was at this stage that they first observed stacking fault loops by electron microscopy.

Price (27,28,31,32,33) has studied loops produced by tensile strain in zinc and cadmium in the electron microscope. By a dislocation reaction mechanism only he deduced that initially all the loops formed had Burgers vectors equal to \( \mathbf{a}+\mathbf{a} \). These loops had uniform ring contrast and showed no interior contrast. Within short space of time these loops acquired

(i) Varying ring contrast

(ii) Lines of zero contrast in strong {10\bar{1}0} and {1\bar{1}20} reflections with the lines of zero contrast parallel to these planes.

(iii) Some loops had dark centres in {10\bar{1}0} reflection.

He concluded for (ii) that the loops had Burgers vector \( \mathbf{b}=\mathbf{a} \), not \( \frac{1}{2}\mathbf{a} \), since no stacking fault contrast was ever observed within these loops. For (i) he envisaged the dislocation reaction \( \frac{1}{3}\mathbf{a} \rightarrow \frac{1}{3}\mathbf{a}+\mathbf{a} \). i.e. the contrast observed resulted from the contrast produced by both loops individually. Eventually he concluded that the \( \frac{1}{3}\mathbf{a} \) loop collapsed by glide leaving only a \( \mathbf{a} \) loop which exhibited the contrast given by (ii).

Loops exhibiting dark centres in 10\bar{1}0 reflections he regarded as being formed by the dislocation reaction

\[
\frac{1}{3}\mathbf{a} \rightarrow \frac{1}{6}\mathbf{a}+\mathbf{a}
\]

with the subsequent growth of one loop at the expense of the other. The final size of the loop was double its initial size.

Michel and Ogilvie (35) have studied vapour platelets of
of zinc and cadmium by X-ray topography and electron microscopy (only cadmium in the case of the latter). Time lapse studies at room temperature were made on both metals by X-ray topography. These time lapse studies showed the formation of dislocation loops with time. In zinc "stacking fault contrast was usually observed in \( \{10\bar{1}0\} \) reflections" (no pictures shown) but not \( \{11\bar{2}0\} \), but in both types of reflection the dislocation ring had a minimum parallel to the diffracting planes. They concluded that these observations were consistent with the loop comprising a stacking fault with Burgers vector in the \( \langle 0001 \rangle \).

In cadmium few loops were observed to contain stacking faults. They have reported that the Burgers vector of the unfaulted loop "appeared" to lie in the \( \langle 0001 \rangle \).

Cadmium specimens in the electron microscope exhibited loops the contrast of which often changed after 10-15 seconds; the loops became less visible and the residual contrast faded so as to be almost unobservable.

Harris and Masters (30) have studied annealed quenched foils of zinc and magnesium by electron microscopy. They observed faulted and unfaulted loops, the unfaulted loops showed lines of zero contrast, which they attributed to having a Burgers vector \( b = 0001 \). To the faulted loops they assigned a Burgers vector \( b = \frac{1}{6} \langle 20\bar{2}3 \rangle \).

Hirsch et al (57) have explained the unpublished electron-microscope micrographs of N. Brown showing large dislocation loops in zinc exhibiting triple and double ring contrast and lines of zero contrast by computed image profiles obtained using the dynamical equations of Hirsch et al (see page 263, Electron Microscopy of thin Crystals, Hirsch et al: Butterworths) They concluded that the Burgers vector of these loops was "probably" \( b = \frac{q}{2} + p \).

The information given in this section is summarised in table 7.6.
7.7. Discussion of Contrast of loops observed by X-ray Topography

7.7.1 Initial Loop Contrast in (12\bar{1}0) and (1\bar{2}10) reflection

This section will be concerned with the initial loop contrast exhibited by crystal A6 (prints 6.11, 6.12 page 111). By considering the contrast of these loops it is possible to determine their Burgers vector: this is not only of inherent interest but also permits light to be cast upon their origin.

We shall confine ourselves specifically to print 6.11 page 111 from which by comparison with the time lapse topograph shown in the print below it that little change in contrast could have occurred, if any, between the time of retrieval from the annealing tube and its subsequent examination, as a consequence of recovery at room temperature. With the help of a detailed literature survey (the results of which are related in sec. 7.6), the conclusion was reached that the loops had Burgers vector equal to either \(c\) or \(c+a\). Specifically, those exhibiting lines of zero contrast in 1100 perpendicular to the \(g\)-vector were most probably \(c\) loops, while those exhibiting lines of minimum contrast perpendicular to the \(g\)-vector most probably had Burgers vector equal to \(c+a\), i.e. lines of zero contrast or minima limit possibilities to loops with an edge component.

That some of the loops had a Burgers vector with an edge component was deduced from the stereo pair of topographs taken in (12\bar{1}0) and (1\bar{2}10) reflections (prints 6.16, 6.17 page 113). As was pointed out in sec. 6.3.2, the image contrast is different in these two reflections and as was mentioned in sec. 7.2 such a difference occurs if the dislocation has an edge component. This difference in contrast arises as a consequence of the intensity of the dynamical image of the dislocation affecting the total image
intensity differently in (hkl) and (hkl) reflections. If a dislocation has no edge component the image intensity in (hkl) and (hkl) is invariant.

Consideration of the kinematical theory of electron diffraction in thin crystals due to Hirsch et al (57) also led to the conclusion that the Burgers vectors of the loops were probably distributed among c and c+a. If for a pure edge dislocation g.b=0, (this is so for a loop having Burgers vector equal to c and lying in the basal plane, and observed in symmetrical Laue transmission) this term in the general displacement vector R in the equations of Hirsch et al obviously does not contribute in producing contrast and if the contrast was purely a function of g.b the loops would be invisible. The contrast of such a loop having Burgers vector equal to c and lying in the basal plane, is generated by the \( g \cdot b \cdot c \) term in their equations. The magnitude of this term varies around the loop and in particular is zero for parts of the loop parallel to g. For a loop of Burgers vector b=c+a, g.b\neq0 and g.bxu does not go to zero at any position around the loop. A loop having such a Burgers vector is likely to produce full ring contrast or minimum contrast for the part of the loop parallel to g.

However the simple considerations outlined in the previous paragraph took no account of the position of the loop within the foil. It was considered conceivable that a loop having a Burgers vector c, showing a line of zero contrast at one position within the foil could at another position exhibit a line of minimum contrast and therefore be mistaken for a loop having Burgers vector equal to c+a.

It was this possibility which led to the initiation of the computation of the image profiles of dislocation loops having Burgers vectors equal to c or c+a at varying depths within the foil in h.c.p
metals using the two beam dynamical equations of Hirsch et al and using displacements predicted by isotropic elasticity theory. Although from the X-ray viewpoint it represents a crude approximation to the solution of the problem of distinguishability, it was still carried out, since only the gross features of the profiles obtained were intended to be compared with the experimental observations.

The problem was tackled by assuming the loops to comprise an infinite mixed dislocation wrapped around upon itself. This enabled loop self interaction to be ignored which was a reasonable approximation since the loops observed are large (50um in diameter). The details of the computation etc and resultant image profiles are given in appendix 1. Now it is pointed out in that appendix and shown that for a loop lying in the basal plane of an h.c.p metal and for reflections taken from planes perpendicular to the basal plane that the term $g \cdot b \cdot x \cdot u$ is independent of $b$, the Burgers vector. Furthermore it is shown in appendix 1 that dislocations having Burgers vector $c$ or $c+a$ can be distinguished in any one $\{11\bar{2}0\}_1$ reflection, this is a consequence of the $g \cdot b$ values for this reflection. The distinguishability is only possible however because $g \cdot b \cdot x \cdot u$ is independent of $b$ in this reflection. It is not possible to distinguish in one $\{10\bar{1}0\}_1$ type reflection between $c$ and $c+a$ loops, even though again for this reflection $g \cdot b \cdot x \cdot u$ is independent of $b$: this is a consequence of the $g \cdot b$ values in this reflection. As was pointed out in Chapter 6 the subgrain warpage within the crystal and the recovery occurring at room temperature did not permit the same subgrain to be picked up with constant reflectivity and with no change in the dislocation configuration. It is thus fortuitous that in one $\{11\bar{2}0\}_2$ reflection one can distinguish between $c$ and $c+a$ loops.

Inspection of the image profiles for varying $\theta$ for a $\{11\bar{2}0\}$ reflection in appendix 1 (these are at a depth of $4\frac{1}{2}g$ which was one
depth at which good contrast was observed, and good loop contrast is observed on the topograph under consideration) shows that for 
\( g.b=0 \) (this is true only for \( c \) loops see appendix 1), that double contrast loops with a line of zero contrast perpendicular to the \( g \)-vector is predicted. For \( g.b=1 \) \((c+a \) loops only) we see predicted loops showing lines of minimum contrast and for \( g.b=+2 \) \((c+a \) loops only), full loops, showing no line of minimum or zero contrast, and also slightly wider in parts, than the loops predicted for \( g.b=+1 \). The electron microscopy calculations showed that \( b=c \) and \( b=c+a \) loops did not markedly alter their contrast with depth in the foil, provided the loops were not positioned near the surface (at which positions computations could not be carried out). This work confirmed the simple considerations discussed earlier and that they were valid for a range of foil thickness. In conclusion and summing up this work showed that loops in \( \{1120\} \) exhibiting lines of zero contrast have Burgers vector equal to \( c \) while those exhibiting minimum contrast or full contrast have Burgers vector equal to \( c+c \), at all loop depths, except perhaps near the surface at which computing difficulties prevented computation being carried out.

7.7.2 Time lapse loop contrast in (10\( \bar{1} \)0) and (1010) reflection

The main features of topographs taken in this reflection from crystal A6 have been set out in sec. 6.33

One of the most striking features on these topographs are the large "double D" loops referred to in the section quoted above. With time lapse and in stereo reflection the contrast of these loops has become enhanced and the image width has increased. Considering the first topograph taken in this reflection print 6.25 page 116, it is proposed that this type of contrast is a consequence of the loop being near a surface of the crystal: most probably at the X-ray exit surface. This explanation is put forward to explain
this type of contrast, since its known sec. 7.2, that the direct image width is very dependent upon the lattice tilt around the defect: at a surface the lattice tilt around a vacancy or interstitial loop, will not be the same above and below the vacancy or interstitial layer, and this difference in lattice tilt above and below could give rise to the contrast observed. Significantly loops exhibiting this contrast are a relative rarity in this topograph.

The effect of lattice curvature is most likely to be observable, if it occurs at the X-ray exit surface, since the defect contrast of the crystal $\frac{3}{5}\mu g$ from the entrance surface is not observable ($75\mu m=3\frac{3}{5}\mu g$ in $(10\overline{1}0)$ reflection). Theoretical calculations would be necessary to confirm this contention.

In the later time lapse topograph in stereo reflection print 6.24 page 116, it is seen that the image width of these loops have increased, although the loops are still "double D" in nature. This change in image width could be a consequence of both flimb (tending to decrease the width of the loop) and glide (tending to bring it nearer to the surface). Moreover if such loops have an edge component (in one $\{10\overline{1}0\}$ reflection one cannot distinguish between $c$ and $c+a$ loops) then a further possibility is that the dynamical image of the dislocation is contributing in a positive manner in this topograph to the total image intensity.

Image profiles of either $c$ or $c+a$ loops in $\{10\overline{1}0\}$ reflection were obtained (see appendix 1) no "double D" contrast was predicted at any position in the foil. An attempt was made to explain this "double D" contrast effect by assuming it to be a surface effect and thus positioning the loop near the surface. However the computer programme broke down when applied near the surface, as evidenced by the diffracted beam intensity exceeding the incident beam intensity and no information regarding these loops could be
obtained using the dynamical theory of Hirsch et al in $\overline{1}0\overline{1}0$ reflection.

Why two of the loops exhibiting the contrast discussed above should have an angle of about $10^\circ$ between their lines of zero contrast is not clear; it is pointed out however, that the criterion that the line of zero contrast should be perpendicular to the $g$-vector is predicted from isotropic elasticity theory and assuming that the loop is bounded by an infinite isotropic matrix. Perhaps this effect would be more likely for $c+a$ than $c$ loops.

7.8. Ageing effects in specimens prepared from slices cut parallel to the Basal plane and annealed at $220^\circ C$ (Crystals A6, A7)

The ageing effects that will be considered are those associated with (a) Recovery at room temperature leading to loop shrinkage (b) The deterioration of Crystal quality.

7.8.1 Recovery effects at room temperature

Topographs taken of crystal A6 showed many interesting features associated with room temperature recovery and such changes which were noted were listed in Chapter 6.

In sec. 6.3.1, 6.3.2 it was pointed out that associated with the disappearance of loops in the former, and shrinkage in the latter that the dislocation line length emanating from close proximity subgrain boundaries increased. These observations are consistent with a climb mechanism operating. In the topographs obtained in (1210) reflection, the loop shrinkage with time was observed in some detail (prints 6.21-6.23 page 115). Such topographs have enabled annealing kinetics in cadmium to be studied.

Now Price (e.g 29) has studied the shrinkage of loops having Burgers vector equal to $c$ in cadmium and zinc in the electron microscope and obtained a value of $U_D$, the activation energy for a vacancy at room temperature, using an equation for loop shrinkage.
with time obtained by Silcox and Whelan (85). The basic premises underlaying this equation are (i) that climb occurs by the diffusion of vacancies to or from a loop depending upon whether it is a vacancy or interstitial type and (ii) the surfaces alone are such good sinks and sources of vacancies that the equilibrium concentration value is maintained during annealing. Friedel (86) has given an equation relating the change of loop radius with time which takes into account both the line tension \( t \) of the dislocation loop and the chemical stress \( F_s \), acting on the loop, which is the stress acting due to the deviation of the concentration of vacancies in the vicinity of the loop from the equilibrium value at temperature \( T^\circ C \).

Silcox and Whelan (85), have shown that for a thin foil that the chemical stress \( F_s \) maybe neglected, since a vacancy emitted from a loop will be absorbed at the surface before a further vacancy is emitted: this is equivalent to saying that the equilibrium concentration of vacancies at the temperature \( T^\circ C \) is maintained. However for thicker foils this will not be so and supersaturation effects will come into play. Since the equation given by Friedel takes \( F_s \) into account it was this equation which was used to study the annealing kinetics of \( c+a \) loops in cadmium at room temperature observed by X-ray topography.

The equation relating the loop radius with time given by Friedel is

\[
r^2 = \frac{2ab^4D}{KT} (t_c - t)
\]

where \( r \) is the radius of the loop at time \( t \), \( u \) the shear modulus, \( D \) the diffusion coefficient, \( b \) the shortest Burgers vector and \( t_c \) the time for loop collapse. Now

\[
D = D_0 e^{-\frac{U_M}{KT}}
\]

where \( U_M \) is the energy of motion of a vacancy at temperature \( T^\circ K \) and hence the equation given above enables this quantity to be determined. It is worthwhile noting at this juncture that the loop shrinkage with time equation obtained by Silcox & Whelan, enables \( U_D \) to be determined and \( U_D = U_F + U_M \), where \( U_F \) is the energy of formation.
of a vacancy.

Using this equation \( r^3 \) versus time has been plotted plot 7.1 for the two sets of shrinking \( c+a \) loops shown in prints 6.21-6.23 page 115. An extra pt has been inserted, the print from which this has been obtained has not been included.

Straight lines for the least squares fit have been drawn in. From the intercepts of these lines and taking \( b=2.98\), \( u=2.46\times10^{11} \) dynes per cm\(^2\), \( T=293^\circ\)K, a value of \( 9.2\times10^{-9} \) cm\(^2\) per sec, has been obtained for \( D \) for the loops of larger radii and \( 6.6\times10^{-9} \) cm\(^2\) per sec for the other set of loops.

\[
D = D_0 e^{-\frac{U_M}{KT}} \quad \text{and} \quad D_0 = 0.10 \quad \text{(perpendicular as to the c-axis)} \quad \text{and} \quad D_0 = 0.05 \quad \text{(parallel to the c-axis)}. \]

Using the values of \( D \) above \( U_M \) has been calculated to be \( 0.405\)eV \( (D=9.2\times10^{-9} \) cm\(^2\) per sec) and \( 0.410 \) \( (D=6.6\times10^{-9} \) cm\(^2\) per sec) perpendicular to the c-axis and \( 0.39\)eV \( (D=9.2\times10^{-9} \) cm\(^2\) per sec) and \( 0.39\)eV \( (D=6.6\times10^{-9} \) cm\(^2\) per sec) parallel to the c-axis. These values are in good agreement with known values of \( U_D \) assuming that \( U_D = U_F + U_M \) and \( U_F = U_M \). Friedel (86) gives \( U_D \) perpendicular to the c-axis as \( 0.83\)eV and parallel as \( 0.79\)eV.

To investigate if the increase in dislocation line length associated with the shrinkage of these loops was consistent with the idea of vacancies migrating from the loops to them, the distance a vacancy can move in the time interval between obtaining the two topographs shown in prints 6.22, 6.23 page 115 was calculated. Using the relationship \( x = (Dt)^{\frac{1}{2}} \) and knowing \( t \) to be equal to \( 25\times10^4 \) secs and taking \( D=9.2\times10^{-9} \) cm\(^2\) per sec, \( 6.6\times10^{-9} \) cm\(^2\) per sec a distance of \( x \) equal to about \( 450\mu m \) was determined. Now the distance of the loops from the subgrain boundary dislocations on the topographs referred to is about \( 50\mu m \) at most and hence we see that the vacancies had ample time to migrate from these loops to the dislocations emanating from the subgrain boundary. It is interesting
to note that the foil thickness was around 50µm and thus the loops were positioned at a maximum of about 30µm from a surface, yet diffusion still took place preferentially at least for some of the vacancies to dislocations at a distance away from the loops comparable to that of a free surface.

In conclusion it seems clear that the loops which have been observed are vacancy loops and vacancy kinetic calculations have indicated that vacancies will migrate to internal sinks within the crystal which are at comparable distances from the surface of the specimen. An average value of $U_M$ parallel to the c-axis of 0.39eV, and perpendicular to the c-axis of 0.41eV has been obtained.

7.8.2. Loss of dislocation visibility after a given period

Both crystals A6, and A7, exhibited a deterioration in quality after a period of time. Crystal A6 was examined over a period of eighteen days, whereas crystal A7 deteriorated after a shorter period of about seven days. Marked deterioration occurred over a short period in both crystals. The features associated with this effect were observed to be (i) A streakiness associated with individual defects (loops and dislocations). (ii) Loss of visibility of Pendellosung fringes (iii) in the case of crystal A7, the observation at the time of bad dislocation visibility of bend contours in the proximity of the subgrain observed.

The quality of crystals A6 and A7 were initially comparable, yet they deteriorated after markedly different times. Such a difference in time is not consistent with the idea of the formation alone of a film on the surface followed by the subsequent injection of vacancies into the crystal leading to an increase in dislocation density, since the formation of a film and its subsequent growth would no doubt be comparable for both crystals of similar quality and such an ageing mechanism one would expect to be operative over
the same period of time for identically oriented crystals, and the same thickness.

It is contended that the most likely explanation of this effect is that the crystals have become bent between exposures even though they had only been left on the goniometer stage of the camera; and that bending could have occurred only as a result of air draughts circulating in the vicinity of the crystal. The evidence supporting this is the appearance as mentioned in (iii) of bend contours with time and particularly at the time when the quality of crystal A7 had markedly deteriorated and of local increases in dislocation density. This explanation would account for the time difference in crystal deterioration and the fact that it occurred at all. The possibility of vacancy injection as a consequence of the formation of a surface film leading to crystal deterioration is not consistent with the observation on crystal A6 of the observed decreases in loop and dislocation density over large areas with time prior to final deterioration of crystal quality.

7.8.3. Comparison with other work

As has been mentioned on several occasions throughout this thesis, vapour grown platelets of cadmium have been subjected to X-ray topographic examination by Michel and Ogilvie (35). The platelets studied were about 5μm thick and CuKα radiation was used. The platelet thickness and radiation used limited the volume of crystal that could be examined (see sec. 7.3.).

The platelet studied in detail was initially dislocation free and with time the platelet became steadily less perfect: loops, line defects, and hexagonal arrays became nucleated and grew continually over a period of two months. After this period the defect arrangement remained static. The contrast of the loops observed (see sec. 7.6) was different to the contrast of the loops
shown in the prints of topographs in chapter 6. They explained their results by invoking an oxide film growth mechanism operating on the platelet surface which led to the injection of vacancies into the initially defect free specimen; these vacancies subsequently they proposed aggregated into loop and line defects; as confirmatory evidence for this proposal they point out that platelets stored in growth tubes for periods up to six months prior to examination were still defect free upon initial examination and only became less perfect when exposed to air at 20°C. Their results could be explained by assuming that the defects were introduced by bending (as a result of air draughts) and that the dislocation arrangement eventually became static as a consequence of the hardening of the crystal due to fatiguing.

As has been remarked upon by A. Lang (87), the dislocation detail in the subgrain containing the loops, upon which annealing kinetic calculations were made, bear a striking resemblance to some peculiar crystals of magnesium oxide examined by the latter (88), especially the appearance of the "hairy" dislocations emanating from the subgrain boundary, and the subgrain shape and size.

7.9. The Origin of Loops

It was concluded from sec. 7.7 that the initial contrast exhibited by the loops indicated that their Burgers vector was either $a$ or $a+a$. Any explanation as to the origin of these loops must account for loops of different Burgers vector.

The most likely explanation as to the origin of loops generally is the the $a$ loops are formed as result of vacancy condensation during cooling on pre-existing $a$ loops which were still present at the anneal temperature and $a+a$ as a consequence of the pinching off of loops from helical dislocations formed by the condensation of vacancies during slow cooling (1°C/hr) on screw dislocations.

- 153 -
To test this hypothesis it is necessary to estimate the number of vacancies required to produce the number and size of the loops observed and see if this number is a reasonable fraction of the equilibrium concentration at the anneal temperature. The activation energy $U_D$ for a vacancy in cadmium is 0.79 eV parallel to the c-axis and 0.83 eV perpendicular to it. $U_F$, the energy of formation of a vacancy in cadmium is not known, but assuming $U_M=U_F$, then the energy of formation is approximately 0.4 eV. The equilibrium concentration at $220^\circ$C is $n = \frac{n}{N} \exp(-\frac{0.4}{0.9\times493}) \approx \exp(-10)$. Therefore $n \approx 10^{-4}N$.

Drawing attention to print 6.11 region a page 111. We see that in an area approximately 350 μm x 350 μm there are in order of magnitude 10 dislocation rings of average diameter approximately 50 μm. The formation of these by vacancy condensation would have required $\pi (25 \times 10^4)^2 \times 10$ vacancies i.e. $\approx 2 \times 10^{12}$. The total number of vacancies in equilibrium at $220^\circ$C in this region is $10^{-4}N$ and if the foil thickness is taken as 50 μm a region of crystal $(35\times35) \times 10^{10} \times 5 \times 10^5$ (Å$^3$) in volume contains about $5 \times 10^{18}$ atoms. The total number of vacancies is therefore of the order $10^{18} \times 10^{-4}$ i.e. $10^{14}$. Thus $2 \times 10^{12}$ represents about 1% the total number of vacancies present at $220^\circ$C.

It therefore seems clear that a high proportion of vacancies of the order 1% do not migrate to the surface even during very slow cooling but condense on dislocation rings. It was shown in sec. 7.8 that vacancies at room temperature migrate to interior sinks from c+a loops, which are situated at a distance comparable to a free surface and it would seem plausible to assume that some vacancies at least will on slow cooling, still go to interior sinks and not necessarily all to the surface. If we assume that some of the dislocation rings were there in the first place we must further assume that the density of these rings was comparatively low even at the relatively high temperature of $220^\circ$C for cadmium. The fact that there must have been many other dislocations present and that vacancies no doubt
condensed on these, would further indicate that a high proportion greater than the estimated do not migrate to the surface. This could be a consequence of the sealing of the crystal surface by an oxide film as proposed by Harris and Masters (30) hence trapping in the equilibrium vacancy concentration at 220°C or that loop growth simply occurs because some of the excess vacancies are bound to be nearer a loop than the free surface. It is pointed out that in the crystal under consideration (A6), the foil thickness is about 50µm, whereas, foils observed by electron microscopy by Harris and Masters were around 1000µm thick and hence surfaces in the latter case were likely to act as more effective sinks for vacancies and hence the mechanism of surface sealing proposed by them was more pertinent in order that they could explain their observations, than in the present consideration. Crystal A7 which was also annealed at 220°C and slowly cooled also exhibits loops on X-ray topographs. The loops observed within crystal A7 are however smaller than those observed in crystal A6; though the temperature of anneal was the same for both crystals, although the temperature of anneal was the same for both crystals, the mode of cooling was not. (See plot 6.1). Crystal A7 was cooled linearly over a period of twelve days, whereas crystal A6 was cooled linearly for approximately four days and then non-linearly down to room temperature over the subsequent three days. The linear cooling of crystal A7 could have allowed loops to grow continually and also to slip completely out of the crystal; the only loops observed, being small, could be those which are still in the incipient state of growth. In crystal A6 however the configuration has been trapped so that the loops which are observed have grown but on faster cooling have not had time to slip out of the crystal prior to examination.

The presence of pre-existing loops still present at the anneal temperature can be explained by invoking the dislocation reaction which are observed have grown but on faster cooling have not had time to slip out of the crystal, prior to examination.
mechanism, leading to the formation of \(c\) and \(c+a\) loops due to Price. In sec. 7.6 it was reported that Price observed \(c+a\) loops on deformation of cadmium platelets, some of which degenerated into \(c\) loops, by the collapse of \(\frac{1}{3}\langle1120\rangle\) loops. Since the loop density at the anneal temperature is low, very little deformation would be required to produce the observed number. Such slight deformation could easily have occurred at room temperature during the cutting and thinning of the basal slices. This is the most likely explanation of the observation of \(c\) loops. If all \(c+a\) loops formed by deformation degenerate into \(c\) loops, then the appearance of \(c+a\) loops at room temperature after anneal can be explained by assuming condensation of vacancies onto existing screw dislocations, which subsequently during cooling or at the anneal temperature ejected dislocation loops (this is a well known mechanism). If the ejection took place at high temperatures the loop itself could subsequently grow by vacancy absorption. Figs 7.9.1, 7.9.2 show diagrammatically how \(c\) and \(c+a\) loops could be formed.
Table 7.3.2. The fraction of dislocations invisible in an h.c.p metal (assuming all Burgers vectors are equally represented)

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Perfect dislocations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;11̅20&gt; type</td>
</tr>
<tr>
<td>10̅10</td>
<td>1</td>
</tr>
<tr>
<td>0002</td>
<td>1</td>
</tr>
<tr>
<td>10̅11</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>11̅20</td>
<td>0</td>
</tr>
<tr>
<td>10̅13</td>
<td>0</td>
</tr>
<tr>
<td>11̅22</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.3.1.

<table>
<thead>
<tr>
<th>Reflecting Plane (Symmetrical Laue Case)</th>
<th>Structure factor F</th>
<th>Atomic scattering factor f</th>
<th>Extinction distance g μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10̅10</td>
<td>f</td>
<td>38.8</td>
<td>22</td>
</tr>
<tr>
<td>11̅20</td>
<td>2f</td>
<td>31.4</td>
<td>12</td>
</tr>
<tr>
<td>0002</td>
<td>2f</td>
<td>39.8</td>
<td>11</td>
</tr>
<tr>
<td>10̅13</td>
<td>(3) 1/2 f</td>
<td>37.8</td>
<td>13</td>
</tr>
<tr>
<td>Investigators</td>
<td>Material, and Mode of specimen preparation</td>
<td>Manner of specimen examination</td>
<td>Contrast observed</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Fourdeux et al (83)</td>
<td>Zinc vapour grown platelets</td>
<td>e.m and X-ray topography</td>
<td>(i) e.m: circular loops, with light microscopy; or dark interior dark circular disc (~200μm). conclusions from tilting, interference fringes</td>
</tr>
<tr>
<td>Berghezan et al (23)</td>
<td>Zinc cold rolled foils</td>
<td>e.m</td>
<td>As in (i) above plus rings with lines of non-uniform contrast</td>
</tr>
<tr>
<td>Harris &amp; Masters (30)</td>
<td>Zinc Annealed quenched foils.</td>
<td>e.m</td>
<td>Same as Berghezan et al</td>
</tr>
<tr>
<td>Investigators</td>
<td>Material, and Mode of specimen preparation</td>
<td>Manner of specimen examination</td>
<td>Contrast observed</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------------------------</td>
<td>-------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>N. Brown (57)</td>
<td>Zinc (mode of preparation not known)</td>
<td>e.m</td>
<td>Loops exhibiting triple and double ring contrast. No interior contrast. Line of zero contrast perpendicular to g-vector</td>
</tr>
<tr>
<td>Price (27,28,29,32,33)</td>
<td>Zinc and cadmium vapour grown platelets</td>
<td>Strained in e.m</td>
<td>(i) Full circular rings (ii) Rings with varying contrast (iii) Rings with lines of zero contrast (iv) Loops with dark centres</td>
</tr>
<tr>
<td>Investigators</td>
<td>Material, and Mode of specimen preparation</td>
<td>Manner of specimen examination</td>
<td>Contrast observed</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------</td>
<td>-------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Michel &amp; Ogilvie (35)</td>
<td>Zinc and cadmium vapour grown platelets</td>
<td>e.m. and X-ray topography</td>
<td>(i) e.m.: (a) Cadmium loops frequently changed contrast; the loops becoming less visible and lines of residual contrast fading. (b) Zinc. Not reported.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(ii) X-ray topography: (a) Zinc: All loops faulted. Exhibited interior contrast in (1010) reflections but not in (1120). Ring of loop exhibited minima in both cases in direction parallel to diffracting planes. (b) Cadmium: Few faulted loops.</td>
</tr>
</tbody>
</table>

(a) consistent with stacking fault loop having Burgers vectors in <0001>
7.1. \((\text{Radius})^3\) v time for shrinkage of \(c+a\) loops at room temperature.
Fig. 7.9.1.

Stages in the formation of a loop by a screw dislocation which has become jogged in attempting to cross-glide around an obstacle. Proposed initial mode of formation of $a$ loops.

Fig. 7.9.2.

Possible growth of a helix from a screw dislocation with ejection of screw orientation loop. Proposed mode of formation of $c+a$ loops.
SUMMARY

The original aims for this thesis were the observation of the substructure detail in high purity melt grown single crystals of cadmium, by optical and X-ray microscopy and in particular the direct correlation between etch pits on the (10\bar{1}0) plane, produced using a dilute Nital solution and dislocations within the crystal as observed by X-ray microscopy.

The substructure detail of cadmium has been studied by X-ray microscopy and a correlation between etch pits and dislocations obtained, although not a direct one. Consistency was found between dislocation densities as determined from X-ray topographs and etch pit densities on the surfaces of specimens examined.

Technical difficulties associated with the aims necessitated much time being spent on overcoming them. Specimen preparation for X-ray microscopy presented by far the greatest problem and this was aggravated by the difficulties encountered in obtaining the basic units of the Lang X-ray equipment by import from the U.S.A.

X-ray microscopy studies on cadmium single crystals, by the Lang method, necessitated the development of spark erosion cutting techniques of Bridgman grown bulk crystals, which imparted the minimum machining damage to the specimen and the subsequent thinning of these specimens to a uniform thickness of 75\textmu m at most over a region of several square millimetres, in such a way that the specimen during thinning and during subsequent handling was not damaged, particularly by bending. A chemical polishing technique has been developed which permits the above requirements to be met.

Such specimens produced, although damage free were found to be highly imperfect from the X-ray microscopy viewpoint, even thought etching experiments had indicated that their dislocation density was of the order $10^5-10^6$ per cm$^2$, a level of dislocation
density which has been known to allow the observation of individual
defects in some other materials. The improvement of these specimens
led to an intensive investigation of various annealing techniques.
The conclusion was drawn that very slow cooling of the order
1°C/hr after anneal was necessary in obtaining high quality crystal
and that stringent precautions during the anneal and cooling and
subsequent mounting of the specimens was also necessary. These
conclusions led to the development of a particular specimen annealing
and mounting technique and to the development, in conjunction with
another person in this department of a novel temperature programmer,
permitting very slow controlled cooling after anneal which has
subsequently been patented by N.R.D.C. (Provisional U.K. Patent
No.23966/68), with a view to commercial exploitation.

The Nital solutions used for etching and polishing cadmium have
been examined. Little is known of alcohol based nitric acid
solutions generally and the fact that Nital in various concentrations
is known to act as a dislocation etch, chemical and electro-chemical
polish over a wide range of temperature on cadmium and that such a
property is unique to the cadmium-Nital system led to the interest
in the chemical properties of these solutions.

Examination of the Nital solutions was carried out within the
department of Chemistry of the University of Surrey. The examination
by electrical and spectroscopic methods led to the determination of
the molecular and ionic constituents of Nital in various concentrations
and to the elucidation of certain ageing characteristics of them.
A general conclusion drawn from this work was that the general
effect upon the classical equilibrium constant of alcohol based
nitric acid solutions as compared with aqueous solutions in change
of composition of the medium is very pronounced.

X-ray topography techniques have generally been advanced by the
ability now to produce damage free crystals in any orientation, which will permit the spatial relationships of defects in cadmium to be studied.

The substructure and dislocation configurations which have been observed, must be more representative of the bulk, than those of platelets which have been observed by other workers, even though specimens obtained from the bulk were subjected to an exacting heat treatment prior to X-ray examination. Moreover since the specimens examined were thick i.e. of the order 0.1mm, this permits the substructure observed to be more directly related to the bulk, than the substructure detail observed by electron microscopy (where specimens examined are of the order 100 times as thin).

X-ray topographic studies have been carried out on specimens prepared from slices cut parallel to (10\overline{1}0) plane. This is the first time an X-ray topographic study has been made on any h.c.p. metal, in an orientation other than basal.

Large edge type dislocation loops (of the order 50µm diameter) have been observed in basal specimens annealed at 220°C and slowly cooled down to room temperature. The majority of the loops observed have been provisionally attributed to having Burgers vectors \( c \) and \( c+a \). This conclusion was arrived at by initiating the computation of the intensity profiles of loops at varying depths within a basal foil, using the two beam dynamical theory of electron diffraction in thin crystals due to Hirsch et al and using displacements predicted by isotropic elasticity theory. Some elucidation of other X-ray contrast effects observed has been achieved. Previous observation and studies on dislocation loops have been carried out by electron-microscopy and in these specimens loop formation has been achieved by quenching from an anneal temperature or by deformation of vapour grown platelets in situ in the electron microscope.
The kinetics of loop annealing at room temperature in cadmium has been investigated and estimates of $U_M$ (the energy of motion of a vacancy at room temperature) made which compare favourably with the value of $U_M$ deduced from the known value of $U_D$. A tentative conclusion has been drawn concerning the mechanism of loop annealing at room temperature.

The origin of the dislocation loops observed has been tentatively explained on the assumption that their Burgers vectors are distributed among $\mathbf{c}$ and $\mathbf{c} + \mathbf{a}$.

The dependence of room temperature dislocation density and subgrain size has been found to be critically dependent upon the cooling history of the specimens examined. Not only has the crystal perfection of cadmium specimens prepared from the bulk been found to be a function of cooling rate after anneal, but the substructure detail observed to be very dependent upon the temperature regime of anneal. Dislocation loops were found to be the predominant defect in basal specimens annealed at $220^\circ C$ and cooled at the order of $1^\circ C/hr$, whereas basal specimens examined which had been annealed at higher temperatures and cooled at faster rates were observed to contain few loops if any.

**SUGGESTIONS FOR FURTHER WORK**

The X-ray microscopy studies on cadmium reported in this thesis indicate that defect studies in this metal over a wide range of temperature would be very informative. By working at elevated temperatures the dislocation density would be low and studies by X-ray topography of creep and annealing could be carried out. Of particular interest would be the observation of the formation and growth of the dislocation loops observed at room temperature produced on slow cooling from $220^\circ C$. The construction of an annealing stage would not present many problems and the oxidation of the specimen
could easily be prevented by surrounding the specimen with a metal vacuum jacket, having for instance Mylar windows, permitting entry and exit of the X-ray beam. The temperature programmer described could be used in conjunction with a high stability temperature controller and small heater coil in close proximity to the specimen, thus permitting X-ray topography to be carried out during or after cooling or heating through any temperature range.

Observation of dislocations at low temperatures would also be of interest, since by cooling a specimen after anneal below room temperature one could stabilise the dislocation configuration and make detailed observations of dislocations without recovery markedly altering the dislocation structure with time, a problem encountered by the author when examining specimens at room temperature. Of particular interest in this respect would be the observation at low temperatures (possibly as low as liquid nitrogen temperatures by surrounding the specimen with a vacuum jacket and radiation shields and using a cryotip) of specimens cut parallel to the (1010) plane, the dislocation configuration of which appear to be particularly mobile at room temperature (as evidenced by electron-microscopy studies being carried out on foils in this orientation at present in this department). The annealing kinetics of dislocation loops in basal specimens could be more quantitatively investigated by keeping the temperature at such a level below room temperature that the loop annealing rate was much reduced. Moreover the lifetime of these basal specimens would probably be greatly lengthened by the prevention of draughts which can cause bending of these specimens.

At low temperatures stereo reflections would be extremely useful in allowing contrast effects and the spatial distribution of dislocations as a function of depth to be examined in detail, a technique not applicable at room temperature and temperatures above
as a result of rapid changes with time of the dislocation configuration.

At reduced temperatures the direct correspondence between etch pits and dislocations could be attempted. By annealing and slowly cooling a (10\bar{1}0) specimen in situ on the Lang apparatus to below room temperature one could possibly also etch this specimen at this temperature before topographic examination and thus overcome the double problem of handling after anneal and of preventing room temperature recovery. The etch pit distribution at this reduced temperature could subsequently be recorded after X-ray topographic examination of the specimen by removing the specimen from the camera and photographing it at room temperature.

Warpage between subgrains in basal oriented specimens has prevented larger volumes of such specimens to be examined. The static orientation of the crystal relative to the X-ray beam on traversing permits normally only one subgrain to be picked up since their angular misorientation relative to each other is greater than the angular divergence of the beam. The examination of more subgrains per specimen could be achieved by continually reorienting the crystal during traversing. The manner in which this could be achieved without damaging the crystal has to some extent been considered. A servo-mechanism linked into the vernier drum which permits rotation of the traversing stage and crystal horizontally could be made to act in response to a signal proportional to the total integrated intensity diffracted from the crystal. A device could be constructed which if the level of the integrated intensity as recorded on the ratemeter fell below a certain level would activate the servo-mechanism linked to it and to the traversing stage so it rotated the latter back and forth until a new peak value of intensity was obtained i.e. a new subgrain picked up. In this way the topograph obtained would contain
more subgrains and hence more information could be obtained per unit specimen. This would also enable the same subgrain to be examined in different reflections and would prevent drift on long exposures on specimens being examined at room temperature, as a consequence of changes in the ambient temperature.

Anomalous transmission and contrast effects in thicker specimens and in different reflections could be investigated. Coupled to this, theoretical calculations of dynamical intensities could be carried out.

There is also scope for further investigation of the Nital solutions, particularly a more detailed investigation of the formation of etch pits on the (1010) plane using 1% Nital. An attempt has been made by other workers to elucidate this mechanism. The molecular and ionic constituents of 1% Nital are known, but the way in which these react on the surface of the exposed (1010) plane of cadmium to produce etch pits has remained elusive. The discharge potentials of the ions in 1% Nital solution are not known. A knowledge of these and of the potential of cadmium in 1% Nital relative to this solution would permit the effect of these ions on the (1010) to be investigated. By adding overpotentials to a cadmium crystal one could prevent in turn each of the ions in solution from reaching the cadmium surface and by examining the subsequent surface structure on the (1010) plane attempt to elucidate the etching mechanism. By using 100% nitric acid produced by distillation and Analar ethyl alcohol contaminants could be kept from affecting etch pit formation.
APPENDIX 1


In an attempt to identify the nature and the Burgers vector of some of the loops of varying character observed by X-ray topography, use was made of the two beam dynamical theory of electron diffraction due to Hirsch, Howie and Whelan\(^{(57)}\) using displacements predicted by isotropic elasticity theory.

Only the gross features of the computed profiles were intended to be compared with the observations since the dynamical theory of electron diffraction is not directly applicable to X-ray diffraction.

In determining the image profiles of the dislocation loops, the loops were approximated to an infinite mixed dislocation wrapped around upon itself. Since the loops observed are large of the order 50 \(\mu\)m diameter loop self interaction was ignored. Two reflecting planes were considered, a \{(10\overline{1}0)\} and a \{(1\overline{1}20)\} and the foil thickness expressed in terms of X-ray extinction distances for a foil 75 \(\mu\)m thick. These are \(3\xi_g\) and \(6\xi_g\) for \{(10\overline{1}0)\} and \{(1\overline{1}20)\} reflections respectively.

The loops were assumed to have a Burgers vector equal to \(\mathbf{c}\) or \(\mathbf{c} + \mathbf{a}\). Tables 1 and 2 in this appendix give the values of \(g \cdot \mathbf{b}\) for \(g\) equal to \{(10\overline{1}0)\} and \{(1\overline{1}20)\} and \(\mathbf{b}\) equal to \(\mathbf{c}\) or \(\mathbf{c} + \mathbf{a}\). Inspection of table 1 shows that for any one reflection from \{(10\overline{1}0)\} type planes Burgers vectors of \(\mathbf{c}\) and \(\mathbf{c} + \mathbf{a}\) are indistinguishable. Table 2 shows that Burgers vectors of \(\mathbf{c}\) and \(\mathbf{c} + \mathbf{a}\) can be distinguished in any one \{(1\overline{1}20)\} reflection.
The computation was carried out in order to

(a) Distinguish in a \(\{1\overline{1}20\}\) reflection between loops having Burgers vector equal to \(\mathbf{c}\) and \(\mathbf{c} + \mathbf{a}_2\), knowing that the initial loop contrast in this reflection comprised either loops having lines of zero contrast perpendicular to the \(g\)-vector or minima.

(b) Elucidate the nature of the 'Double C' and 'Double D' loops observed in \(\{10\overline{1}0\}\) reflection and explain the rotation of the lines of zero contrast of some of these 'Double D' loops.

Although the computation represents a crude first approximation in explaining the observed X-ray effects, the results are directly applicable to the electron diffraction case, provided the loops are assumed to be large enough to allow loop self-interaction to be ignored.

Expression for \(\mathbf{g} \cdot \mathbf{b} \times \mathbf{u}\) for Basal Dislocation Loops

Using the 3-axis hexagonal coordinate system and solving the following two equations for \(A\) and \(B\)

\[
\begin{align*}
\mathbf{u} \cdot \mathbf{a}_1 &= A \mathbf{a}_1 + B \mathbf{a}_2 - \mathbf{a}_1 \\
\mathbf{u} \cdot \mathbf{a}_2 &= A \mathbf{a}_1 + B \mathbf{a}_2 - \mathbf{a}_2
\end{align*}
\]

One obtains the following expression for \(\mathbf{u}\), the unit vector along the positive direction of the dislocation line.

\[
\mathbf{u} = a^{-1} \left( a_1 \frac{\cos \theta}{\sqrt{3}} - \sin \theta \right) + 2a_2 \frac{\cos \theta}{\sqrt{3}}
\]

We define a general vector \(\mathbf{b} = \mathbf{c} + \eta_1 \mathbf{a}_1 + \eta_2 \mathbf{a}_2\)

\[
\begin{align*}
\text{e.g.} \quad \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}_1, \mathbf{c} - \mathbf{a}_3, \mathbf{c} + \mathbf{a}_2, \mathbf{c} - \mathbf{a}_1, \mathbf{c} + \mathbf{a}_3, \mathbf{c} - \mathbf{a}_2
\end{align*}
\]

\[
(\eta_1, \eta_2) (0, 0) (0, 1) (1, 1) (0, 1) (-1, 0) (-1, -1) (0, -1)
\]
where $\gamma = \frac{c}{a}$ is the axial ratio and $g_i \ (i = 1, 2, 3)$ are the components of the reciprocal space lattice vector.

Now for reflections taken from (10\overline{1}0) and (1\overline{1}20) $g_3 = 0$ and $g \cdot \hat{b} \times \hat{u}$ reduces to

$$g \cdot \hat{b} \times \hat{u} = -\gamma g_1 \left(\frac{\sin \theta}{\sqrt{3}} + \cos \theta\right) - 2\gamma \frac{\sin \theta}{\sqrt{3}} g_2$$

i.e. $g \cdot \hat{b} \times \hat{u}$ is independent of the Burgers vector of the loop.

In general $g \cdot \hat{b} \times \hat{u} = A \cos \theta + B \sin \theta$ and of course $\sin^2 \theta + \cos^2 \theta = 1$ and therefore a given value of $g \cdot \hat{b} \times \hat{u}$ occurs at two positions on the loop at $\theta_1$ and $\theta_2$.

Putting $g \cdot \hat{b} \times \hat{u} = 0$ gives $\tan \theta_o = -\frac{g_1 \sqrt{3}}{(g_1 + 2g_2)}$ (for $g_3 = 0$) and $\frac{d}{d\theta} (g \cdot \hat{b} \times \hat{u}) = 0$ gives $\tan \theta_M = \frac{g_1 + 2g_2}{g_1 \sqrt{3}}$. Therefore $\tan \theta_o \tan \theta_M = -1$ and the angle between $\theta_o$ on $\theta_M = \frac{\pi}{2}$.

Computation of Image Profiles of Basal Loops in h.c.p. Metals, having Burgers Vectors Equal to $c$ or $c + \hat{a}$.

The basic equations of Hirsch et al.\(^{(57)}\) are

$$\frac{d\phi_o}{dz} = -\frac{\pi \phi_o}{\xi_o} + \pi \left(\frac{i}{\xi_\hat{g}} - \frac{1}{\xi_\hat{g}}\right) \phi_\hat{g}$$

$$\frac{d\phi}{dz} = \pi \left(\frac{i}{\xi_\hat{g}} - \frac{1}{\xi_\hat{g}}\right) \phi_o + \left(-\frac{\pi}{\xi_o} + 2\pi i (s + \hat{g} \cdot \hat{u}')\right) \phi_\hat{g}$$

- 172 -
Let \( \phi_o = a_o + i b_o \), \( \phi_g = a_g + i b_g \), where \( \phi_o \) and \( \phi_g \) are the amplitudes of the transmitted and diffracted beams.

Equating real and imaginary parts and multiplying through by \( \xi_g \) and letting \( z = \xi_g \), \( \xi_g' = \xi_o' \), \( \xi_g = \xi_g' \) leads to

\[
\begin{align*}
\frac{da_o}{dz} &= -\frac{\pi a_o}{\xi_o'} - \frac{\pi a_g}{\xi_g'} - \pi b_g \\
\frac{db_o}{dz} &= -\frac{\pi b_o}{\xi_o'} + \frac{\pi a_g}{\xi_g'} - \pi b_g
\end{align*}
\]

\[
\begin{align*}
\frac{da_g}{dz} &= -\frac{\pi a_o}{\xi_g'} - \pi b_o - \frac{\pi a_g}{\xi_g'} - 2\pi (s + \beta_g') \xi_g' b_g \\
\frac{db_g}{dz} &= \pi a_o - \frac{\pi b_o}{\xi_g'} + 2\pi (s + \beta_g') \xi_g' a_g - \frac{\pi b_g}{\xi_o'}
\end{align*}
\]

where

\[
\beta_g' = g \cdot \frac{dR}{dz} \text{ and } R = \frac{1}{2\pi} \left[ b \phi + \frac{b c \sin 2\phi}{4(1 - \nu)} + bxu \left\{ \frac{1 - 2\nu}{2(1 - \nu)} \ln \frac{r \cos 2\phi}{4(1 - \nu)} \right\} \right]
\]

where the notation for \( R \) used is that of Hirsch et al.

For loops lying in the basal plane i.e. parallel to the foil surface \( \phi = \phi \) in the notation of Hirsch et al.

Using these equations N. Ross\(^{(89)}\) has used the Runge-Kutta 4th, order numerical integration procedure to compute the image intensity profiles of basal loops for \( g \)-vectors (10\(\overline{1}0 \)) and (11\(\overline{2}0 \)), positioned at varying depths within foil, assuming \( b = c \), or \( b = c + a \).
The values of the auomalous absorption parameters were set at 0.125, so the angular derivation from the exact Bragg diffracting position was set at zero and the angular changes in \( \theta \) around the loop at 18° intervals. In (10\bar{1}0) reflection values of \( g \cdot b = 0, g \cdot b = \pm 1 \) were used in (11\bar{2}0) \( g \cdot b = 0, g \cdot b = \pm 1, g \cdot b = \pm 2 \).

The image intensity profiles for the diffracted beam for a \( \{11\bar{2}0\} \) reflection with \( g \cdot b = 0, g \cdot b = \pm 1, g \cdot b = \pm 2 \) at a loop depth of 4 \( \xi \) are shown in plots 1, 2, 3 and those for (10\bar{1}0) at the same loop depth of 2 \( \xi \) are shown in plots 4, 5 for \( g \cdot b = 0, g \cdot b = \pm 1 \) respectively. The profiles are typical for positions within the foil where good contrast was found to occur.

The programme developed by Ross was subjected to a series of tests before any loop profile computation was carried out.

He -

(a) Checked the programme against known profiles of Hirsch et al. (Electron Microscopy of Thin Crystals: Butterworths, p.253, Fig.11.5).

(b) Investigated loop profile at a fixed depth within the foil for different angular positions around the loop.

(c) Investigated how many positions within the foil to consider concluded large changes occurred near the surface, little dependence upon position near the centre of the foil.

(d) Investigated the integration step; the number of steps was varied. To conserve computing time used the largest integration step compatible with the known profiles of Hirsch et al.
General Conclusions from the Computation

A. $\mathbf{g} = (10\overline{1}0), \mathbf{g} \cdot \mathbf{b} = 0$

(a) For all loop depths within the foil (taken in steps of $0.5 \xi_g$) there was always detected a line of zero contrast perpendicular to the $g$-vector. This leads to the possibility of 'Double C' or 'Double D' loops.

(b) The profile was symmetrical about the foil centre.

(c) The contrast was enhanced in the vicinity of the foil centre.

(d) The loops of 'Double C' nature were well explained when the loop was within $0.5 \xi_g$ of the foil centre.

$\mathbf{g} = (1010), \mathbf{g} \cdot \mathbf{b} = \pm 1$

(a) Computation characterised by no line of zero contrast, but minimum contrast perpendicular to the $g$-vector.

(b) Reciprocity as in (b) for $\mathbf{g} \cdot \mathbf{b} = 0$.

(c) Considered profile near the surface ($0.25 \xi_g$, nearer to the surface than this then computation broke-down), no 'Double D' loops predicted.

B. $\mathbf{g} = (1\overline{1}20), \mathbf{g} \cdot \mathbf{b} = 0$

(a) Computed profiles applicable to $\mathbf{b} = \mathbf{c}$ loops.

(b) Good 'Double C' contrast at all loop depths except at $1 \xi_g$ and $5 \xi_g$, where contrast was poor.
\( \mathbf{g} = (1 \bar{1} 2 0), \mathbf{g} \cdot \mathbf{b} = \pm 1 \)

(a) Computed profiles applicable to \( \mathbf{b} = \mathbf{c} + \mathbf{a} \) loops.

(b) At all loop depths broad loops showing minima, perpendicular to the \( \mathbf{g} \)-vector.

\( \mathbf{g} = (1 \bar{1} 2 0), \mathbf{g} \cdot \mathbf{b} = \pm 2 \)

(a) Computed profiles applicable to \( \mathbf{b} = \mathbf{c} + \mathbf{a} \) loops.

(b) At all loop depths loops showing fall ring contrast.
Table 1. values of $g.b$ $g=\langle 0110 \rangle$

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<th>$g$</th>
<th>$[1010]$</th>
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Table 2. values of $g.b$ $g=\langle 1120 \rangle$

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<th>$[1120]$</th>
<th>$[1210]$</th>
<th>$[2110]$</th>
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<tbody>
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</table>
Plot 2. Reflection (1120). Loop depth = 4\(\gamma \), \(\varepsilon \beta = 1\)
Plot 4: Reflection (10\(\overline{1}0\)). Loop depth = 2\(\bar{g}\). \(g\cdot b\)=0
Plot 5. Reflection (10\bar{1}0). Loop depth $=2\frac{\varphi}{\varphi_g^*}$, $g\cdot b = 1$
In sec. 5.2 was described an electronic programmer which was developed for producing slow furnace cooling rates. It was related in that section that such an instrument capable of producing the cooling rates required and with inherent stability was not commercially available. The development of this instrument resulted purely from a need, which no industrial concern could meet.

Both the author and Mr. B. Selway after it had been in use for some time realised that it was of potential industrial use. This possibility was discussed with Professor K.E. Puttick who subsequently informed the Science Research Council (the granting authority who have supported the author financially for the period of research for a higher degree at the University of Surrey) of its potential. The Science Research council in turn forwarded the information supplied to them by Professor K.E. Puttick to the National Research Development Corporation.

Under normal circumstances the procedure of N.R.D.C. is to investigate the industrial potential of any devices or systems brought to their notice and in the light of this assessment by technical qualified assessors decide whether or not such a device or system is worth attempted commercial exploitation. If in their opinion it is they proceed to lodge provisional patents describing the device or system and claiming the novelty thought by their Patent Agents to be inherent in it.

In the present case the N.R.D.C. after assessing the instrument on the details forwarded to them by S.R.C. and after discussion by telephone with the author lodged a provisional patent on the device prior to on site assessment, since several industrial concerns after being approached by Mr. B. Selway had shown an interest in it. At a later date an N.R.D.C. official confirmed that the N.R.D.C. would continue support of the exploitation of the device. At the
time of writing the Patent specification is under review by several firms, notable among these being Ether Ltd who have a majority interest in the U.K. temperature programmer market.

It is of interest to relate some of the uses to which temperature programmers are put to in the industrial sphere. In the Potteries industry, they are used for the baking and "firing" of ceramics. Here the desire is for a programmer which takes the kiln temperature at a specific rate up to a temperature of about 99°C, at which it is held for some hours to drive off water vapour within the ceramic material. The temperature is then raised again at a fixed rate to a temperature of around 1100°C-1200°C and there again held for a fixed period. This is the "firing" temperature. Finally the kiln is controllably lowered back to room temperature.

Within the electronic component manufacturing industry, discrete electronic components are heat cycled many times before being marketed to stabilise their characteristics against changes in ambient temperature to which they will be subjected when in use by the consumer. Specific welding techniques within the ship-building industry are being used at present, which require temperature programmers in order to standardise the welding technique.

Until the present time the electro-mechanical programmers which have been produced have been adequate but now according to what industrial representatives from industrial concerns with whom the author has come into contact have related, the industrial sector is now demanding higher stability more versatile programmers, than are at present being produced in order to cope with allied technologies being developed. For example within the semi-conductor technology field, programmers which give greater reproducibility of required temperatures and higher dwell stability are necessary where reproducible diffusion depths of impurities injected into solid state
The advantages of the electronic programmers described over existing ones are (i) its low cost. (ii) Its potential versatility.

As will be recalled from sec 5.2 the device described was not automated (this was not necessary from the viewpoint of the author) and was constructed to produce only slow cooling from the anneal temperature. From what has been said concerning the industrial applications of temperature programmers, automated furnace rise rates, cooling rates and dwell periods at elevated temperatures are required. These requirements can easily be incorporated into the device described by having a second pulse generator $P_2$ linked into the other pulse generator $P_1$ via a series of resistors $R_n$ which would replace the variable resistor controlling the pulse rate of the system described. The second pulse generator $P_2$ by switching in any one of the $R_n$ resistors would set the rise rate of the furnace by setting the pulse rate $P_1$ and this rate could be maintained until a preset temperature was attained. Dwell periods would involve the second pulse generator $P_2$ switching in open circuit to the other pulse generator $P_1$ again this could be for any given period depending upon the pulse rate of this pulse generator $P_2$. Cooling rates from an elevated temperature at a given rate would be achieved again by switching a resistor in the $R_n$ sequence thus setting the pulse rate of $P_1$ and by reversing simultaneously the direction of the staircase waveform from the staircase generator. These are the general lines upon which such an automated programmer could be built.

Revenue sharing agreements have been agreed upon by N.R.D.C. and the University of Surrey. The scheme being such that each receives 50% of any royalties which may accrue should any firm market the instrument. The University has further agreed that should
any royalties accrue the inventors would receive the 50% due to the University, in equal division.
My Supervisor Professor K.E. Puttick, for suggesting the programme of research carried out and for encouragement and interest during its execution.

The Science Research Council for a maintenance grant during the period of research.

The Managers and Professor R.E. King of the Royal Institution of Great Britain for providing various facilities and space for the first eighteen months of the research period.

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Dr. A.G. Crocker and N.D.H. Ross, the former for showing interest in X-ray topography studies on cadmium, which led to useful discussion and the latter for carrying out the computation of dislocation loop profiles in h.c.p metals.

Dr. C.M. Luke a colleague and co-worker for useful discussion.

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Mr. A.E. Jenkinson of Mullards Research Laboratories Salfords for help in the initial assembly of the Lang X-ray equipment.

Mr. B. Selway, chief Technician in the Electrical workshop for assisting in development and for constructing the temperature programmer used for slow cooling of specimens.

Mr. F. Bristow and associates in the Mechanical workshop for producing various pieces of equipment.

Mr. D. Leong and the Audio Visual Aids unit for producing photographic prints.

My sister Gillian for typing this thesis and my wife Alexandra for encouragement and help.

My family in general without whose help my higher education generally would not have been possible.
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