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Some Effects of Deformation and Gamma
Radiation on Sodium and Potassium
Chloride Crystals.

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by

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Abstract

The strain rate sensitivity of the flow stress of KCl is measured over a wide range of temperatures, strains and strain rates for both primary and secondary slip systems.

On the primary slip system the dependance of dislocation etch pit velocity on applied stress is found to follow the relation

$$v = \left(\frac{\tau}{\tau_0} \right)^{m^*}$$

between 190°K and 325°K for normal stresses of constant strain rate tests. Only at lower temperatures are the strain rate tests consistent with a thermally activated process. An analysis of the strain rate and temperature cycling data which are independent of strain under all conditions, indicates that a thermal stress from point defect interactions predominantly controls yield at the low temperatures. Work hardening is consistent with the athermal interactions that have been extensively developed for NaCl.

Deformation on the secondary slip system is investigated by accurately aligning compression in the $\langle 111 \rangle$ direction. The strain rate and temperature cycling tests are consistent below 300°K with a thermally activated strain independent process. Experimental results give close agreement with the theoretical parameters of a Peierls mechanism, probably due to the large repulsive forces between chlorine ions due to their close approach during secondary deformation.

Comparison of the temperature dependance of

slip on the secondary system and previous reports on the deformation of KCl polycrystals suggests the plasticity of polycrystals is unlikely to be controlled by the onset of slip on the secondary systems. Consequently, the beginning of macroscopic cross slip is a more probable limiting process giving plasticity.

The influence of deformation and grain boundaries on the formation of F centres by Co^{60} γ -radiation is investigated. Comparison between the stress strain curves of the deformation and the F centre enhancement by the deformation can be interpreted in terms of work hardening and dislocation debris production. This suggests Stage II work hardening is the result of a higher rate of production of dislocation debris. The increase of F centre colouration with tilt angle of zero twist grain boundaries is determined. At low angles of tilt where the boundary is considered as a dislocation array there is only small enhancement. At higher tilt angles F centre enhancement is greater, corresponding to a grain boundary structure that probably contains large concentrations of vacancies which may act as favourable regions for F centre formation similar to the influence of dislocation dipoles.

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5.1. Conclusions

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1.1. General Introduction

Recent experiments by Evans and Pratt, 1970 have shown that a consistent analysis of thermally activated dislocation obstacles may be obtained for alkali halide crystals by applying theory similar to that successfully employed for the strain rate and temperature cycling experiments for metals. However, the experiments on alkali halide crystals were only conducted at one temperature 244° K on nominally pure material for which subsequent analysis has indicated 30 to 40 molar ppm of polyvalent cation impurity (Kirk 1968). Evans and Pratt concluded from their results that yield was controlled by thermal obstacles whilst work hardening was completely athermal in origin. Hesse 1965 from dislocation etch pit studies has suggested for crystals at this temperature that both yield and stages I and II work hardening are controlled mainly by athermal obstacles: these results indicated a small thermal stress which also increased with strain.

Strain rate and temperature cycling tests on high purity crystals over a wide temperature range will be important to distinguish between these alternatives. This type of analysis has not been made over such a wide temperature range, thus, particular care must be taken to ensure the validity of the theory used. Direct observation of dislocation velocity using etch pits should give the same parameters as those derived from macroscopic measurements if the theory is applicable.

Electron microscope studies of slip lines have confirmed that for compression of crystals in the $\langle 111 \rangle$ direction the resolved shear stress along the primary $\{110\} \langle 110 \rangle$ systems is too small for dislocation

motion and slip occurs mainly on the $\{100\}\langle 110 \rangle$ secondary slip system (Matucha 1968). Secondary slip may be controlled by large anion repulsion (Huntington 1955) giving a Peierls interaction which has been considered theoretically by Dorn 1967.

With increasing temperature the onset of the ductility of ionic crystals may be due to the operation of five independent slip systems (Von Mises criterion) or to the onset of diffusion controlled processes, e.g. Nabarro Herring creep, grain boundary diffusion or the climb of edge edge dislocations.

The primary slip systems $\{110\}\langle 110 \rangle$ provide two independent systems (Groves and Kelly 1963). If the secondary $\{100\}\langle 110 \rangle$ systems provide the other three, then a comparison between the temperature dependence of slip on the secondary system using $\langle 111 \rangle$ compression tests and the ductile brittle transition temperature for KCl (Stoloff 1963) may indicate whether secondary slip controls ductility.

The increasing rate of work hardening, observed at room temperature when deforming NaCl and KCl single crystals in the $\langle 100 \rangle$ direction on the primary slip systems, e.g. Evans 1970, has been attributed to an increased rate of dislocation dipole and debris production. Also, the enhancement by prior deformation of the F centre concentration formed by ionising radiations is believed to be due to the influence of dislocation dipoles (Chang 1965). Thus, by

monitoring the rate of production of dislocation debris by the stress and strain during deformation, it should be possible to relate the transition from Stage I to Stage II of the stress strain curve to a corresponding increase in the rate of F centre enhancement with strain.

Commercial lithium fluoride thermoluminescent dosimeters have recently been developed to monitor ionizing radiations. To stabilise the colour centres produced by the radiation, impurities have been incorporated into the crystal. Recently, pure polycrystals have been successfully used; the grain boundaries have been suggested as the regions where the trapping of radiation products may occur. This trapping process is not known. Conductivity and mechanical studies of bicrystal grain boundaries in NaCl have been reported (McQuhae 1969 and Stokes 1965 respectively). These results can be related to the various models of grain boundary structure in terms of vacancies and dislocations. Bicrystals of NaCl with boundaries of zero twist are irradiated in this work for different angles of tilt and the F centre enhancement is compared to previous conductivity tests on similar specimens.

Unlike polycrystals, bicrystals allow a close study of boundary regions as a function of such variables as the degree of misorientation across the boundary, without the complications arising from the interaction between grains in a polycrystalline piece formed under stress.

Summarising, the experimental investigations are carried out in the following manner:

- (1) Growth of pure KCl single crystals and NaCl bicrystals and the preparation of suitable test specimens.
- (2) Strain rate and temperature cycling deformation tests for both primary and secondary slip systems of KCl are compared with a parallel study of dislocation velocities using etch pits.

- (3) Correlate the states of work hardening from the stress strain curves of KCl to the enhanced F centre concentration caused by the previous deformation of the irradiation specimens.
- (4) Measure the effect of the grain boundary region of bicrystals on the F centre concentration of NaCl as a function of tilt angle.

1.2. Dislocations in ionic crystals.

The aim of this section is to summarise the possible dislocation slip systems to be expected in KCl and NaCl crystals, to assess their relative occurrence during deformation and indicate how the dislocations contribute to the observed stress strain curves. Qualitatively KCl and NaCl crystals have shown similar deformation characteristics. The unit cell of the rock salt structure, two interpenetrating f.c.c. lattices, is shown in fig. 1.1.

1.2.1. Slip system geometry.

Compared to metals, dislocations in ionic crystals have added constraints due to the different sizes of the ions, to ion charge interactions and to the need to maintain charge neutrality. Consequently slip on the plane of closest packing does not normally occur.

Past work has claimed to observe slip in NaCl and KCl under particular conditions on three types of slip plane: $\{110\}$, $\{100\}$, & $\{111\}$ (e.g. Kear et al 1966). In each case the Burgers vector of the slip is a $\frac{a}{2}\langle 110 \rangle$. This is the shortest displacement between ions of the same sign (see Fig.1.2).

The primary slip planes are the six $\{110\}$ planes. These require lower shear stress for dislocation motion than the closer packed $\{100\}$ slip plane, probably due to the large repulsive force between anions for slip on $\{100\}$ planes, (Huntingdon et al 1955), ~~because~~ use of their close approach during dislocation motion. Fig 1.3.

illustrates the configuration of an edge dislocation on $\{110\}$ planes in ionic crystals with the rock salt structure: the dislocation may be considered as two extra half planes inserted perpendicular to the slip plane to preserve charge neutrality. In the figure, it is indicated with broken lines that the dislocation may be considered equally as a single line of ions alternating in sign inserted into the crystal in a direction inclined to the slip plane. The end of such a line carries a charge equivalent to half the charge of an ion i.e. $\pm e/2$.

To preserve charge neutrality, the ion type at the end of each half plane may be expected to alternate along the dislocation line as indicated in Fig. 1.4. Jogs of the dislocation line are also shown in the figure. With the discontinuity at the jog there may be a charge imbalance which gives the dislocation jog an effective charge $\pm e/2$. Overall charge neutrality is maintained by the presence of a similar number of jogs of opposite sign. Measurements have shown that edge dislocations in alkali halide crystals can carry a net charge of either sign depending on the impurity content or other crystal conditions (Turner and Whitworth 1963, Zagoriuko 1966). Thus, deformation gives a charge flow to surfaces and dislocations move in an electric field.

Edge dislocations move considerably faster than the screw component on the primary slip system (approximately ten times - Gutmanas et al 1963). Thus, dislocation loops rapidly become mainly rectangular and the dislocation is then predominantly either of pure edge or pure screw orientation. Since the screw dislocations are the slower moving, the

interactions between obstacles and this component of the dislocation probably control the dislocation velocity. These screw dislocation interactions are now considered further. Possible types of dislocation obstacle are summarised in Table 1.1. This table distinguishes between defects that lie in the slip plane and those that repel the dislocations when they pass near the defect. Screw dislocations interacting with (i) nearby polyvalent impurity vacancy pairs and dislocation debris, both of which are asymmetrical defects, (ii) the direct interaction of dislocations with one another and with dislocation debris, and (iii) the thermal production of sessile jogs on screw dislocations have all been suggested as important dislocation obstacles for KCl and NaCl. The geometrical nature of these interactions is now explained as follows.

The six possible $\{110\} \langle 110 \rangle$ slip systems may be divided into three pairs: the planes of any one pair intercept each other at right angles in a $\langle 100 \rangle$ direction and are designated as conjugate slip planes. Intersection with another $\{110\}$ plane not the conjugate plane occurs at an angle of 60° in a $\langle 111 \rangle$ direction and is called oblique slip.

For intersection between conjugate slip systems, the dislocation interaction between dislocations (S_1) in the one plane with edge (E_2) or screw (S_2) dislocations in the other, is shown in Fig. 1.5(a) and (b) respectively. In both cases a jog is produced on the dislocation line. The dislocation that constitutes the jog can only move in a plane defined by its Burgers vector and dislocation line: this is a $\{100\}$ plane perpendicular to the direction

of the moving screw dislocation. Thus, this jogged part of the screw dislocation cannot move forward conservatively with the screw dislocation and is probably pinned at lower temperatures (Day & Stokes 1966). The moving screw dislocation bows out on either side of the jog (Groves & Kelly 1963b) forming ~~parallel~~ to the motion a pair of dislocation lines on planes separated by a distance equal to the jog height. This pair of dislocation lines are of edge orientation and of opposite sign, so they constitute an edge dislocation dipole. Cross slip of the two separated segments of S_2 may occur to form an isolated prismatic loop of debris in the slip plane. Thus, dislocation dipoles are interstitial or vacancy sheets on $\{110\}$ planes and are comparatively long in the $\langle 110 \rangle$ direction and short in the $\langle 100 \rangle$ direction.

A similar dipole formation process may occur during thermally activated cross slip of the screw dislocation. This process may also lead to glide band broadening (Washburn et al 1960) but Evans & Pratt (1970) have suggested that it is the subsequent formation of blocking obstacles that mainly is responsible for slip on new planes. The height of the thermally activated jogs may be too small for the dipoles to be stable.

Both processes outlined above for dipole production, form debris parallel to the direction of the screw dislocation motion. The interaction of these dipoles with screw dislocations slipping on oblique slip planes is expected to be much larger than for further slip on the active conjugate planes. Thus, this model predicts slip predominantly on one pair of conjugate slip planes.

Dislocations moving on oblique slip systems may react to give sessile dislocations on the $\{112\}$ plane according to the equation

$$\frac{a}{2} [110] + \frac{a}{2} [\bar{0}11] = \frac{a}{2} [101] \quad \dots\dots (1.1)$$

See Fig. 1.6 (Groves & Kelly 1963, Washburn et al 1960). These sessile dislocations may act as barriers to further slip on the oblique planes.

In a real crystal multiple intersection of the dislocations and debris must occur giving rise to a tangle of dislocation lines. This has been observed for MgO using electron microscopy (e.g. a review by Langdon & Pask, 1969) but the same technique cannot be successfully used for alkali halides due to the radiation damage that is simultaneously produced by the beam. Since MgO is an ionic crystal that has the same primary slip systems as NaCl and KCl, the dislocation interactions may be expected to be similar.

Huntington et al 1955 have suggested the possible configuration of edge and screw dislocations on both $\{110\} \langle 110 \rangle$ and $\{100\} \langle 110 \rangle$ slip systems. Table I.II lists the energies they have calculated for dislocations on these systems by allowing the ions away from the dislocation are to relax elastically to minimum energy and calculating the core energy from ion interactions. The screw dislocation has the same configuration, along a $\langle 110 \rangle$ direction, in both planes, but the energy of the core of an edge dislocation on a $\{100\}$ plane is considerably greater than on the primary $\{110\}$ planes.

Stacking faults of 2 to 5b have been calculated to be stable on $\{110\}$ and $\{111\}$ slip planes but not on the $\{100\}$ planes. The dissociation into partials occurs according to the reaction

$$\frac{a}{2} [110] \rightarrow \frac{a}{4} [110] + \frac{a}{4} [110] \dots\dots\dots (1.2)$$

and its formation may lead to an appreciable dilation of the lattice (Fontaine 1968, Fontaine and Haasen 1969)

1.2.2. Stress Strain Curves.

(a) Primary slip system $\{110\} \langle 110 \rangle$

(i) Yield Stress.

Yield stresses for NaCl and KCl have been measured as a function of temperature. (Hesse 1965, Johnston and Nadeau 1964 - See Section 3.1.1). The temperature dependance is similar to that observed for metals. At low temperatures the yield stress is temperature and strain rate sensitive. This is consistent with thermally activated dislocation motion controlling yield. At higher temperatures the yield is comparatively temperature independant, indicating that yield is controlled by long range elastic interactions.

(ii) Three stage work hardening.

At room temperature KCl and NaCl crystals have three stage work hardening curves. Deformation during the first two stages has been compared to the similar stress strain dependance for f.c.c. metals. Both materials have the Taylor relationship between athermal stress and total dislocation density N suggesting elastic dislocation interactions in the first two stages of work hardening (Schmitten & Haasen 1961 Davidge & Pratt 1964 Hesse 1965, Matucha et al 1969.)

$$\tau \propto N^{\frac{1}{2}} \dots\dots\dots (1.3)$$

But Davis and Gordon 1970 have added that the

Taylor relation does not necessarily indicate elastic dislocation interactions. Nabarro et al (1964) have suggested that jog dragging, cutting of dislocation forest or attractive intersections also lead to this equation.

However, the rates of work hardening are much higher for the ionic crystals: they do not have the initial region of easy glide and low work hardening rate of metals. In f.c.c. metals slip line observations indicate slip on the set of parallel planes for Stages I and II, but with ionic crystals predominantly single slip occurs during Stages I and II with some initial conjugate slip and during Stage II slip lines are observed for limited slip on oblique slip systems (Davidge and Pratt 1964).

Evans and Pratt. 1970 using NaCl of similar purity, about 30-40 molar ppm polyvalent cation impurity (Kirk 1968) have reported that both Stages I and II of work hardening at 244°K may be attributed to athermal obstacles. Strain rate and temperature cycling tests were used - see chapter 3.1.3. They suggested the screw dislocation - obstacle interaction during Stage I is due to (1) the back stresses of blocking obstacles formed previously on nearby parallel slip planes at the regions of screw dislocation cross slip and subsequent dislocation pile up and intersection, (2) the intersection with the forest of dislocations around, a blocking obstacle, and (3) the drag due to sessile jogs on the screw dislocation. Blocking obstacles in f.c.c. metals are more difficult to form by this method since the large separation of dislocations into partials restricts cross slip thus explaining the difference between rates of work

hardening. The limited dislocation motion on oblique systems during Stage II work hardening of ionic crystals gives greater intersection and debris production on inclined systems which then interacts strongly with the predominant dislocation motion parallel to the slip planes of Stage I.

The Taylor relationship between athermal stress and dislocation density has been found to be valid between 133°K and 294°K for NaCl (Hesse 1965) suggesting work hardening may be predominantly due to elastic interactions over a wide temperature range. The experiments relating the dislocation etch pit density to stress were carried out for deformation at two constant strain rates. If during deformation of two specimens, one at each strain rate, the dislocation density is the same, then Hesse assumes the dislocation configuration and athermal stress are the same for each crystal: if this is valid, any difference between the flow stresses is due to the strain rate dependence of the thermal interactions for this structure. This technique gives a small increase of thermal stress with strain. Thus, this is not consistent with the observations of Evans & Pratt. Hesse suggests that the decrease of the stress for the onset of Stage III with increasing temperature is consistent with a thermally activated process: the thermally activated cross slip of screw dislocation would give the observed work softening during this Stage III. This cross slip would become easier due to the recombination of dissociated dislocations in the stress concentrations of dislocation obstacles.

The effect of hydrostatic pressure on the deformation of ionic crystals at room temperature has been shown

to be consistent with partial dislocations occurring during deformation (Davis and Gordon 1968, 1970, Haasen et al 1970, Aladag, Davis and Gordon 1970). They propose from the pressure dependance of the flow stress that Stage I stress may arise from both elastic interactions and the creation or diffusion of point defects; Stage II is controlled solely by elastic interactions and, during Stage III deformation, there is dynamic recovery by the athermally activated cross slip of screw dislocations following the recombinations of partial dislocations at the stress concentrations around obstacles.

Fontaine 1968 has suggested possible mechanisms for the formation of barriers to block active sources as part of the model involving partial dislocations.

The discrepancies between authors may be due to the different dislocation interactions in crystals with differing impurity contents: Hesse claimed purity of 2 ppm polyvalent impurity, estimated from conductivity, a technique which may be unreliable (see Chapter 2): Aladag, Davis and Gordon 1969 have suggested their results apply equally to Harshaw crystals with less than 10 ppm impurity: chemical analysis of crystals, similar to those used by Evans and Pratt, indicate 30 to 40 ppm of polyvalent cation impurity. Alternatively, the different conclusions may be the result of invalid assumptions involved in the techniques used. Strain rate cycling tests on high purity crystal may resolve this.

(iii) Latent hardening

Latent hardening experiments consist of deforming a crystal in a $\langle 100 \rangle$ direction to a particular stress and strain then reorientating the crystal so that the original slip planes are parallel to the new $\langle 100 \rangle$

compression direction. The deformation is then continued and the latent hardening is the increase in stress required to move the dislocations on the new slip systems through the slip band of the original deformation. Conclusions may be reached about the relative production of dislocation obstacles on the different slip systems. When the first deformation is halted within Stage I work hardening, the latent hardening increases with strain, Alden 1964, Evans and Pratt 1970. This suggests that obstacles produced on the inclined planes during the original deformation, are not so effective to the original slip as the dislocation obstacles produced on the original slip planes are to the subsequent slip planes after reorientation. This is consistent with the latent hardening arising from dislocation debris, produced parallel to the active slip systems during the original deformation. This debris has a large interaction with dislocations on inclined planes than with dislocations moving on the active slip planes during the original deformation. The latent hardening remains constant for a crystal deformed into Stage II, suggesting that equal quantities of debris are produced on both the active slip planes and on the inclined planes during the original deformation.

1.2.2. (b) Secondary Slip Systems $\{100\}\langle 110 \rangle$

Stepanov and Bobrikov 1957 have observed $\{100\}\langle 110 \rangle$ slip for tensile specimens of natural rock salt stressed in the $\langle 111 \rangle$ direction. The resolved shear stresses along all the primary slip systems are zero for this orientation of the deformation axis. Yield stresses were measured as a function temperature. Above 600°K they reported the yield stress was independent of temperature and below this temperature yield was temperature dependant. The purity of the

crystals is unknown: "Rock salt obtained from the Artemorsk region was used." "For the purposes of making tests we selected the purest pieces: these consisted of specimens which were as free as possible from visible inclusions in the form of blisters or regions of turbidity".

Electron microscopy studies of carbon replicas of slip steps of high purity NaCl crystals compressed in the $\langle 111 \rangle$ direction confirm that slip occurs predominantly on the $\{100\}$ planes at low strains (Matucha, 1968). After torsional deformation of cleaved KCl crystals Gilman 1959 used etch pits to observe that slip had occurred only on the secondary slip systems $\{100\}\langle 110 \rangle$.

Huntington et al 1955 have proposed a configuration for edge dislocations slipping on the $\{100\}$ planes, Fig. 1.3(b), and have indicated that this edge motion on the secondary planes may be restricted by the 'large' lattice potential barrier between the anion closed shells. Such a barrier would act as a Peierls potential hill controlling the dislocations moving forward. Guyot and Dorn 1967 and Dorn and Rajnak 1964 have reviewed the experimental parameters to be expected from this type of short range thermally activated interaction.

When the applied stress is zero, the dislocation line occupies the position of lowest energy in the potential valley midway between the two Peierls potential hills of chlorine ions. Without thermal fluctuations (i.e. 0°K) a shear stress applied to the slip plane would be sufficient to move the dislocation over the potential barrier in the direction of the Burgers vector, a distance equal to the chlorine ion spacing in a $\langle 110 \rangle$. At normal

temperatures, the thermal energy may be sufficient to activate a segment of dislocation into the next potential valley. The theory relates the increase in line energy of the dislocation to the thermal and mechanical energy. The shape of the Peierls potential along the slip planes has to be assumed in the calculation, consequently theoretical parameters are calculated for different values of a variable which can be related to the different models of the Peierls hill.

Fontaine, 1968 and 1969, has calculated that the stacking fault energy is too high for partial dislocations to form during slip on $\{100\}$ planes.

1.2.3. Individual dislocation motion.

The position of individual dislocations can be observed under the optical microscope from dislocation etch pits. Dislocation velocities as a function of stress have been measured for NaCl on the primary slip planes: a simple power relation exists between the velocity of edge or screw dislocation V and the stress at normal stresses i.e.

$$V = \left(\frac{\tau}{\tau_0} \right)^m$$

where the index m is sensitively impurity dependant and has values between 8 and 17 for pure crystals, (Gutmanas et al 1963, Evans & Pratt, 1970).

Experimentally, the technique consists of producing fresh dislocations with an indentation on the specimen surface which produce a "rosette" etch pit pattern around the indent. The velocity is calculated from the distance moved by the outer most edge or screw dislocation after a known load has been applied for a given time.

The etch pits observed around the indent correspond to dislocations on all slip planes of the

primary system that intersect the crystal face indented. The type of dislocation depends on the relative orientation of the slip plane and surface (see Section 2.2.5). Gilman and Johnston 1962 and Nadgornyi and Stepanov 1963 have considered the production of motion of dislocations in this type of indentation, etch pit rosette.

1.2.4. Deformation of KCl

Compression of KCl in the $\langle 100 \rangle$ direction at 295°K moves the dislocations on the primary $\{110\}\langle 110 \rangle$ system which gives stress strain curves with similar three stages of work hardening to NaCl. The transition from Stages I to II work hardening occurs at lower strain for KCl, both crystals show a similar dependance on specimen dimensions: a larger ratio of height to diameter gives lower rates of work hardening (Alden 1964).

The variation of yield stress with temperature has been reported by Johnston & Nadeau 1964 for high purity KCl (analysis indicated about 10ppm alio-valent impurity ions) below 297°K and by Stoloff et al 1963 above this temperature. At low temperatures the yield stress increases more rapidly with decreasing temperature than the slow approximately linear increase at higher temperatures. The yield, particularly at low temperatures, increases rapidly with greater impurity content (e.g. Johnston & Nadeau 1964). Latent hardening experiments at 295°K are similar for KCl and NaCl. See Section 1.2.2. (Alden 1964). The only strain rate cycling tests that have been reported for KCl are those at 295°K by Johnston & Nadeau 1964. From the extrapolation of m values to zero strain (see section 3.1.1) they quoted m^* values between

30 to 40 for pure crystals. No etch pit measurements were made in conjunction with these strain rate cycling tests to check the validity of this m^* value.

Komnik et al 1967 using impure KCl could not detect any strain rate sensitivity of the flow stress at room temperature and suggested that changes of dislocation density completely accommodated the increase of strain rate.

Slip on the secondary $\{100\}\langle 110\rangle$ planes of KCl has been observed by Gilman 1959 using etch pits following torsional tests which exert stresses parallel to $\{100\}$ plane and perpendicular to the slip direction of the primary slip systems. Comparison with this yield stress with normal $\langle 100\rangle$ compression of the crystals gave an approximate ratio of the yield stresses of the two systems

$$\frac{\sigma_{\{100\}}}{\sigma_{\langle 110\rangle}} = 10.5$$

Micro-hardness tests have been made on KCl between 230°K and 670°K (Johnston & Nadeau 1964): the logarithm of microhardness was found to decrease linearly with temperature. The microhardness results were interpreted as a measure of the ease of slip on the secondary slip system. Since the indenter gives an arbitrary deformation, to accommodate this the crystal must deform on five independent slip systems (Von Mises 1928) if no cracks form. They suggested the results indicate a slow variation of the yield stress with temperature for slip on the secondary system, as similar measurement on LiF showed a sudden increase in hardness at the lower temperatures tested.

The onset of wavy slip during $\langle 100 \rangle$ compression of KCl has been observed at a temperature 50°K lower than the ductile - brittle transition for polycrystalline KCl at 420°K (Stoloff et al 1963).

1.3. Radiation damage in ionic crystals.

The understanding of radiation damage processes in alkali halides has been greatly increased in the past few years but exactly how impurities and deformation of the crystal affect the colour centre formation in the crystal is still not clear.

This section will summarise the present knowledge of this topic from work undertaken recently. Books written on colour centres by Schulmann and Compton 1962 and Markham 1966 give a comprehensive summary of the properties known up until about 1961. However, much work relevant to this field has been carried out since then and has sometimes contradicted previous experiments and theory due to the development of high purity crystals.

1.3.1. Radiation Damage at room temperature.

If a crystal is irradiated with photons which have an energy greater than the fundamental optical absorption limit, this causes excitation of the most loosely bound electrons from the valence band of the halide ion to an excited state, i.e. the creation of an exciton states of bound electron-hole pairs which are mobile at room temperature: these pairs can either recombine or interact with ions or imperfections of the lattice. High energy irradiations not only produce multitudes of electron-hole pairs continuously but can impart sufficient energy to the lattice to cause direct or indirect ion displacement. Thus, at room temperature certain defects are mobile and, in equilibrium, the radiation damage is the complex statistical result of many interactions between the defects within the lattice.

KCl irradiated at room temperature in the dark becomes magenta and NaCl yellow. A spectrophotometer shows these crystals have a large error function shaped absorption peak, in the visible region, called the F band. This F band is due to the major colour centre introduced at room temperature: it consists of an anion vacancy, which in the lattice has an effective positive charge, with a trapped electron. Other more complex colour centres are formed particularly at higher doses. These will not be considered in detail.

The optical density at the maxima of a particular band is proportional to the colour centre concentration. Thus, one can easily plot a graph of F centre concentration against irradiation dose. Typically for a crystal irradiated at room temperature this F colouration "growth" curve has two stages - see Fig. 1.7. There is a stage I in which F concentration increases rapidly: this saturates and a Stage II starts which is approximately linear and the rate of F centre formation is much lower. Stages I and II are affected differently by extrinsic conditions of the crystal such as deformation, impurity and irradiation intensity: The dose dependance of other properties of the crystal differ depending on whether colouration is within Stage I or II e.g. volume expansion, yield stress. Gordon and Nowick 1956 suggested the mechanism for the formation of Stage I F centres is different from those formed in Stage II. These mechanisms will be discussed separately.

(a) Stage I colouration.

Stage I F centres are associated with defects initially present in the crystal.

Early workers assumed that this first Stage I colouration was due to anion vacancies, initially present in the crystal from thermodynamic arguments, which trapped electrons: when all are filled with electrons a saturation level is reached. Mitchell et al 1961 Harrison 1963 and Agullo Lopez et al 1967 have suggested that several simultaneous mechanisms operate to give Stage I, each a saturating process freeing anion vacancies from different environments. The formation of F centres preferentially at sites along dislocation lines can be excluded from the failure of dislocation etch pits to move during irradiation. Processes involving electronic trapping of radiation products would stabilise the damage produced, preventing recombination and may thus contribute to Stage I (Sibley & Russel 1964).

Such mechanisms must account for the dependance of Stage I on the following factors, Stage I is enhanced by some impurities and not others, and is sensitive to the intensity of the radiation, deformation and heat treatment.

(1) Stage I mechanisms: impurity effects.

Divalent cation impurity appears to be important in the colouration process and will be considered briefly here. Divalent cation impurity enters the lattice substitutionally on cation sites. It must be accompanied by a charge compensating cation vacancy. From the law of mass action

$$N_+ N_- = A \exp \left\{ \frac{-E_s}{KT} \right\} \quad (1.6)$$

where N_+ = concentration of free cation vacancies
 N_- = concentration of free anion vacancies
 E_s = energy of formation of a pair of vacancies.

This equation infers that if the cation vacancy concentration is considerably enhanced by doping with divalent cations, then the concentration of anion vacancies will be drastically reduced. Thus, if F centres are simply formed by the anion vacancies trapping electrons, divalent impurity may almost completely suppress Stage I colouration.

On the contrary, Etzel¹⁹⁵² and many subsequent authors (e.g. Sibley et al 1965) have shown that certain divalent cation impurity greatly enhances stage I colouration.

Several explanations have been given for this enhancement: the mechanism of Crawford and Nelson 1960 has been well supported by experiment but recently Ikeya¹⁹⁶⁵ has offered an equally satisfactory alternative. These mechanisms will now be discussed.

Etzel thought the impurity enhancement was either due to the excess cation vacancies aiding the diffusion of anion vacancies away from dislocations where they had been created by the irradiation, or the cation vacancies trapped holes, reducing the electron-hole recombination so enhancing the trapping of electrons by the anion vacancies.

Crawford & Nelson suggested that Stage I colouration was due to the conversion of the cation vacancies into anion vacancies. The conversion may take place by an anion adjacent to a cation vacancy capturing a hole. The anion thus becomes effectively a halide atom of zero charge and may relax into the cation vacancy leaving an anion vacancy; the energy released in the hole capture may be used to free the anion vacancy. If the remaining halide atom combines with its neighbouring anion this gives a halide molecule ion Cl_2^- which

lies in a $\langle 100 \rangle$ direction, see Fig. 1.8(i) Hayes 1962 & Hayes and Nichols 1960 have observed a Cl_2^- centre at 77°K in a $\langle 100 \rangle$ direction but suggested this was adjacent also to the divalent cation. Thus, Hayes suggested a model similar to Crawford and Nelson with an impurity - cation vacancy pair at the beginning rather than just the cation vacancy, see Fig. 1.8(ii). If crystals are grown without hydroxyl ions, then no complexing between the hydroxyl ion and divalent impurities can occur and this enables the number of isolated cation vacancies to be calculated from:

$$N_+^2 = \frac{N N_m}{12} \exp \left(- \frac{E_A}{KT} \right) \quad (1.7)$$

where N = concentration of lattice sites;

N_m = concentration of divalent impurities

E_A = association energy of an impurity - vacancy pair.

Both Sibley and Russel 1964 and Ikeya 1965 grew OH free crystals and were able to compare the number of isolated cation vacancies from this equation to the concentration of F centres at the saturation of Stage I colouration $(N_f)_0$, found by extrapolating Stage II colouration back to zero irradiation time as in Fig. 1.7. They both found these concentrations to be almost equal strongly suggesting the Crawford type of mechanism.

At room temperature, d.c. steady state conductivity is due to the diffusion of single cation vacancies, thus this is a measure of the isolated cation vacancy concentration of the crystal. Ikeya 1966 measured this conductivity as a function of radiation dose. He observed the fractional increase of the F band and decrease of conductivity; when plotted against

irradiation time both follow the same curve for stage I in NaCl: Ca^{++} i.e. one cation vacancy is destroyed for each F centre produced, again consistent with the Crawford and Nelson mechanism. However, in high purity crystals, irradiation does not decrease the conductivity.

Ikeya suggested that while his results supported the Crawford and Nelson model, they are really only supporting an enhancement of colouration by isolated cation vacancies rather than the divalent impurity atoms. He proposed an alternative model which equally satisfies the results. Ikeya noted that colouration increased with temperature between 200°K to room temperature giving an activation energy of 0.08eV for the process of colouration: this is very close to the value of 0.07eV that Schnatterly and Compton 1964 observed as the activation energy for mobile interstitial halogen ions. Ikeya said it would be quite possible for the cation vacancies to trap interstitial halogens so reducing recombination of F centres and interstitials. This gives F enhancement at the expense of the cation vacancies. Such a mechanism is supported by Sonder and Sibley 1965 who concluded that F enhanced colouration at liquid nitrogen by divalent impurity is due to the stabilisation of interstitial halogen ions by the impurity.

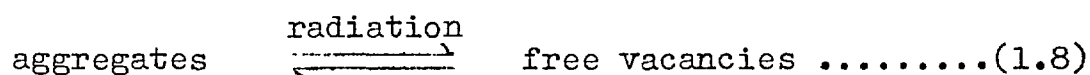
Rabin 1959 examined the change of density by measuring the change of linear dimensions as a function of irradiation dose for pure and doped crystal. Stage I gives no density change whereas the density decreases in Stage II. Etzel's stage I model involves the production of new vacancies which would decrease stage I density. This is not observed. The models of Crawford & Ikeya do not involve the production of

vacancies and so satisfy Rabins observations. The work of Paus & Thonmen 1963 contradicted the work of Rabin: they saw a density decrease for stage I. Sibley and Russel 1964 found the flow stress of crystals, both pure and doped, does not increase with irradiation in Stage I. This again rules out the model of Etzel which would give interstitial ions that would have caused hardening of the crystal. The models of Crawford and Ikeya would not produce interstitials or other hardening centers and are thus compatible with these flow stress measurements.

(ii) Stage I mechanisms: pure crystal.

Mitchell 1961, Harrison 1963 and Agullo-Lopez 1967 have all suggested more than one mechanism contributes to stage I colouration of pure crystals. The models were derived to fit the observations of the intensity and deformation dependance of the colouration. Mitchell used only low intensity x-rays, about 15,000 R/hour, whereas Agullo-Lopez used irradiation about 1.8×10^6 R/hr and, since colouration in stage I is sensitively intensity dependant, an exact comparison between their results and calculations is difficult. Both explanations considered the trapping of electrons by two or more types of anion vacancies from different environments. Mitchell proposed that one type of anion vacancy is randomly distributed throughout the crystal, a bulk process, and the other type is concentrated in particular regions of the crystal. The latter type is probably located with dislocation debris, so a more comprehensive study of this work will be given later under deformation enhanced colouration. Agullo-Lopez and Harrison considered the intensity dependance of Stage I. They analysed Stage I into

fast and slow components and proposed tentatively from these results that the initial fast component is due to the easy capture of electrons by isolated anion vacancies. Such trapping would not be intensity dependant. The slow component may be due to vacancies having to be released from aggregates by the radiation before they can form F centres like the fast component. With higher intensity γ - rays more vacancies may be produced to maintain the equilibrium of:-



More free vacancies will increase the contribution of the slow component. This increase of the slow component with intensity will saturate when there is equilibrium for the process of trapping electrons by freed vacancies.

(b) Stage II colouration

We have seen that Stage I results from the easy conversion of initially present defects into F centres with an activation energy as low as 0.08 eV. During Stage II the anion vacancies have to be created by the radiation itself; this requires an energy of the order of electron volts, consequently the rate of formation of F centres is much slower in Stage II. As with Stage I, the mechanism of Stage II for the production of F centres is not definitely known. One difficulty has been that ionising radiations have small momenta; thus it is impossible for them to supply sufficient momenta to directly knock out a lattice ion.

Below room temperature, interstitial centres are observed using electron spin resonances, Schoemaker 1966. The hardening and expansion of crystals increasing with dose during Stage II irradiation at room temperature is consistent with Frenkel pairs being produced by the radiation at this temperature. Thus in Stage II colouration the anion vacancy for F colouration is probably produced together with an interstitial anion. Two possible mechanisms have been suggested for this Frenkel pair production: an ionisation mechanism and an excitonic mechanism.

(i) Stage II coloration - ionisation mechanism.

Prior to 1966, it was generally accepted that the exchange of energy between radiation and ion occurs by an ionisation process. The Varley 1954 mechanism involves multiple ionisation of an anion giving it an effective positive charge. This ion is highly repelled by its neighbouring positive cations and is ejected into an interstitial position

in a $\langle 110 \rangle$ direction.

Dexter 1960 objected to this sort of mechanism involving double ionisation of lattice ions. He calculated the lifetime of a double ionised state before electron capture on the basis of the band model and found it to be too short to cause ejection of the anion, but Howard and Smoluchowski disagreed.

To satisfy these objections, Klick 1960 put forward other possible models. Either a halide ion is doubly ionised as above or two adjacent halide ions were ionised, see Fig. 1.9; both lead to the formation of a halogen molecule ion, X_2^- V_K centre; this may move in a $\langle 110 \rangle$ direction and may eventually become localised at a halogen site, i.e. formation of an anion vacancy and interstitial centre.

Williams 1962 showed that a single ionisation mechanism is possible to form Stage II F centres. The single ionisation of an ion leaves a halide atom uncharged, X^0 , which forms a molecule ion, X_2^- , by combining with an anion neighbour. This molecule ion has symmetrical electrical forces acting upon it, but its movement is caused by momenta imparted to it by quantum mechanical asymmetry considerations and it would then move as for a double ionisation mechanism.

Seitz 1956 suggested that a vacancy production mechanism might require less energy if it takes place near existing defects e.g. excitons moving dislocation jogs. But this mechanism does not produce interstitials which the measurements on flow stress and density have suggested and so this model has been ruled out. Ionisation mechanism fail to account for several Stage II F centre properties.

- (i) Production of F centres by U.V. radiation,
Ikegawa et al 1967.

(ii) Stage II growth is very sensitive to small impurity concentrations. e.g. Sibley et al 1964.

(iii) Stage II growth depends on temperature, Hall et al 1964.

(ii) Stage II colouration: Exciton mechanism.

The failure of the ionisation model to predict certain Stage II properties suggests an alternative mechanism causes the Frenkel pair production.

In 1966, quite independantly, Hersh and Pooley proposed a similar excitonic (non-ionising) mechanism for anion vacancy production.

During electron hole pair formation in the lattice, the radiation removes the valence electron from the halide ion leaving the halide in an effectively uncharged state, X^0 . The neighbouring anion X^- in a $\langle 110 \rangle$ direction is no longer in a symmetric position. The asymmetry splits the triple degeneracy of the p electron of this neighbouring ion and the energy will decrease if the X^0 and X^- move towards one another (John Teller effect) forming a halide molecule ion which at low temperatures is the stable form of a trapped hole - the V_K centre.

Electron-hole recombination occurs all the time.

Kabler 1964 and Murray and Keller have shown how this recombination may take place: the electron bound to the V_K hole center i.e. X_2^- ion captures another electron and is then the excited state $X_2^{\bullet}$ of two anions, $2X^-$. At low temperatures this excited centre usually relaxes to the perfect lattice structure and the extra energy is emitted as a phonon of luminescence. At higher temperatures it is more likely to relax to its ground state without a radiative emission. The extra energy of the excited state, in this case, remains with the

halide ions. Then the ion with the larger energy might start a replacement sequence in the $\langle 110 \rangle$ direction leaving behind an anion vacancy and forming an interstitial halide a few lattice spacings away, see Fig. 1.10. This anion vacancy traps an electron to become an F centre. The replacement sequence satisfies the requirements of the transfer of energy from ions of equal size and minimisation of coulombic forces by replacing one ion with a similar one. Radiative transitions and F centre production from the decay of the excited state are just two of the competing processes: Table I-III lists other mechanisms.

The success of this exciton model is that it predicts properties that the ionisation model is unable to do. It is possible to calculate the intensities of the non-radiative transition to the radiative transition, luminescence, as a function of temperatures and compared this to F centre production. Fig. 1.11 shows the behaviour of the F colouration and luminescence of KI measured about 100°K ; there is small colouration and large luminescence below 100°K and small luminescence and large F colouration above. (Hall et al 1964, Konitzer and Hersh 1960). Experimentally, the rate of colouration at temperature above 100°K decreases. This model suggests this is due to the hole no longer being immobile and recombination of electron and hole can take place at impurities.

This model would then predict the large suppression of Stage II F colouration by impurities which act as recombination centres for electrons and holes instead of at the halogen X_2^- ion. The efficiency

of the suppression depends on the impurity type: 6ppm of lead impurity has been shown to nearly completely suppress Stage II but calcium and strontium are not nearly so effective, Sibley and Russel 1964.

The ionisation model has failed to explain the F centre formation observed after W irradiation

However, ultra violet radiation in 6 to 10 eV range forms electron hole pairs and consequently self trapped hole centres, which with subsequent recombination by the exciton mechanism may give F centres.

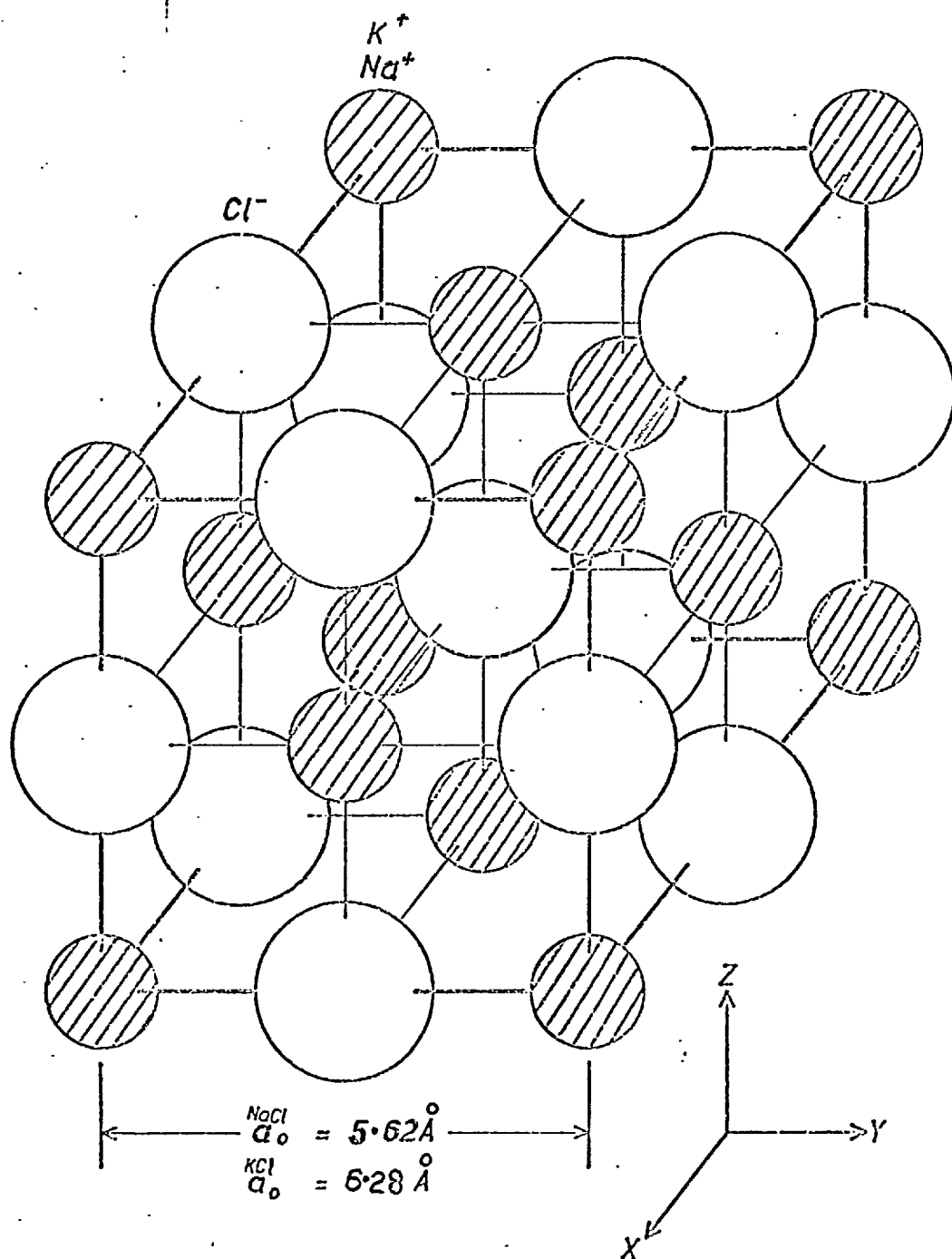
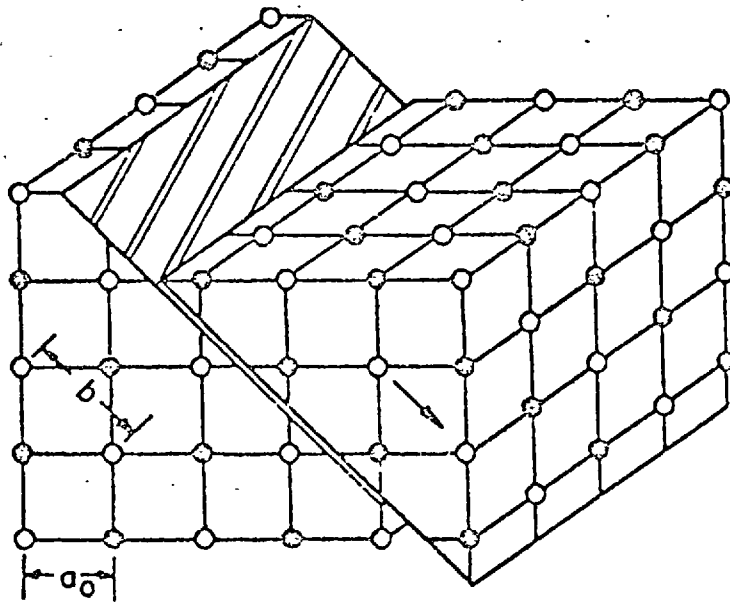
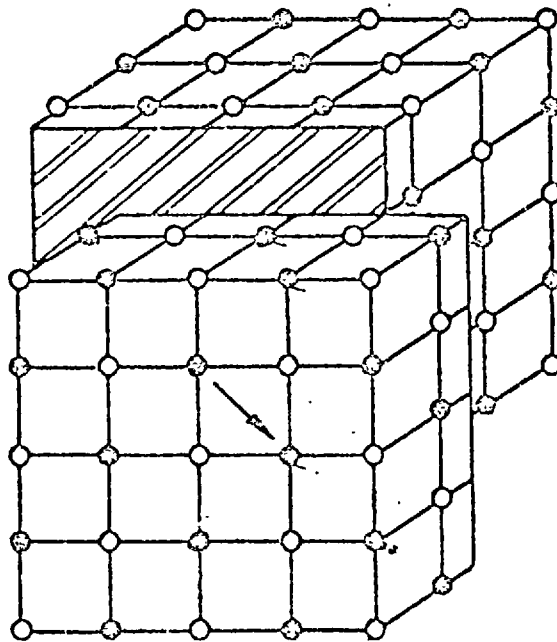


Fig.1.1 UNIT CELL OF NaCl & KCl



$\{110\} \langle 110 \rangle$ GLIDE



$\{100\} \langle 110 \rangle$ GLIDE

Fig 1.2 Glide planes

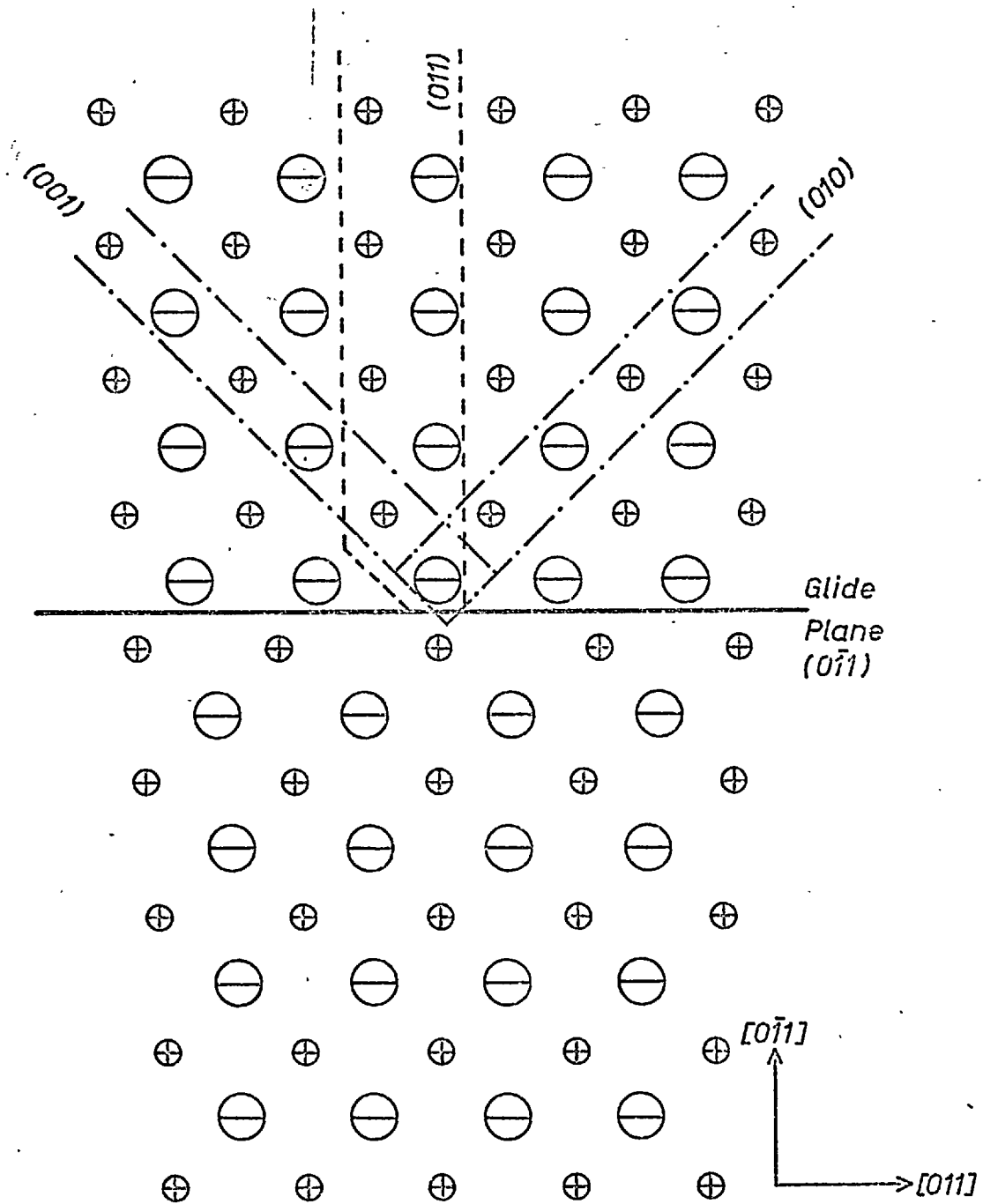


Fig.1.3(a) EDGE DISLOCATION IN NaCl

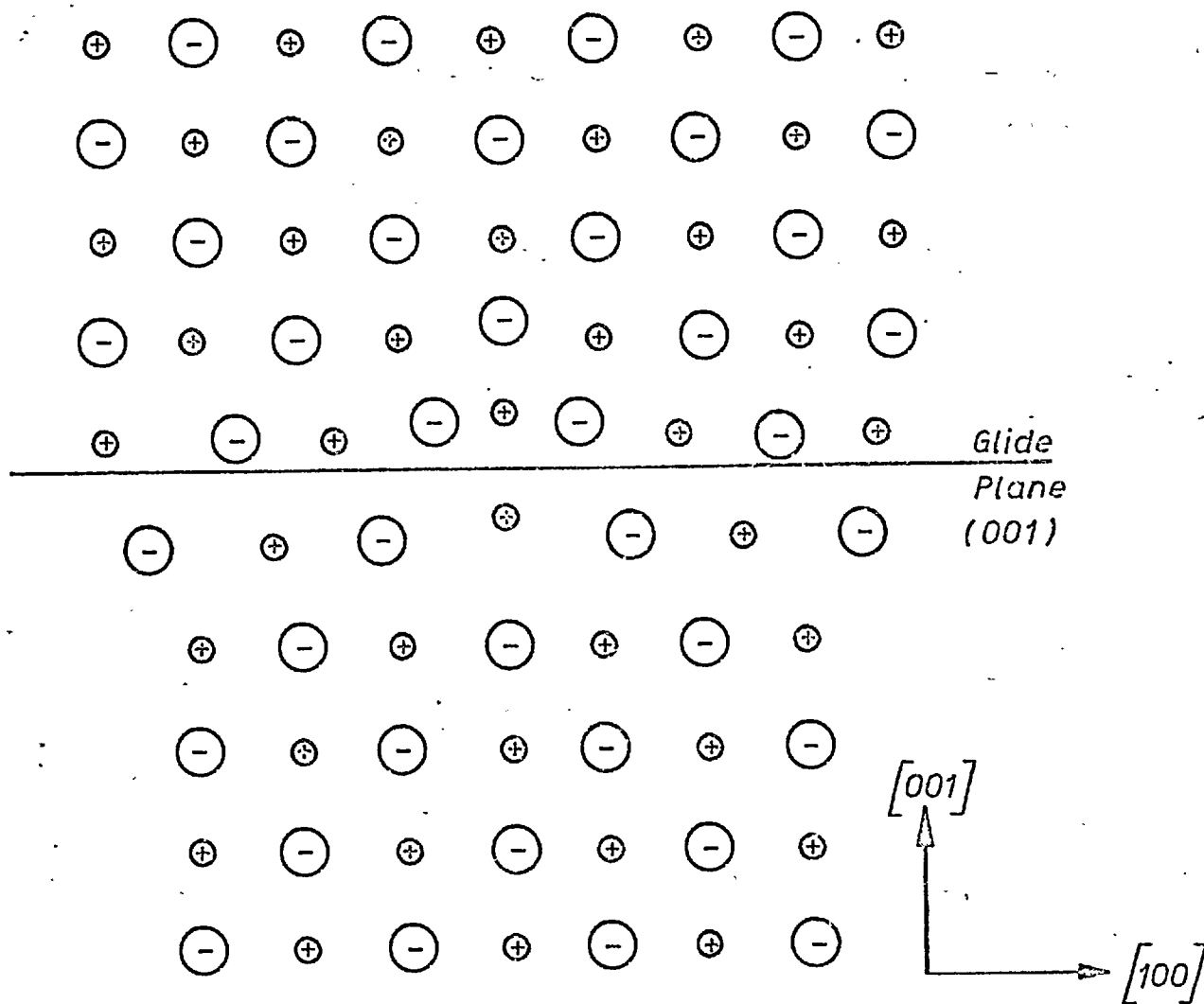


Fig. 1.3(b) EDGE DISLOCATION ON $\{100\} \langle 110 \rangle$

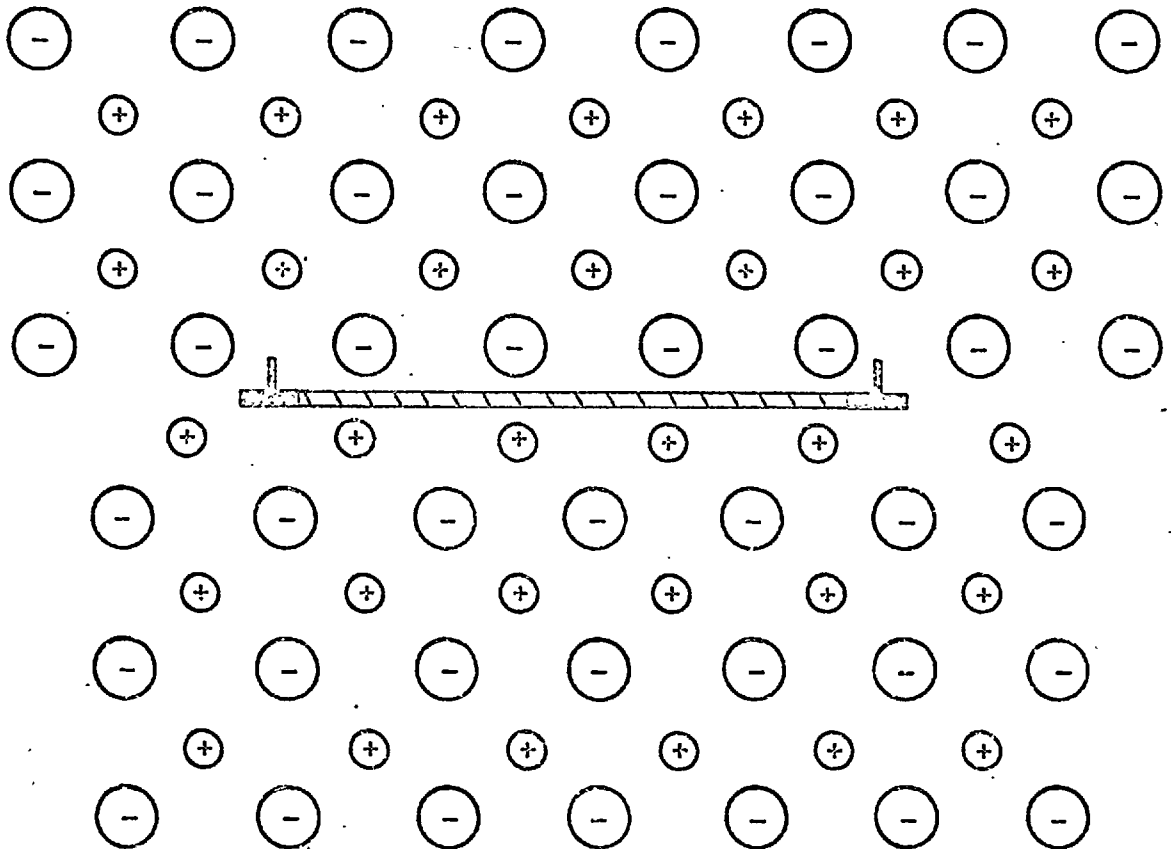
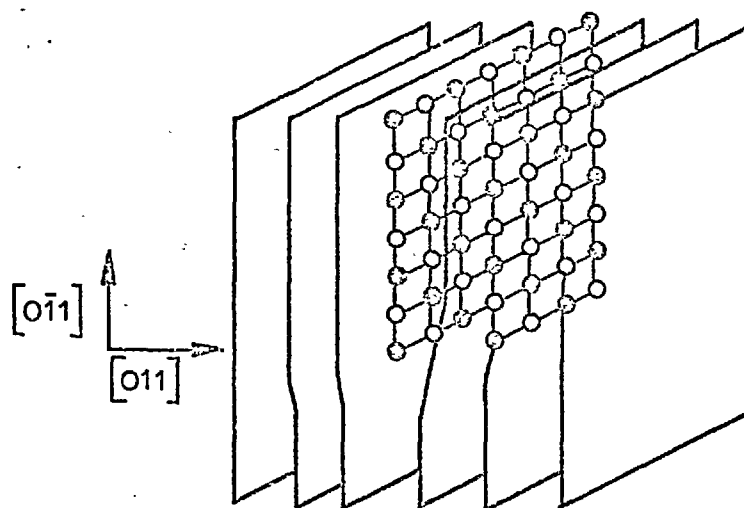
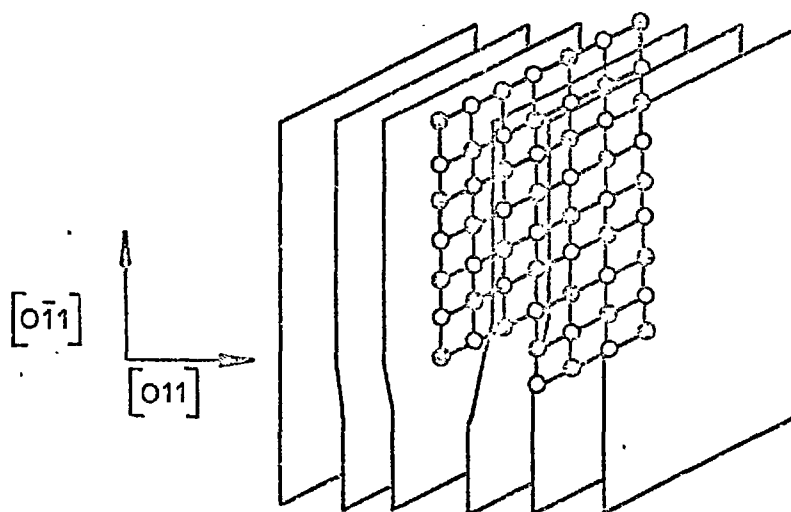


Fig.1.3(c) EXTENDED EDGE DISLOCATION ON
 $\{110\} \langle 110 \rangle$



(a) charged jog



(b) uncharged jog

Fig.1.4 JOGS ON EDGE DISLOCATIONS
ON $\{110\}$ $\langle 110 \rangle$

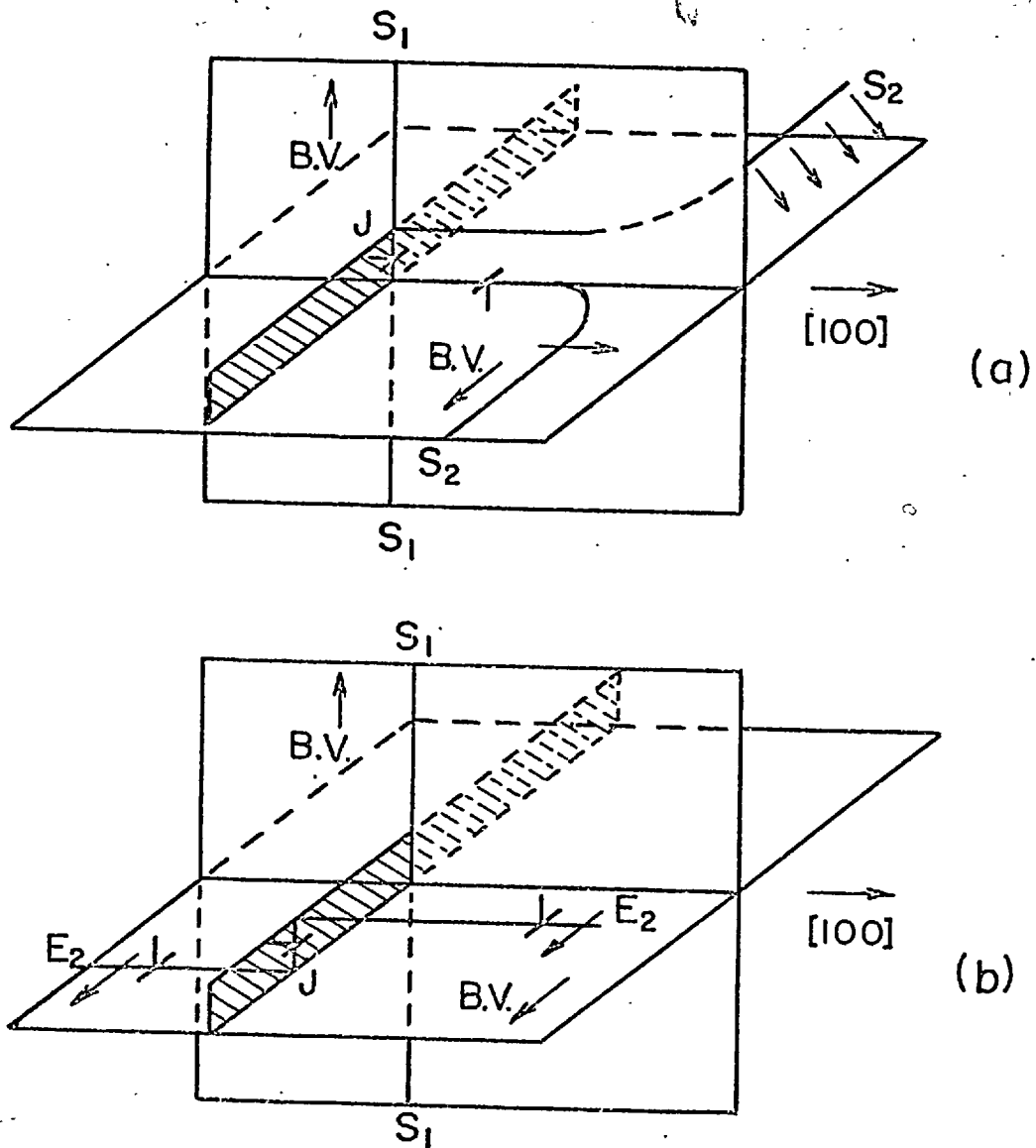


Fig 1.5 Dislocation intersection

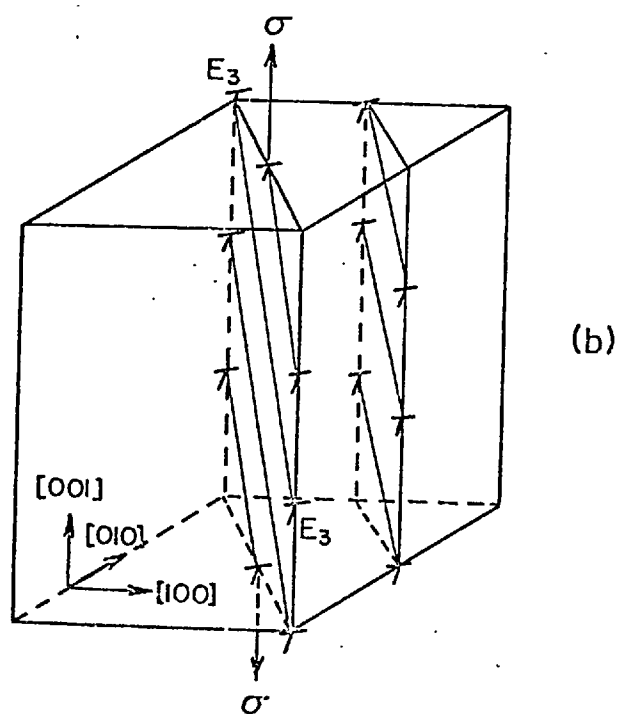
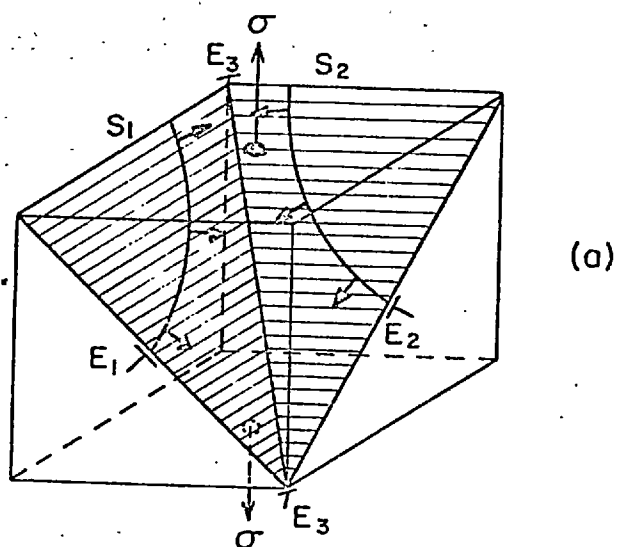


Fig 1.6 Dislocation interaction

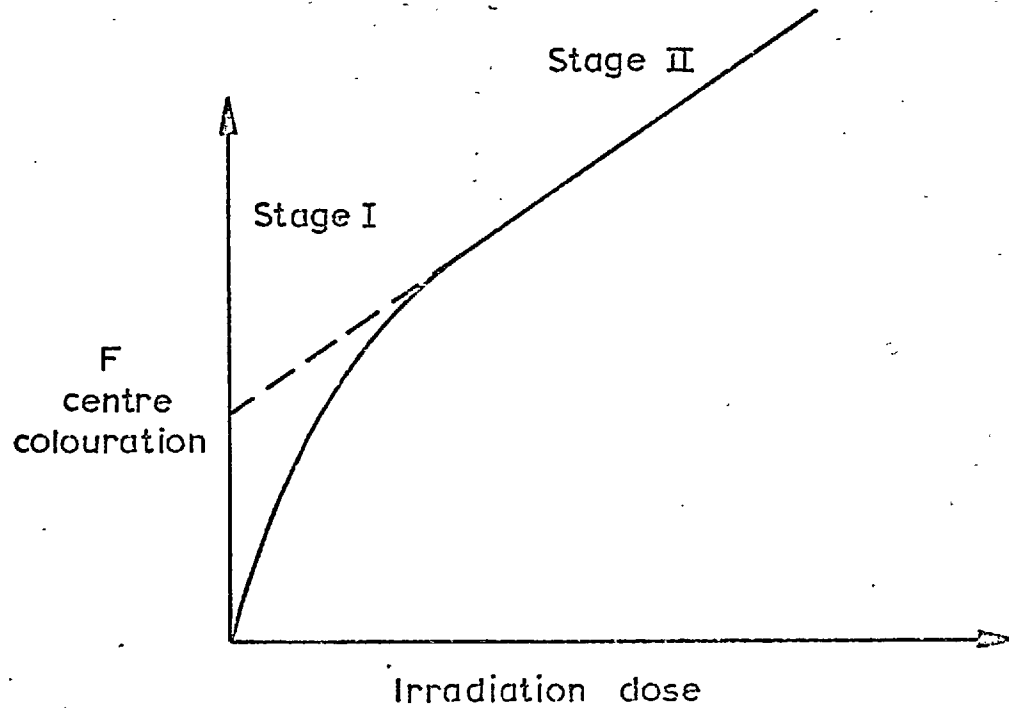
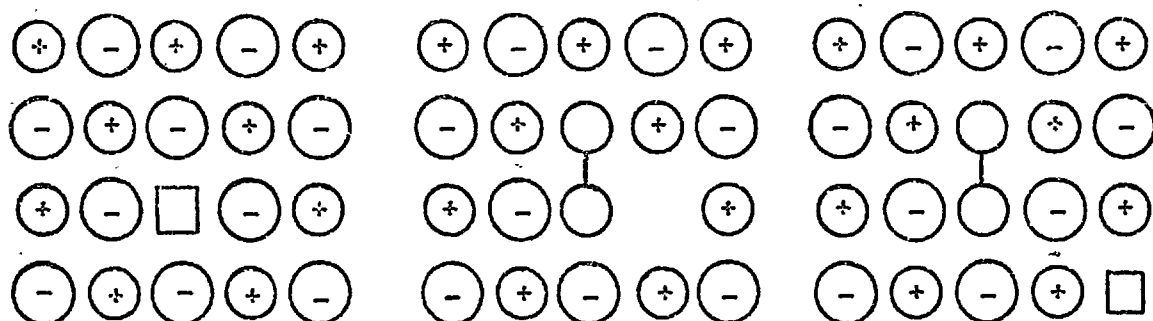
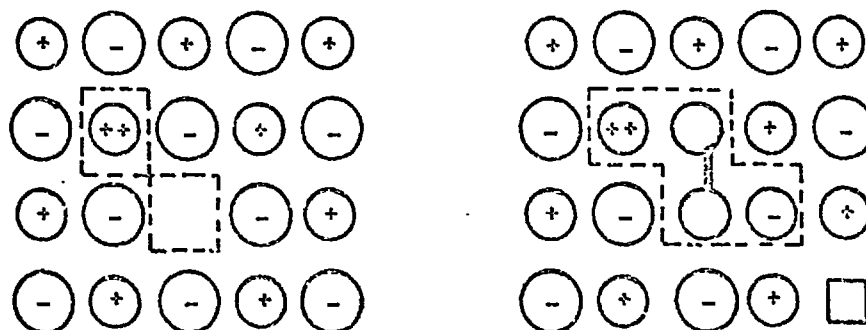


Fig.1.7 THE TWO STAGES OF F CENTRE COLOURATION AT ROOM TEMPERATURE.



(a) Cation vacancy $\square$ (b) $\square + X^- + X^- + h\nu \rightarrow \square + X_2^=$ (c) Anion vacancy motion

(i)



(a) Cation impurity (b) $I^{++} + \square + X^- + X^- \rightarrow I^{++} + X_2^= + \square$
vacancy pair

(ii)

Fig.1.8. STAGE I F CENTRE COLOURATION.
THE CONVERSION OF CATION VACANCIES
INTO ANION VACANCIES.

(i) Method of Crawford & Nelson

(ii) Method of Hayes

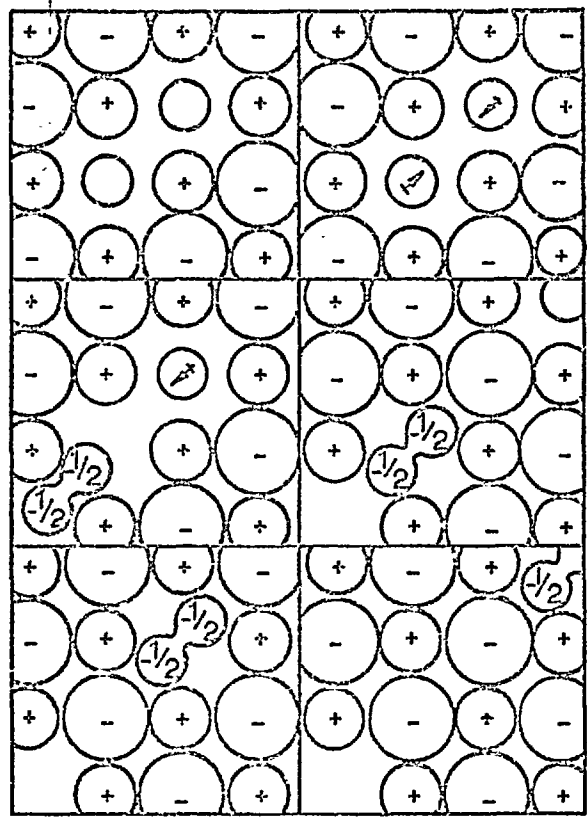
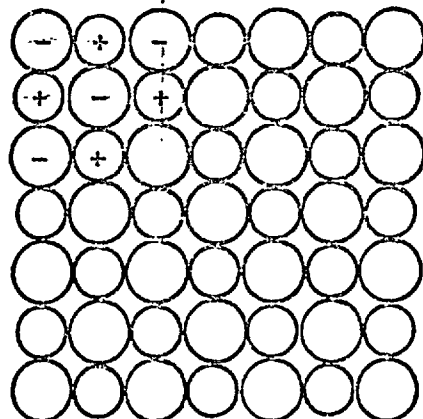
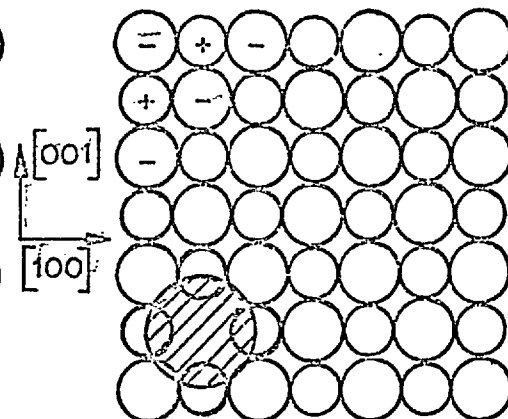
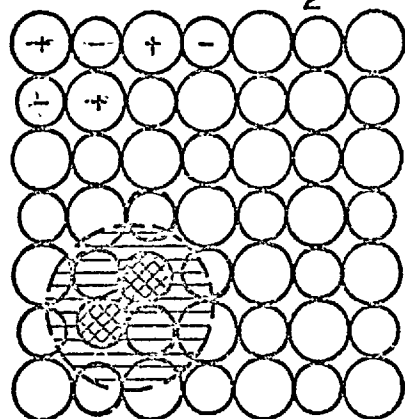
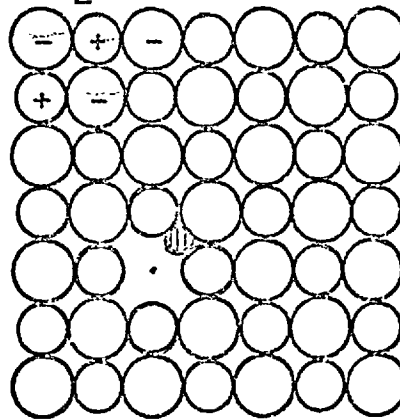


Fig.1.9

STAGE II F CENTRE COLOURATION
 ANION VACANCY AND INTERSTITIAL
 FORMATION FROM AN IONISATION
 MECHANISM

(a) Perfect crystal

(b) $X^- + h\nu \longrightarrow X^{-*}$ (c) $X^{-*} + X^- \longrightarrow X_2^{-*}$ (d) $X_2^{-*} \longrightarrow X^- + e + X_{int}$ 

(e) Interstitial motion

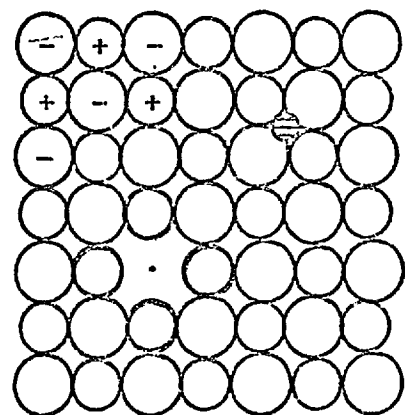
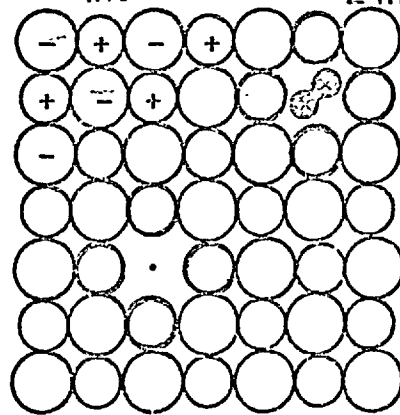
(f) $X_{int} + X^- \longrightarrow X_{2int}^-$ 

Fig.1.10. STAGE II F COLOURATION: EXCITONIC MECHANISM

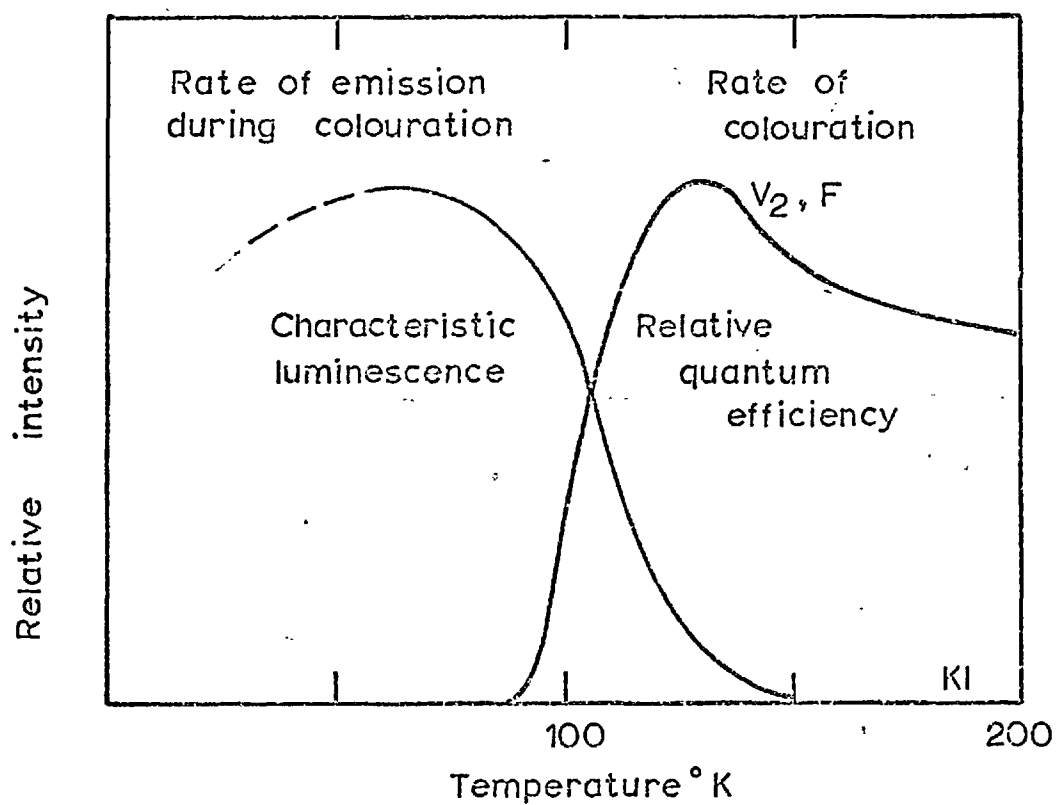


Fig.1.11. THE TEMPERATURE DEPENDENCE OF
STAGE II F CENTRE COLOURATION
AND LUMINESCENT EMISSION OF KI

INDIRECT INTERACTION OF STRESS FIELDS	SYMMETRICAL DEFECTS	Impurities Vacancies	Solid solutions (same valence) Quenching F centres
	ASYMMETRICAL DEFECTS	Impurities Vacancies Interstials Dislocations	Solid solutions (different valence) Precipitates Prismatic loops Irradiation damage Dislocation debris (Taylor, dipole)
DIRECT INTERACTION BY CUTTING		Impurities Vacancies Dislocations	Precipitates Prismatic loops Dislocation debris (Multipoles, forest)

Table 1 - I' Dislocation interactions.

Table I - II Dislocation energies.

Slip plane	Component	Elastic Energy eV/cm	Core
{110}	edge	$1.81 \ln R/r_0$	1.37
	screw	$1.37 \ln R/r_0$	0.39
{100}	edge	$1.62 \ln R/r_0$	3.8
	screw	$1.37 \ln R/r_0$	0.39

R = distance between dislocations

r_0 = dislocation core radius ($\sim 2 \text{ \AA}$)

Table 1-III Possible decay processes of excited X_2^*

0	Formation	$X^- + h\nu \rightarrow X^{*-}$ primary exciton $X^{*-} + X^- \rightarrow X_2^{*}$ relaxed exciton
1	Luminescence	$X_2^{*} \rightarrow 2X^- + h\nu$
2	Heat	$X_2^{*} \rightarrow 2X^- + \text{heat}$
3	Ionisation	$X_2^{*} \rightarrow X_2^- + e$
4	Dissociation	$X_2^{*} \rightarrow X_2^{**} - X \text{ int} + X + 0 + e$
5	Formation of halogen molecules	(a) $X_{\text{int}} + X^- \rightarrow X_2 \text{ int} - V \text{ center}$ (b) $X_{\text{int}} + X_{\text{int}} \rightarrow X_2 \text{ int}$

Chapter 2. Production of Specimens.

2.1. Introduction.

All the properties to be investigated depend sensitively on impurity. Thus the aim is to grow high purity single crystals to reduce the extrinsic effects of impurity.

The athermal forces acting on a dislocation depend on the dislocation density of the crystal; consequently, deformation specimens need to have a low dislocation density which is consistent for the range of specimens used. The specimens should be free from low angle boundaries since these may be considered as dislocation arrays.

The purification and growth of alkali halide single crystals has been reviewed by Dreyfus 1963. Zone refining KCl produces crystals with very low concentrations of most cation impurities but this process is not satisfactory for purifying NaCl since the impurity rejection ratio between solid and melt for Ca⁺⁺ is close to unity. In addition, the single crystal areas in the purified material are small and badly stressed from the constraints of the container and by thermal gradients, Butler et al 1966: this results in high dislocation densities and many low angle boundaries in the specimens. Thus, it is difficult to obtain a sufficient number of consistent, low dislocation density specimens using this technique. The Stockbarger method suffers from similar problems from the container unless it is large.

Crystal growth using the Kyropoulos (or Czochralski) process yields large strain free crystals, since there are no constraints from the container. This process is used to prepare the crystals for this work. Crystallisation is initiated on the surface of

the molten salt with a seed crystal which is then slowly withdrawn. Bicrystals with zero twist boundaries are grown in the same apparatus using twin seeds.

The Kyropoulos technique itself involves only a small purification from the favourable rejection ratio for certain impurities at the interface between solid and melt during crystal growth. Thus, the impurity content of the starting material must be as good as that required for the crystal specimens.

2.2. Experimental.

2.2.1. Starting material.

Sufficiently pure KCl can be reasonably purchased as 'Spcc-Pure' material from the Johnson Matthey Chemicals Ltd. (London). The impurity level varies considerably between batches. Only KCl from the batch with the lowest impurity content is used: analysis gives the total polyvalent cation content as 4 ppm and sodium content as 3 ppm. (See Analysis Table 2-I). High purity alkali halide material by chemical processes has been prepared recently by Butler et al 1966 and McQuhae 1969. Similar ion exchange techniques are used to purify the NaCl, starting from reagent grade material: this is indicated schematically in Fig. 2.1. Chelating agents purify the salt solution since they more readily form compounds with multivalent ions rather than alkali ions, due to the directional nature of their bonding, e.g. Samuelson 1963.

The NaCl is dissolved in deionised water and agitated with an immiscible phase of chloroform in which is dissolved the chelating agents dithizone and oxine and then separated from it. This stage is effective for the removal of Ba, Cu, Fe, Pb, and

partly removes Ca and Mg, since they form complexes which do not dissolve in the aqueous phase and can be removed by filtration and with the chloroform.

The solution is then passed at 25 cc per minute through four 60 cm long, 2 cm diameter columns containing three chelating resins. Each resin is in its sodium form, converted by previous washing with NaOH solution followed by deionised water.

Resin 1 De-Acidite E resin with the tertiary amine group replaced by chloroacetic acid (McQuhae 1969).

Resin 2 Oxine treated with formaldehyde then resourcinol (Pennington et al 1959)

Resin 3 Dowex Al (Commercial Resin)

The final solution is boiled to give a saturated solution then evaporated to dryness in an oven. The effectiveness of this purification process is shown in Table 2.1. All cation impurity was below the detection limit of the analysis.

Before use all glassware is thoroughly rinsed with sulphuric and chromic acid, then with the commercial deionising solution Decon and washed with deionised water.

2.2.2. Crystal Growth.

Hydroxyl ions hydrolyse the salt at high temperatures and cannot be removed by heat alone. If present they may enhance the F centre colouration, Etzel and Patterson 1958, and the grain boundary regions of bi-crystals, Cabane 1962. Sibley 1962 has suggested that heating the material near the melting point under high vacuum before melting considerably reduces the OH concentration in the crystals.

Patterson 1962 has shown that the hydroxyl ion content of melt grown crystals is reduced for the growth in the absence of oxygen, particularly if a dry inert gas is used. Bubbling chlorine or hydrogen chloride through the melt reverses the hydrolysis, Butler 1966. Hydroxyl ion concentrations were found to be lower from melt grown crystals in silica containers rather than platinum, Etzel and Patterson 1958, probably due to OH ions forming compounds with the silica. This may be responsible for the solidified melt adhering to its container after crystal growth if no initial precaution is taken to remove OH.

The Kyropoulos technique crystal grower is of essentially standard design but includes the following items to prevent contamination of the melt and modification to grow bicrystals. The seed and melt are completely surrounded by a vacuum tight chamber (McQuhae 1969), see Fig. 2.2., which consists of a six centimeter diameter transparent high purity silica tube mounted at each end with water cooled 'O' ring seals and stainless steel end plates. The furnace and thermocouple are fixed externally to prevent contamination. The rotating stainless steel beaker support and seed holder are both water cooled to limit corrosion. An umbrella is attached to the seed rod to collect any deposit that may be loosened as the rod is withdrawn during crystal growth. A high purity silica tube covers the seed rod below the umbrella to prevent any salt deposit contaminated by the stainless steel rod from falling back into the melt.

Seed withdrawal and beaker and seed rotation are mounted on ball races and driven at variable speeds

through flexiote couplings to give a vibration free growing jig. High purity silica 250 ml beakers are used to contain the melt. Silica has never been found to be dissolved in melt grown crystals and the silica removes hydroxyl ions from the melt (Wartenburg 1957, Warren 1965). Before the salt is placed in the beaker, the beaker is cleaned as outlined for glassware in section 2.2.1, then heated in air to 1000°K to remove any tenacious carbon deposit.

Before melting the salt, a vacuum of 5×10^{-5} mm of Hg is applied to the growth chamber and the temperature slowly raised to 920°K and the apparatus left under vacuum over night. The growth atmosphere of argon is then admitted up to atmospheric pressure after passing through drying columns of silica gel and anhydrous calcium sulphate: this gas is then replaced twice before the powder is melted. Single crystals 4 cms in diameter and 8 cms long are grown: these are lifted just above the melt after growth and the apparatus slowly cooled at 0.5°C per minute to minimise strains from thermal gradients.

The technique outlined by Fuschillo 1966 and McQuhae 1969 is employed to grow bicrystals with planar boundaries using two identical single crystals seeds by the Kyropoulos technique: the seed chucks, Fig. 2.3, are used to hold the seed symmetrically at the particular angle of misorientation required*. Careful alignment is necessary to eliminate twist between the seeds. Bicrystals with tilt angles from 10° to 80° are grown. A cleaved bicrystal boule is shown in Fig. 2.4: the cleavage plane is perpendicular to the boundary. The absence of discontinuities on this cleavage plane indicates there is no twist at the boundary.

*i.e. the tilt angle is the angle between the seed crystals.

2.2.3. Crystal Purity.

The most likely source of impurity in the crystal grower is from vapour collecting on the stainless steel seed holder, becoming contaminated and falling back into the melt. The stainless steel is slightly attacked, losing its polish, and analysis shows the salt is contaminated with iron. The umbrella restricts the visibility of the growing crystal. Consequently, there is a possibility of a small quantity of contaminated salt returning to the melt. Below the umbrella the stainless rod is covered with silica which is supported by stainless screws holding the seed. These screws and the recess for the seed remain exposed; these may also be sources of contamination. The analyses given in Table 2.1, if not due to experimental error, may be attributed to small contamination from either of these sources. Several authors have deduced the polyvalent cation impurity of their crystals from the "knee" temperature of the conductivity reciprocal temperature graph (e.g. Hesse 1965, Peech 1967). However, Kirk 1969 has shown that anion impurities form complexes which give an apparent lower cation impurity level. The knee temperature of the KCl of this work is $(770 \pm 10)^{\circ}\text{K}$ using the technique of Kirk 1969. This indicates a free cation impurity of (1.0 ± 0.2) molar ppm from the equation:-

where S_s is the entropy, H_s the enthalpy of Schottky pair formation and c the impurity concentration

$$c = x_o = \exp\left\{\frac{S_s}{2k} - \frac{H_s}{2kT}\right\} \quad \dots(2.1) \text{ (Lidiard 1957)}.$$

Similarly for the NaCl, the knee temperature is $(768 \pm 8)^\circ \text{K}$ corresponding to a free cation impurity concentration of (2 ± 1) molar ppm. The actual cation impurity level cannot be deduced until the anion impurity concentration has been determined unequivocally.

Any free hydroxyl ion causes optical absorbance peaks in the infra-red and ultra-violet wavelengths of KCl (Fritz et al 1963). These peaks are too small to see for KCl and NaCl with a Perkin Elmer 137 infra-red grating spectrophotometer and a Perkin Elmer 450 ultra-violet spectrophotometer, even for 3cm thick crystals. For low levels of divalent cation impurity in KCl, the hydroxyl ion concentration OH^- in molar ppm has been shown to be approximately (Butler et al 1966)

$$[\text{OH}] = 2.5 \alpha_{\text{OH}}$$

Where α_{OH} is the absorption coefficient (cm^{-1}) at the 204 μm absorption peak of KCl. Since the sensitivity of absorbance at this wavelength is better than 0.1 cm^{-1} , this indicates the hydroxyl ion content of KCl is below 1 molar ppm.

No extensive experiments relating infra-red and ultra-violet absorption peaks similar to those of Fritz et al for KCl, have been reported for NaCl. However, the similarity between NaCl and KCl crystals suggests a comparable hydroxyl ion dependance applies. If this is correct, since no OH^- peak can be detected for NaCl, this probably corresponds to a low hydroxyl ion concentration for NaCl and the precautions to eliminate these ions, as outlined in the previous section, are adequate. In addition, if any correction is necessary to the cation impurity concentration

deduced from the conductivity results then this is probably due to anion impurities other than the hydroxyl ion.

The low temperature yield stress of ionic crystals is impurity dependant. This is discussed extensively in Chapter 3. The yield of the KCl is similar to that obtained by Johnston and Nadeau 1964: they estimated the divalent cation content of their crystals at 10 ppm.

Thus, summarising, the observations suggest the crystals to be used have a cation impurity concentration in the range 2-10 molar ppm.

2.2. Specimen preparation.

Cleaving crystals is the usual manner of specimen preparation for the alkali halides. This has certain disadvantages when a large number of similar deformation specimens are required. Cleaving gives specimens each of slightly different shape, cleavage step pattern and is wasteful in the use of crystal since all specimens with chipped corners or bad cleavage steps have to be rejected. In addition, there may be an impurity gradient through the boule, due to the rejection ratio of impurities between solid and melt during crystal growth. Thus, only a limited number of consistent specimens may be obtained by cleaving the crystals. Most specimens which are produced in the following way, give identical results to cleaved samples within experimental error, but are considerably more consistent especially at larger strains, due to their uniform preparation. In addition, a large number of satisfactory test specimens can be obtained from a crystal. A Capco diamond slitting wheel with internal cutting blade rotated at high

speed is used. To minimise the damage to the crystal at the cutting surface the diamond cutting blade has a fine diamond size, the blade must be in as new condition and the lowest rate of feed of the crystal onto the blade employed. If this care is taken the dislocation damage is limited to within 100 microns of the surface see Fig. 2.5. The surface damage is removed by chemical polishing. The Capco machine incorporates an accurate screw thread to adjust the position of the boule with respect to the blade so that specimens can be cut to ± 20 microns with a series of parallel cuts each with the same spacing. From the boule, two parallel faces are cleaved one of which is attached with adhesive to the moving stage of a two axis goniometer: a further face is cleaved perpendicular to the others. This goniometer can be mounted reproducibly on the Capco and also on another jig with a similar holder to the Capco so that the goniometer can be accurately aligned with the cutting blade parallel to the required crystallographic direction. A thin slice of crystal is removed after alignment and the orientation of the surface checked using the Laue-back reflection X-ray technique. From any misalignment shown by the stereographic projection of the cut face, the goniometer is readjusted and a new cut made until the face lies along the required plane to better than one degree. The standard projections of the cut faces are shown in Fig. 2.6. After cutting the specimens are rinsed in acetone to dissolve the adhesive, then polished for two seconds in a solution of 5mls 880 ammonia diluted in 95 mls of doubly distilled water; this gives a fast polish. The specimens are then placed in a slower polish of a solution of 15 mls of the

fast polish mixed with 85 mls of ethyl alcohol. This polishing procedure removes the damaged surface layer produced by the Capco but also slightly rounds the compression faces of the specimen. The ends of the specimen are polished flat by holding the specimen in a V-groove milled on the side of a metal block and lightly lapping on a fine cloth moistened with a solution of equal quantities of the fast and slow polish.

The yield and stress strain characteristics of the crystals depend on the dislocation density. This density is rendered consistent and small by annealing the specimens at 970°K for six hours, then slow cooling at 0.5°K per minute. Sibley et al 1967 has suggested the diffusion of impurities may be important for pure crystals during annealing. This is avoided by annealing under the same conditions as used for the crystal growth. The crystals are placed inside a clean silica beaker in the sealed enclosure of the crystal growing apparatus. This is evacuated to $5 \times 10^{-5} \text{ mm Hg}$ and refilled twice to atmospheric pressure with high purity argon before the annealing begins.

Bicrystal specimens can be similarly cut with faces parallel to the grain boundary using the Capco slitting wheel. In this case particular care must be exercised when polishing the specimens since water attacks the grain boundary rapidly. Only the surfaces parallel to the boundary are polished on a fine cloth lightly moistened with the polish: no polish is allowed to wet the sides of the specimen that expose the grain boundary.

2.2.5. Geometry of $\langle 111 \rangle$ compression specimens.

The standard (111) projection Fig. 2.6 indicates that there are three $\{100\} \langle 110 \rangle$ secondary slip systems for compression in the $\langle 111 \rangle$ direction equally inclined

to the compression axis: there is no resolved shear stress for slip on the $\{110\}$ $\langle 110 \rangle$ primary slip systems.

In order to understand the dislocation etch pit rosette around an indent and the subsequent dislocation motion and the slip step orientation, the specimen faces need to be planes of low indices, and mutually perpendicular to produce rectangular compression specimens. Thus, from the standard (111) projection, Fig. 2.6, the specimen faces parallel to the compression axis are chosen as the $(10\bar{1})$ plane and the perpendicular plane, close to a $(1\bar{2}1)$ plane. The directions of intersection between the possible slip systems and the crystal faces are tabulated in Table 2.II.

2.2.6. Slip step observations.

Slip steps are observed with the interference contrast attachment on a Reichert Table model microscope. For $\langle 111 \rangle$ compression of KCl at room temperature and for strains less than 1.5% the slip steps are observed only in the $[10\bar{1}]$ direction, at right angles to the compression direction, on the $(1\bar{2}1)$ face of the specimen, see Fig. 2.7. Reference to table 2.II shows that the slip planes (101) , $(1\bar{1}1)$ and (010) intersect this face in the observed direction. However, slip on the (101) plane is parallel to the $(1\bar{2}1)$ face so this cannot produce the slip steps, and slip on the $(1\bar{1}1)$ plane would give simultaneously slip steps of similar height on the $(10\bar{1})$ faces at 55° to the $\langle 111 \rangle$ compression axis, since the possible burgers vectors for this slip $\frac{a}{2} [011]$ or $\frac{a}{2} [110]$ are inclined to all faces of the specimen. Slip steps on the $(10\bar{1})$ face cannot be seen at these strains, thus neither the $\{110\}$ $\langle 110 \rangle$ nor $\{111\}$ $\langle 110 \rangle$ slip systems are active and slip occurs only on the secondary (010) $[10\bar{1}]$ system at low strains.

Since not all the slip steps are parallel, this indicates that some cross slip of the screw dislocations is occurring; if so, this is likely to occur on the primary $\{110\}$ slip planes, since the burgers vector for screw dislocations on the primary and secondary slip planes is the same.

At higher strains, slip steps appear on four faces of the specimen; the directions of the steps are consistent with slip taking place on $\{110\}$ primary slip planes. Probably lattice rotation occurs as slip proceeds until there is sufficient resolved stress along the primary slip planes for dislocations to move on this system.

2.2.7. Dislocation Etch pit observation.

The following etching solution is used to produce dislocation etch pits of good definition for KCl with a controllable etching time of about 20 secs. The etchant is 1.75% by weight of reagent grade barium carbonate dissolved under reflux in freshly distilled proprionic acid (Cook 1961). The specimens are rinsed in petroleum ether which is evaporated in a stream of warm air. The dislocation density of the KCl specimens before deformation is $(6 \pm 3) \times 10^{+4} \text{ cm}^{-2}$.

Dislocation etch pit rosettes around an indent are illustrated in Fig. 2.829. The indent produces dislocations on all the primary slip systems. The movement of the dislocations during subsequent deformation is discussed in Chapter 3.

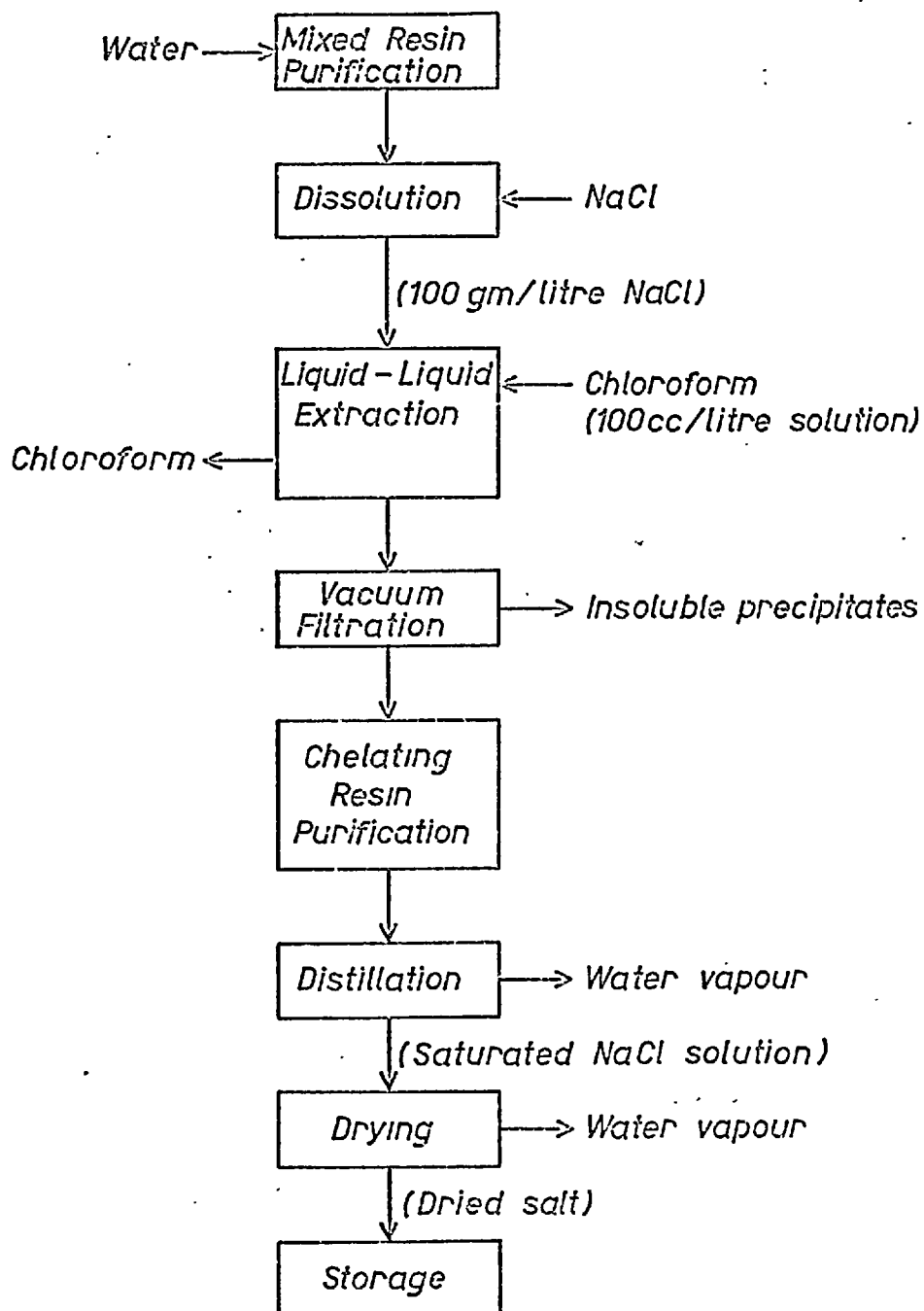


Fig.2.1 FLOW CHART FOR PURIFICATION PROCESS

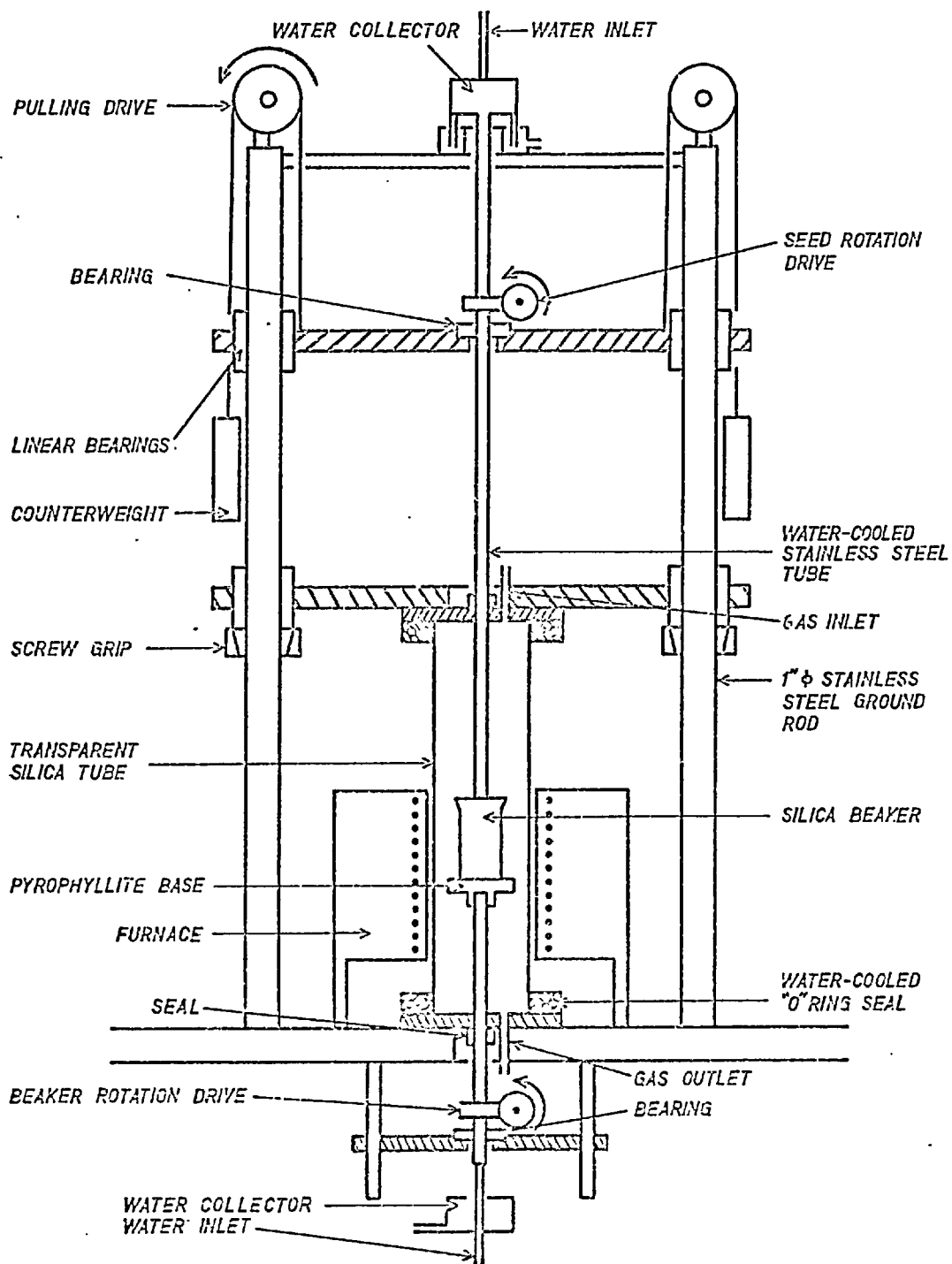


Fig. 2.2 CRYSTAL GROWING APPARATUS

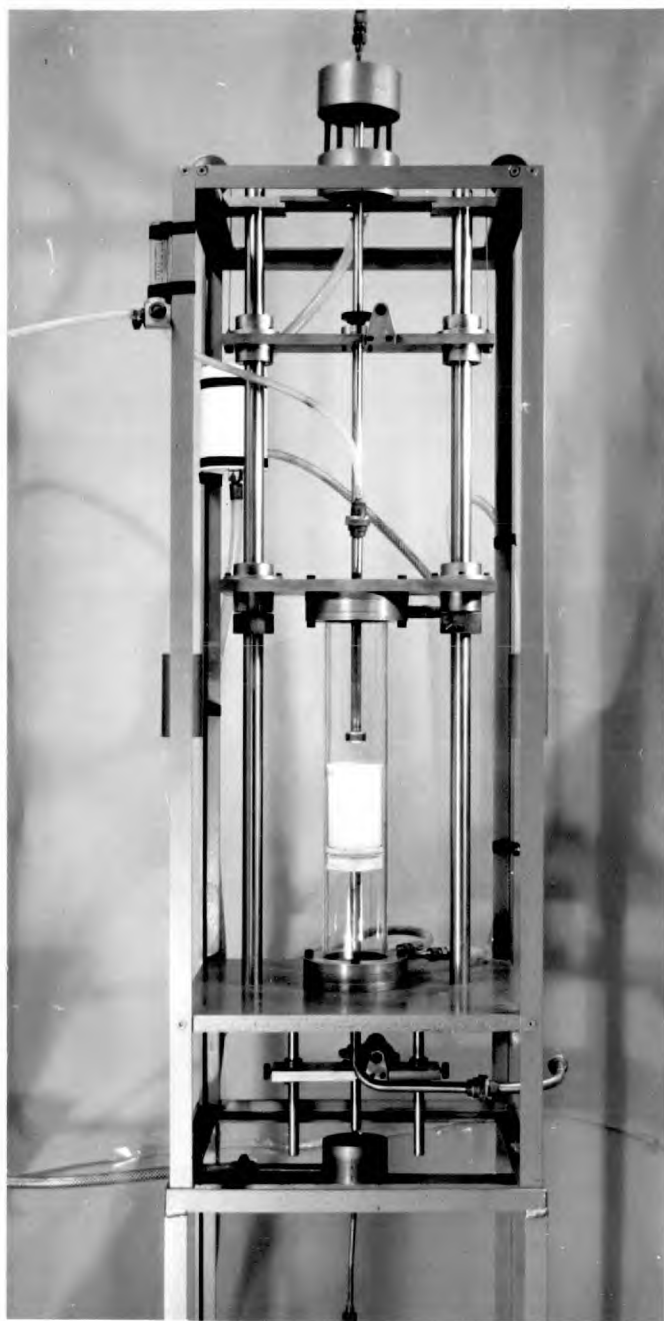


Fig. 2.2.(b) Crystal growing jig.

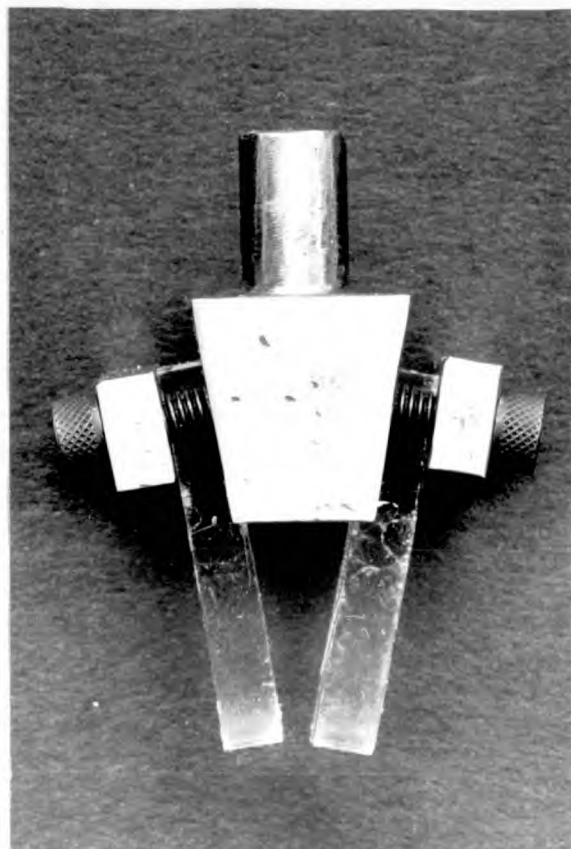


Fig. 2.3.
Bicrystal seed
chucks.



Fig. 2.4.
Cleaved bicrystal.

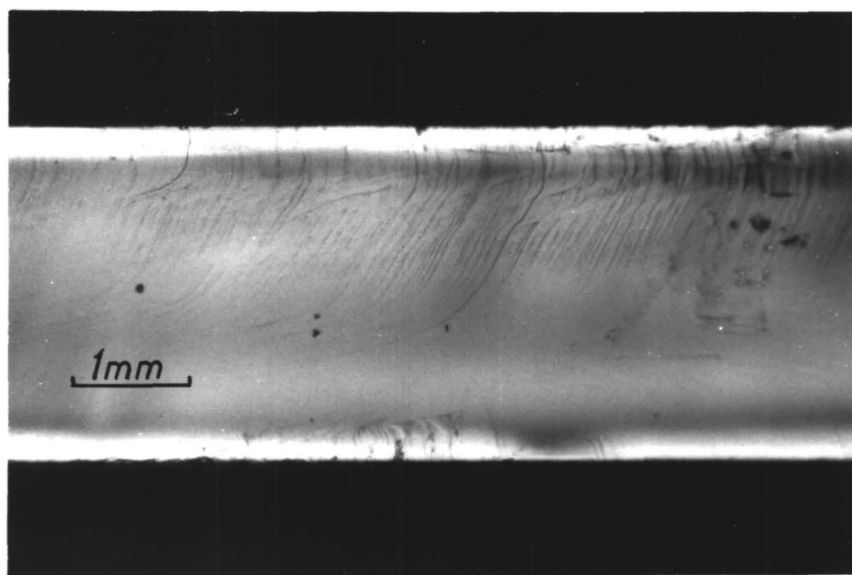


Fig. 2.5. Birefringence at the surface
after cutting.

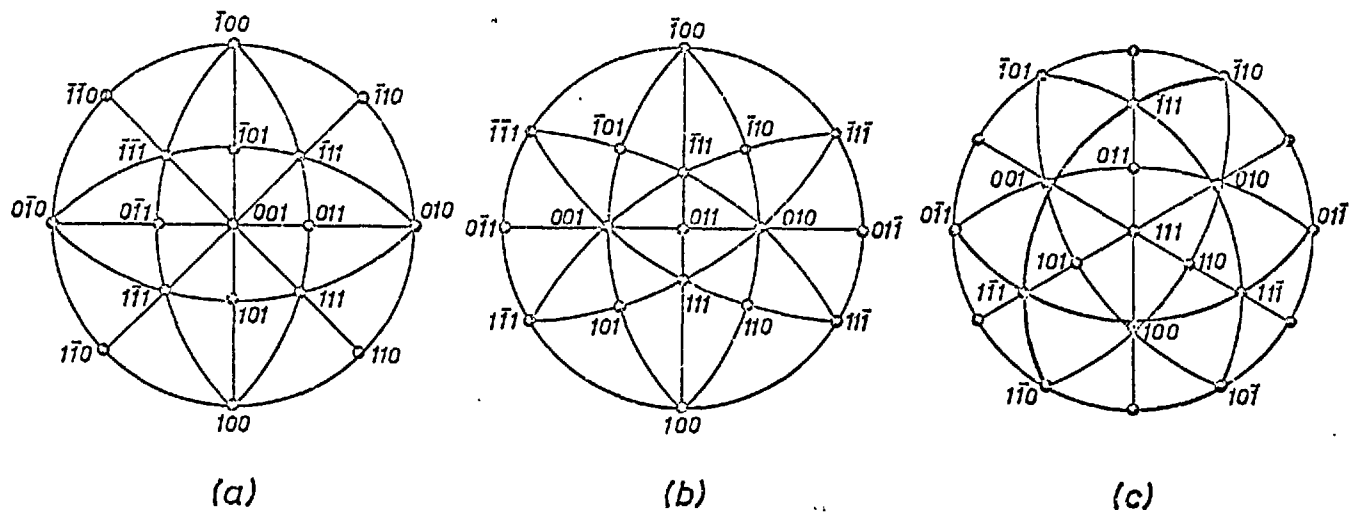


Fig. 2.6 STANDARD PROJECTIONS OF CUBIC CRYSTALS (a) on (001)
 (b) on (011)
 (c) on (111)

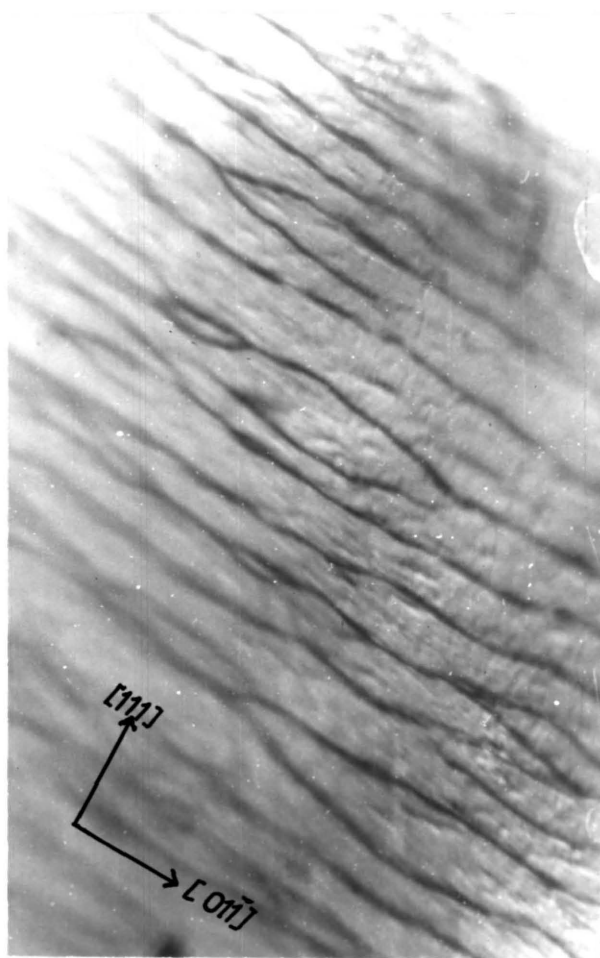


Fig. 2.7 Slip steps on $(1\bar{2}1)$
at low strain

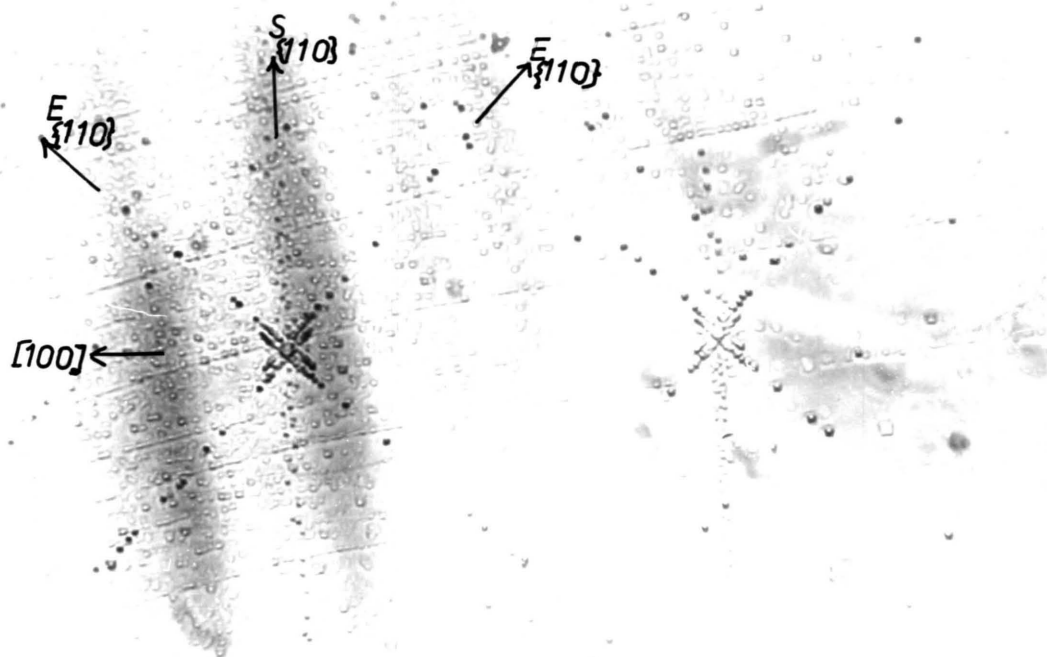


Fig. 2.8. Dislocation etch pit rosette $\{100\}$

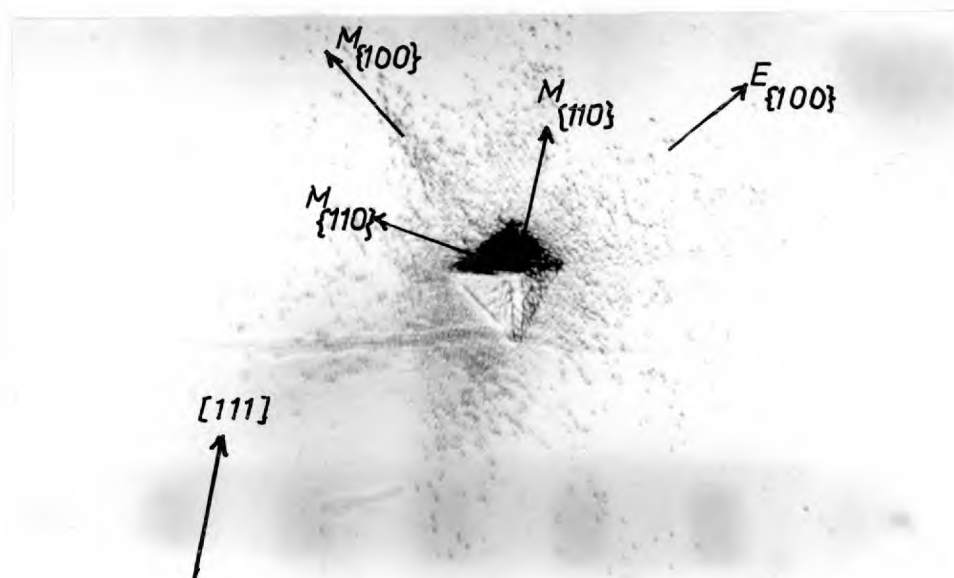


Fig. 2.9 Dislocation etch pit rosette, $\{10\bar{1}\}$

Table 2.I Analysis

	Al	Ba	Ca	Cu	Fe	Mg	Na	Ni	Pb	
KCl starting material										Emission spectroscopy.
Spec pure	<1	N.D	2	N.D	N.D	1	3	N.D	N.D.	All other cations not detected (1)
NaCl purified			N.D <5ppm			N.D <1ppm				Emission Spectroscopy (2)
KCl crystal	N.D	N.D	N.D	N.D	Trace ~1	Trace ~5 _a		N.D	N.D.	Emission Spectroscopy except: a. Atomic absorption. b. Calcrimetric. (2)
NaCl crystal		N.D			Trace ~1 _b	Trace ~5 _a	Trace ~3 _b			Emission Spectroscopy (2)

Sources:

(1) Johnson & Matthey Ltd, London.

(2) Imperial College (Analytical Services Dept.)

TABLE II
Slip Step Orientations

Slip Plane	Intersection with (121) plane			Inter-section with (101) plane	
	Crystallographic Direction	Inclination to $\langle 111 \rangle$ direction.		Crystallographic Direction	Inclination to $\langle 111 \rangle$ direction.
(100)	012	39°		010	55°
(001)	210	39°		010	55°
(010)	101	90°		101	35° (3)
(110)	111	0°		111	0°
(101)	111	0°		-(1)	-(1)
(011)	111	0°		111	0°
(101)	101	90° (2)		010	55°
(110)	111	58°		111	71°
(011)	311	58°		111	71°
(111)	123	22°		101	35°
(111)	321	22°		101	35°
(111)	101	90°		112	19°

1) Slip plane parallel to (101)

2) Slip direction parallel to (121)

3) Slip direction parallel to (101)

CHAPTER 3 Dislocation Motion

3.1. Dislocation Dynamics.

3.1.1. General.

The plastic deformation of ionic crystals is still far from being fully understood. The techniques of strain rate cycling have been successfully used to investigate the deformation of metals over a wide range of temperatures and impurities: no such extensive study has been made for NaCl and KCl single crystals. This technique is particularly useful for probing thermally activated dislocation obstacle interactions. Since the yield stress of both metals and ionic crystals exhibit a large temperature dependance at low temperatures, this strain rate cycling method seems applicable. Those papers that have appeared report only strain rate cycling for primary slip of NaCl and KCl crystals near room temperature between 250 and 300°K, a region where the yield stress of pure crystals is temperature independant: these will be considered in section 3.1.3. The aim of this chapter is to apply these methods to the deformation of single crystal KCl for both the primary and secondary slip systems over as wide temperature range as possible to understand further the thermal activation of dislocation interactions. The applicability of these methods is investigated in detail.

In high purity single crystals the movement of dislocations and hence the relationship between applied stress and strain, is controlled by the relative magnitudes of the resistance of the lattice to a dislocation moving through it and the interaction

between this dislocation with either intrinsic obstacles or dislocation debris caused by those dislocations that have previously moved.

The techniques for experimentally determining these interactions and relating their contribution to work hardening have been recently developed and reviewed. Evans and Rawlings 1969 give a general derivation of the dislocation dynamic theory and Evans 1969 consider the application of this theory to ceramic materials. In these papers concern is given to the extent of the validity of the theory to the experimentally derived parameters from strain rate and temperature cycling tests. The conclusion is reached that considerable care must be exercised in the use of these theoretical equations since even at ordinary temperatures their boundary conditions are not necessarily satisfied.

Since deformation on both the primary and secondary slip systems will be investigated in this chapter, a brief general survey of the theory of thermally activated dislocation motion is necessary, sufficient only to state the limitations of the equations: a more complete derivation can be obtained from the reviews mentioned above. This survey is followed by a review of the previous strain rate cycling data obtained for NaCl & KCl crystals.

3.1.2. Dislocation Dynamics.

(a) Dislocation Velocity.

Certain forces on the moving dislocation limit its terminal velocity along the slip plane. Such obstacles may be separated into two types: those which exert a long range force on the dislocation and those whose force acts over a much shorter distance. Fig. 3.1 shows a schematical variation of the

force on a dislocation from both obstacle types as the dislocation moves through the lattice.

Thermal fluctuations may assist or be completely responsible for the dislocation passing only those obstacles with short range forces, since the fluctuations would be sufficiently coherent over small interaction distances. This type of obstacle is referred to as a 'thermal obstacle' and the part of the applied stress necessary to overcome this type of obstacle **and** not already provided by the thermal fluctuations is called the "thermal" or "effective" stress τ^* (see Fig. 3.2). As the temperature is increased the thermal contribution becomes larger, hence τ^* will be temperature dependant, decreasing as temperature increases for a particular obstacle.

Long range forces between dislocation and obstacles are also overcome by another part τ_μ of the applied shear stress τ . Thus, the applied shear stress necessary to move a dislocation must be the sum of the forces required to move the dislocation past thermal and athermal obstacles. i.e. . . .

$$\tau = \tau^* + \tau_\mu \quad (3.1)$$

It is important to note that all the theory assumes that only one type of thermal obstacle contributes to τ^* and if more than one slip system is operating then these must be equally inclined to the compression axis so that the stress on each system is identical. (See section (C) for Arrhenius rate equation for dislocation velocity).

A valid theory of thermally activated dislocation motion using parameters concerned with macroscopic properties must yield the same results as measurements from the observations of individual dislocations. Etch

pit techniques can be used to see individual dislocations. By applying a known stress for a given time the distances moved by the dislocation can be determined and hence their velocity as a function of the applied stress can be found.

The empirical relationship that has been found by this method for normal flow stresses during stress strain tests is given by Gutmanas 1963, Evans 1970.

$$V = \left(\frac{\tau}{\tau_0} \right)^{m_1} \quad (3.2)$$

where V = dislocation velocity

τ = applied stress

m_1, τ_0 = constants at a particular temperature

Experimentally, this equation does not apply at very high or low velocities, Gutmanas 1963.

If there are no athermal obstacles present at zero strain i.e. $\gamma_0 = 0$ then $m_1^* = \frac{d \log V}{d \log \tau}$ (3.3)

where m_1^* is the value of m_1 at zero . . . (Different subscripts will be used to distinguish values of m^* determined by different experimental techniques).

The velocities are different for edge and screw components. The slowest component at a particular stress must be found from these etch pit studies, since it will be to this component of the dislocation, interacting with its most effective obstacle, that limits the dislocation velocity, and this requires the highest stress to move a dislocation loop at a particular speed.

By equation 3.3, plotting log dislocation velocity versus log stress, gives m_1^* from the gradient.

For a constant strain rate test, the strain

$$\text{rate } \dot{\epsilon} = NbV \quad (3.4)$$

Where N = mobile dislocation density

b = burgers vector of the dislocation

ϵ = strain.

Combining equation (3.4) and (3.2) gives

$$m_2 = \frac{d \log \dot{\epsilon}}{d \log \tau} + \frac{d \log N}{d \log \tau} \quad (3.5)$$

If N is stress independent

$$\frac{d \log N}{d \log \tau} = 0 \quad (3.5a)$$

$$\text{then } m_2 = \frac{d \log \dot{\epsilon}}{d \log \tau} \quad (3.6)$$

Thus values of m_2 can be obtained by change of strain rate tests as a function of strain: these can be extrapolated to zero strain to give m_2^* . If this value of m_2^* agrees with m_1^* obtained from the etch pit studies then the mobile dislocation density does not appreciably vary with stress during a change of strain rate at this temperature, and equation (3.5) is a valid approximation. This comparison should be made to check that the strain rate cycling tests are made at constant structure.

Equation (3.6) can be rewritten:

$$m_2^* \frac{\Delta \tau}{\Delta \ln \dot{\epsilon}} = \tau^* + \frac{\Delta \tau}{2} \quad (3.7)$$

assuming the stress increment during strain rate cycling can satisfy: $\Delta \tau \ll \tau^*$ (3.7a)

If a series of tests are made to give the $\Delta \tau$ values for a range of strain rate increments then a graph of $\frac{\Delta \tau}{\Delta \ln \dot{\epsilon}}$ vs $\frac{\Delta \tau}{2}$ for a set of $\Delta \tau$ values at a particular strain gives m_2^* from the gradient at each strain and τ^* is the intercept on the $\frac{\Delta \tau}{2}$ axis.

(b) Thermal and athermal stress components.

If yield stresses are plotted against temperature, at high temperatures there is usually only small temperature dependence controlled by athermal obstacles. At lower temperatures the temperature variation of the yield stress is much greater (See Fig. 3.3) due to contributions from both thermal and athermal mechanisms. An approximate value of the thermal stress may be obtained by subtraction of the extrapolation of the athermal high temperature yield from the yield at lower temperatures. This method will be strictly valid only if the structure at yield is the same at all temperatures. This is unlikely to be completely satisfied since dislocation motion occurs on a limited scale before yield.

At finite strains the most general equation for determining τ^* from change of strain rate tests is derived from equation (3.8)

$$\tau^* = \frac{\Delta\tau}{(\dot{\epsilon}/\dot{\epsilon}_0)^{m-1}}$$

Thus the conditions applicable to equation (3.8)

must also apply for this equation to be valid i.e. conditions (3.3) (3.3a) (3.5a) and (3.7a) must be satisfied: if they are, then this τ^* value should agree with the value obtained from the graphs of $\frac{\Delta\tau}{\Delta \ln \dot{\epsilon}}$ against $\frac{\Delta\tau}{2}$ using equation (3.7).

If the thermal stress increases with strain, this indicates new thermal obstacles are being created whose production probably depends on the increasing dislocation and debris density.

(C) Activation Volume.

The activation volume V^* is defined such that the work done by the thermal stress during activation of an obstacle is $V^* \tau^*$. When a linear segment, length l (approximately the obstacle interaction distance)

of a dislocation of burgers vector b is thermally activated a distance ΔR reversibly & isothermally past the obstacle

$$V^* = l \cdot b \cdot \Delta R \quad (3.10)$$

(This is not identical to the thermodynamic activation volume. The factors l , b & ΔR are not mutually perpendicular nor are they independent of τ^* for a particular obstacle type).

An Arrhenius rate equation may be expected to apply to the thermal activation of dislocation motion giving dislocation velocity as

$$V = \lambda \nu_0 \exp \left(\frac{-\Delta G + V^* \tau^*}{KT} \right)$$

where λ is the distance moved after a successful activation of the dislocation and ν_0 the dislocation and lattice frequency; ΔG is the Gibbs free energy of the obstacle: V^* can be determined from strain rate cycling tests using:

$$V^* = KT \frac{(\Delta \ln \dot{\epsilon})}{(\Delta \ln \tau)} \quad (3.11)$$

provided equations (3.3a) (3.5a) (3.7a) are satisfied. The variation of l , b and ΔR with τ^* has not been rigorously treated theoretically. For random fixed point obstacles it has been suggested the stress dependence of l & ΔR will cancel out at stress below one tenth of $(\tau^*)_{00K}$, Evans and Rawlings 1969.

Direct correlation of V^* from etch pit velocities may be obtained from

$$V^* = \frac{KT}{\left(\frac{d \ln \left(\frac{V}{\Delta R} \right)}{d \tau} \right)_T} \quad (3.12)$$

Evans has suggested that the $\Delta R \nu_0$ is approximately stress independent.

(d) Activation enthalpy.

If the total activation enthalpy of a particular thermal obstacle

can be calculated, this can be compared with the theoretical values. This enthalpy should be constant over the range for which this type of obstacle limits dislocation motion and should change in value if the predominant obstacle changes.

The total enthalpy of the obstacle, ΔH_0 , is equal to the activation enthalpy ΔH at zero effective stress $\tau^* = 0$.

Experimentally, $\tau^* > 0$ so values of ΔH are calculated and a suitable factor added to determine ΔH_0 for each test.

$$\Delta H = KT^2 \left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \tau} \right)_T \left(\frac{\Delta \tau}{\Delta T} \right)_\dot{\epsilon} \quad (3.13)$$

These factors will be considered separately:

$\left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \tau} \right)_T$ can be derived from the strain rate

cycling tests and the conditions (3.3a) (3.5a) and (3.7a) must be applicable.

$\left(\frac{\Delta \tau}{\Delta T} \right)_\dot{\epsilon}$ requires temperature cycling tests

to be performed at a particular strain and strain rate. There must be no change of the dislocation structure during the temperature increment i.e. $\Delta \tau_a = 0$. Thus values of $\left(\frac{\Delta \tau}{\Delta T} \right)_\dot{\epsilon}$ from the yield stress temperature plot do not necessarily satisfy this condition since the quantity of dislocation motion that occurs before yield changes with temperature.

To obtain the total activation energy ΔH_0 of the obstacle a correction must be applied to ΔH to account for the energy supplied by the thermal stress.

$\Delta H_0 \approx \Delta H + \int_0^{\tau^*} V^* d\tau^*$ This is valid if the entropy term $T(\Delta S_0 - \Delta S)$ is small in comparison to ΔH_0 where ΔS_0 is the entropy at $\tau^* = 0$ and $\Delta S = \beta(\Delta H + V^* \tau^*)$.

where $\beta = -\frac{1}{\mu_0} \frac{d\mu}{dT}$, μ = shear modulus.

The integration can be obtained numerically from a $V^* - \tau^*$ graph.

3.1.3. The strain rate sensitivity of flow stress.

In chapter 2 we have considered the general deformation features of NaCl and KCl and have shown the great similarity between them. This section reviews the deformation literature with particular reference to the strain rate sensitivity and its relation to the theory developed in the previous section.

Until the very recent work of Evans and Pratt 1970 no comparison had been made for KCl and NaCl between m^* values obtained from macroscopic strain rate cycling tests and microscopically from individual dislocation etch pits. Even in this work experiments were made only at one temperature and the NaCl crystals probably contained an impurity level which was higher than other comparable work. Thus this immediately asserts the need of experimental data on purer crystals over a wide temperature range.

The variation of yield stress with temperature indicates (from section 3.1.2(c)) that a thermal mechanism controls deformation at low temperature and is impurity sensitive in KCl and NaCl. Yield is temperature sensitive below 250°K for material of 10 ppm divalent cation impurity and to higher temperatures at greater impurity concentrations, Johnston 1964. The yield stress is not temperature dependant to a large extent above 250°K for purer crystals suggesting yield is controlled by athermal obstacles at high temperatures.

However, Schmitten and Haasen 1961 suggested there is only a small thermal activation of the dislocation motion of NaCl at room temperature from the small changes of flow stress during a change of strain rate test. They reported n values of 10 grm/mm^2 for $\dot{\epsilon}_2/\dot{\epsilon}_1 = 10$ and the C.R.S.S. of their NaCl at room temperature was 41 grm/mm^2 .

Johnston & Nadeau 1964 reported m^* values from strain rate cycling tests at room temperature for NaCl and KCl.

NaCl pure $m^* = 30$ to 40

NaCl impure $m^* = 30$ to 200

KCl pure $m^* = 45$ to 60

Their CRSS and n values are similar to those obtained by Schmitten & Haasen: their total multivalent cation impurity level was calculated at 10 ppm.

Kornik et al 1967 concluded from observations of the rapid fluctuations of flow stress with time that dislocation multiplication was greater for KCl than NaCl at room temperature. On the same crystals they could not detect any stress changes for strain rate cycling of KCl. This was because either dislocation multiplication was occurring, hence equation (3-3a) was not satisfied, or the strain rate increments were too small to give a measurable stress change. The conflicting results between Kornik and Johnston may be the result of different impurity content. Kornik estimates that for their crystal the Mg content, for instance, could be as high as 30 ppm: their room temperature yield stress was also much higher, 100 grm/mm^2 which could also have been the result of this impurity level.

The hydrostatic pressure around deformation specimens was cycled in the experiments of Davis & Gordon 1968,

and the stress changes that resulted were recorded.

Their conclusions assumed that the dislocation density within the crystal did not alter when the stress increased during the pressure cycle i.e. equation (3.5a) is a valid assumption at room temperature. A comparison between m^* values from strain rate cycling and dislocation etch pit experiments would determine the validity of this assumption. Davidge 1966 has reported the small strain rate sensitivity of NaCl at room temperature was constant for all strains and suggested the thermal stress remained constant, thus all work hardening was athermal.

Evans and Pratt 1970 at 244°K have found reasonable agreement between the value of m^* from etch pit velocity observations of NaCl ($m_1^* = 15 \pm 3$) and the values from strain rate cycling tests (from the extrapolation of m_2 values to zero strain $m_2^* = 16 \pm 2$ for a range of strain rate increments and from a graph of $\frac{\Delta\tau}{2}$ against $\frac{\Delta\tau}{\Delta \ln \dot{\epsilon}} = 13 \pm 2$ for all strains. They concluded their results were consistent with the theory of a single thermal obstacle giving a point defect interaction of total enthalpy of 0.5eV probably caused by impurities. The thermal stress was found constant for all strains so the work hardening in Stages I & II had to be completely due to the development of athermal obstacles during deformation. However 244°K was within the athermal region of the CRSS - temperature graph of Johnston and Nadeau 1964 for crystals of 10 ppm impurity. Thus, either yield within the high temperature region is still thermally activated or the crystals used by Evans and Pratt contained a greater impurity than those of

Johnson & Nadeau, sufficient to raise the extent of the athermal region above 244°K .

Gutmanas, Nadgornyi and Stepanov 1963 have made a study of the dislocation velocity - stress relationship from the etch pit motion around rosettes for a complete range of velocity and for pure and doped NaCl. For normal flow stress m^* increased from 8 for purity estimated qualitatively at 10 ppm Ca to $m^* = 17$ for impurity of about 100 ppm Ca^{++} . Screw dislocations moved slower than edge so would be the limiting component.

The onset of macroscopic slip for the pure crystals occurred at 110 gm/mm^2 , a much higher stress than for the crystals of Johnston & Nadeau with the same estimated impurity level.

For NaCl Hesse 1965 and others have shown that the stress may be directly proportional to the square root of the dislocation density observed as etch pits. Thus, they have shown that the stress in Stage I of the room temperature stress strain curve may be predominantly athermal. Matucha 1969 using electron microscope replicas to count the closely spaced etch pits has observed that stage II is also caused predominantly by athermal obstacles. Hesse's results indicate that for two constant strain rate tests at different strain rates and for strains having the same dislocation density (and, hence, same athermal stress) the flow stress difference should reflect the strain rate dependence of the thermal stress. They show that γ^* is small but increases with dislocation density, i.e. with strain, consistent with being caused by forest dislocations, jogs or debris. The purity of these crystals was estimated at 2 ppm from conductivity tests. (This value may be too low if any anion impurities are present, see Chapter 2).

Thus it may be concluded that for the primary slip system there is need for experiments to compare the strain rate cycling data with etch pits studies over a wide temperature range to include thermal and athermal regions of the yield stress temperature graph for high purity crystals.

No strain rate cycling tests have been made for the secondary slip system.

The possibility of a Peierls mechanism controlling edge dislocation motion has been considered in section 1.2.2(b). If this dislocation interaction operates, then the motion will be thermally activated and it will be strain rate sensitive. The experimental results can be compared to the theoretical parameters, reviewed by Dorn and Rajnak 1967 for this type of dislocation obstacle, to deduce whether a Peierls mechanism is operating.

3.2. Experimental

3.2.1. Testing Techniques.

The preparation, orientation, polishing and etching of specimens has been explained in Chapter 2.

Compression is effected in Instron testing machines with compression jigs of the type described at length by Pascoe 1967. They consist of two interpenetrating frames moving relative to one another on adjustable ball races to keep the compression faces parallel. See Fig. 3.4.

Two methods are used to deform at low temperatures. A dewar was constructed Fig. 3.6 & 3.7 which consists of a deformation jig enclosed in a container than can be evacuated or filled with dry nitrogen. The deformation jig inside is held at a constant temperature by a reservoir containing the coolant (or hot oil) isolated from the outer casing.

The specimen can be viewed through glass windows mounted on 'O' ring seals in the side of the finger which is constructed to fit the specimen compartment of a Perkin Elmer 450 Spectrophotometer (see Chapter 4). To prevent thermal shock of the specimen when cooling to liquid nitrogen temperature it is essential to initially partly cool the jig. A much simpler method is to cover the room temperature Instron jig with a polythene bag and seal the top with an elastic band. The jig can be lowered slowly into a vacuum flask containing the coolant. The bag prevents any surface contamination of the specimen by the coolant and allows the specimen and jig to cool slowly as the trapped air acts as an insulator. Temperature cycling tests require the load on the specimen to be removed and the reservoirs of coolant exchanged. The new temperature is reached when the specimen ceases altering its dimensions. This can be monitored from the stress on the Instron Chart, when the small load applied to the specimen no longer changes. The Instron gives a constant strain rate to the specimen from about $1 \times 10^{-5} \text{ sec}^{-1}$ upwards, automatically recording load and time. Changes of strain rate up to 1000 fold increase or decrease can be effected instantaneously on this machine. The chart speed is simultaneously increased in the same ratio as the strain rate so that the time axis of the chart is linear deformation even during strain rate cycling.

To improve the consistency of stress strain results three conditions have to be satisfied for a result to be valid. The elastic part of the stress strain curve must have a linear elastic region and the total plastic strain determined from the Instron

chart must agree within 0.2% strain with the difference of crystal lengths measured with a travelling microscope. During deformation the crystal may be observed with an optical microscope between crossed polaroids.

The birefringence of the slip bands must be uniform along the compression axis: specimens with slip on oblique system at opposite ends of the crystal give large dislocation boundaries at the centre of the crystal and anomalous stress strain curves.

A program is used for an IBM 7090 computer to calculate the activation parameters from the experimental results.

Direct dislocation velocity measurements can be made using an etch pit technique similar to that described by Gutmanas 1963. This requires the introduction of fresh dislocations on to the crystal surface and the distance moved by these, observed by etching, can be measured when a given stress is applied for a known time. The method used differs from that used by Gutmanas in one important respect, since the etching of an indent before compression pins the dislocations. Gutmanas used steel or glass to indent the crystal: this was not reproducible and the size of the indent needed to be known by etching before each compression: this etching may pin the dislocations. Indenting with the diamond microhardness tester on a Reichert table model microscope gives a completely reproducible indent and dislocation rosette etch pit pattern may be obtained. The length of the arms of the indent rosette are measured after etching for a trial test, then similar indents are made in crystals just prior to deformation thus avoiding possible dislocation pinning. Dislocations should move at least 200 microns away from the indent when the stress is applied so that the effects of stress concentrations around the indent may be lessened. Any rounding

of the specimen ends or the specimen defects may give rise to stress concentrations: these give a very large scatter to results using compression specimens. Four point bending gives a uniform surface tensile force between the inner knife edges where the stress is given by

$$= \frac{3WS}{bh^2}$$

W = applied load

S = spacing between lines
and out knife edges.

b = specimen breadth

h = specimen thickness

The jig was machined from pyrophyllite with sapphire rollers see Fig. 3.5.

3.2.2. Deformation on the Primary Slip Systems of KCl.

Specimens are prepared for compression in the $\langle 100 \rangle$ direction by the methods described in Chapter 2.

Resolved stresses for this deformation direction refer to the $\{110\}\langle 110 \rangle$ systems.

(a) Constant Strain rate tests.

(i) Effect of environment

Evans 1970 has reported latent hardening tests at liquid nitrogen temperature made by the technique of surrounding the specimen with a polythene bag as outlined in the previous section. Doubt exists whether atmospheric moisture has any effect on the stress strain curve by condensing on the surface of the specimen. Experiments in the dewar in an atmosphere of dry nitrogen do not give consistently different results from the simpler technique. This may be because any moisture condensing during cooling does so on the coldest surface: this will be the polythene and not the specimen. Any other surface contamination of the specimen must be present in both cases due to crystal

preparation in the air. Thus the simpler technique may be used. Lubricants of oil and vacuum grease were applied to the rams to prevent friction stresses between specimen and ram: this made no difference to the deformation.

(ii) Effect of specimen dimensions.

The stress - strain curve for deformation depends on the shape of the test specimens. The correct size specimen must be determined and the results of size dependance will be used in Chapter 4 to show how the enhancement of F centre colouration depends on specimen dimensions. This dependance is shown typically at 20°C in Fig. 3.8 for crystals of the same cross-section but different heights. (Similar graphs from Alden 1964 are included for comparison). Yield stress is constant but the rates of work hardening decrease and length of Stage I increases as the ratio of height, h , to the diagonal, d , of the cross section increases. Etch pits and birefringence of slip planes show this may be associated with the stress concentrations from end effects between the crystal and the jig. Dislocation motion is uniform in the centre of the specimen but is greater at the ends: this may cause greater debris production and a larger rate of work hardening in these regions (see section 3.2.2. (d)). These end effects may be reduced by having longer specimens: however, if the specimen is too long $\frac{h}{d} > 4$ or has one dimension of the cross section much less than the other, plastic buckling of the specimen occurs giving rise to unknown stress concentrations and an anomalously low rate of work hardening and long Stage I. If $\frac{h}{d}$ is much less than 2 deformation takes place by block slip and the stress strain curve has more than three regions of work hardening as dislocation

boundaries develop. Evans and Pratt 1970 have shown that $\frac{h}{d} = 3$ satisfies the above criteria for NaCl and gives similar results to tensile tests where no end effects are present. Within these limits the stress strain curve and strain rate sensitivity do not depend on the cross sectional dimensions. Hesse 1965 and Matucha 1969 use similar values of $\frac{h}{d}$ and should be quantitatively similar: Gutmanas 1963 $\frac{h}{d} = 4.2$

Similarly the deformation specimens to be used for irradiation should also conform to these dimensions for the structure to be quantitatively interpreted from stress strain curves. Past work e.g. Chang 1965 measuring the influence of deformation upon F centre colouration has used thin specimens, one dimension of the cross section much less than the other; consequently, they must have deformed by plastic buckling with a long Stage I. But absorption measurements at high F centre densities require a thin specimen.

Thus specimen dimensions must have $\frac{h}{d} = 3$ and have one dimension as thin as possible without plastic buckling occurring: test specimens 12.5 x 3.5 x 2.5 mm satisfy these criteria and are used for subsequent tests.

(iii) Variation of the stress strain curve with temperature.

Fig. 3.9 demonstrates the variation of the stress strain curve with temperature. Above 100°C there is a single stage of work hardening: the gradient of this initial stage decreases at lower temperature and a Stage II of higher rate appears followed by a Stage III of lower work hardening rate. The rate of Stage I slowly increases as temperature decreases until at about 120°K fracture occurs within this stage.

This behaviour is similar to that reported for NaCl, Evans 1969^{3.1}
Subsequent tests will investigate the thermal and
athermal components of these stresses.

The insert in the last figure 3.9 shows the methods
for determining the yield stress, 0.2% proof stress and
critical resolved flow stress from the Instron charts.
These values are plotted in Fig. 3.10 as a function of
temperature for two different strain rates. (These are
compared to the CRSS experimental points of Johnston and
Nadeau 1964 which are similar and may be associated with
a comparable crystal purity). Yield stresses are least
consistent. The curves have two temperature regions
of the type indicated in section 3.1.2. The high
temperature region above about 150°K decreases slowly
with temperature and, thus, might be associated with
an athermal dislocation interaction. Below this
temperature yield is much more temperature sensitive
and may be attributed to a thermal dislocation obstacle.
Change of strain rate tests should confirm this change
of obstacle type. The yield stress temperature graph
for the test at higher strain rate shows, in the low
temperature region, the strain rate dependence is
considerably greater than that at higher temperatures the
latter $\Delta\tau$ are nearly of the same order of magnitude
as the experimental error of the observation but in
each case are positive (see Fig. 3.1.8)

(b) Determination of m^*

(i) m^* from Etch Pit Studies.

Values of m^* can be obtained directly by etch pit
studies from the variation with applied stress of the
edge and screw velocities around an indent. A typical
indent rosette after deformation is illustrated in
Fig. 2.8. and the interpretation discussed in Chapter 1.
This method is found to give consistent results for

KCl between 190 & 325°K. At higher temperatures the dislocations around the indent become pinned in the short period of time after indentation and before deformation; at lower temperatures the scatter and error of the calculated velocities renders this technique useless. The consistency of the measured velocity at a particular stress needs to be ascertained. This can be confirmed by deforming specimens at the same load for different periods of time and measuring the dislocation movement in each case: these give the same velocities except at low stresses and short times when the dislocations remain in closer proximity to the indent (see Section 3.2.1). Such a check is not possible at the larger velocities since the maximum time is limited by the dislocations nearing the specimen edge and the shortest time by the speed at which the Instron can load and unload the specimen. However, these higher velocities still follow the same velocity-stress dependence.

The graphs of dislocation velocity versus applied stress for 295°K and 196°K are shown on log scales in Fig. 3.11 & 3.12 for both edge and screw dislocations. Each graph point and its standard deviation is derived from the arms of three indents in a particular specimen used in four point bending. The outermost dislocations in each arm are used to calculate the velocity. A few dislocation arms move much less than the mean: any dislocation velocity that lays outside two standard deviations from the mean is omitted from the set. The method of least squares is used to draw the best straight line through the graph points (and to determine the standard error of the gradient) which is the value of m * (Topping 1961). The graphs show that the edge dislocations move faster than the screw dislocations at all the stresses, so any

dislocation - obstacle interactions considered in later⁹⁶ sections for the rate controlling mechanism will apply to the screw dislocation. Both edge and screw dislocation satisfy an empirical equation of the type

$$V = \left(\frac{\tau}{\tau_0} \right)^{m_1^*}$$

From graph 3.11 & 3.12: screw | edge
 at 295°K, $m_1^* = 14.3 \pm 2.1$ | 12.9 ± 3.2
 at 196°K, $m_1^* = 18.2 \pm 2.9$ | 16.7 ± 3.5

If no dislocation density change occurs during strain rate cycling then these m_1^* values should agree with those from strain rate cycling tests,

(ii) m^* from strain rate cycling tests.

The load extension graph for a typical strain rate cycling test is given in Fig. 3.13. The period of strain at the higher strain rate is kept to a minimum to reduce the effects of the higher strain rate structure, if any, on the lower strain rate test. There is good agreement between the values for strain rate increase and decrease provided the overshoot on decreasing the strain rate is omitted (see Fig. 3.13). This overshoot may be due to increased density of mobile dislocations that result from deforming for the small but finite time at the higher strain rate. Thus for the short period of time after the strain rate cycling at the lower rate, there is an excess of dislocations and the strain can be accommodated by the dislocations moving at a slower velocity, which requires a lower stress. The excess dislocations are then rapidly pinned. The overshoot lasts too long to be due to poor pen response.

The values of m_2 are determined using equation (3.6) for different strains, strain rate increments and base

strain rates at each temperature. These are plotted in Fig. 3.14 for three temperatures 77, 196, 295°K. These tests have been undertaken between 400 and 900°K using a radiation furnace with alumina rams: a small strain rate sensitivity is observed over the whole temperature range (no flow stress drops on strain rate increase were observed like those seen in MgO at high temperatures, Moon and Pratt 1969).

The graphs given in Fig. 3.14 show the m_2 values increase with strain at a particular strain rate, but at each strain m_2 decreases as the strain rate increment increases. These m_2 curves extrapolate to approximately the same value m_2^* at zero strain at a particular temperature. These values are considerably greater than the corresponding m_1^* values found using etch pits.

Both the etch pit velocity-stress graph and extrapolation of m_2 values to zero strain provide m^* values only for small strains. The alternative method using strain rate cycling data in equation (3.7) calculates m_3^* at finite strains. The graphs of $\frac{\Delta\tau}{2}$ against $\frac{\Delta\tau}{\Delta \ln \dot{\epsilon}}$ are plotted in Fig. 3.15 for each

temperature. Since $\frac{\Delta\tau}{\Delta \ln \dot{\epsilon}}$ is found to be independent of strain, m^* is independent of strain. At the low temperature the experimental points give reasonable straight lines whose gradients give values of m_3^* which agree closely with m_2^* : at higher temperatures the points lie on a slight curve, straight lines drawn through these points give m_3^* values less than m_1^* and m_2^* .

The variation of m_1^* , m_2^* and m_3^* with temperature is shown in Fig. 3.16. The significance

of these values will be discussed when the variation of the other thermal activation parameters has been derived.

(c) Thermally Activated Dislocation Motion

(i) Stress Changes during Strain Rate Cycling Tests

The stress changes $\Delta\tau$ for each strain rate increment are independent of strain at each temperature, Fig. 3.17, thus indicating that no new thermal obstacles are produced during deformation. If thermal obstacles cause this strain rate sensitivity then they must have existed at yield. The variation of $\Delta\tau$ with temperature for a particular strain rate increment is shown in Fig. 3.18. Above 240°K, $\Delta\tau$ has low values and is approximately constant with temperature: below this temperature increases rapidly as temperature decreases. This temperature when $\Delta\tau$ increases is similar to the region where the yield stress increases rapidly as temperature decreases. Plotted for comparison in Fig. 3.18 are the difference of flow stress between the two constant strain rate tests at different strain rates. The strain rates are the same as those of the strain rate cycling tests. Approximate agreement is obtained but the errors for the flow stress measurements are considerably larger.

(ii) Thermal Stress

From the previous section, $\Delta\tau$ is constant with strain so there is no measurable increase of thermal stress with strain at any temperature. Thus all work hardening must be predominantly athermal. The methods for determining the magnitude of the thermal stress have been outlined in section 3.1.2 and each is given in Fig. 3.19 as a function of temperature. The thermal stresses derived from equations (3.7) and

(3.8) both assume that the athermal stress is zero at zero strain while the value calculated from the flow stress temperature graph includes an approximate correction for a non-zero athermal stress.

All three values converge at lower temperatures where τ^* has larger values. This suggests that these assumptions are valid at these temperatures but not at any higher temperature. The small difference between the τ^* values from equations (3.7) & (3.8) at low temperatures is probably due to a small athermal stress at the yield stress, but the progressively larger difference at higher temperature suggests the parameters of a thermally activated interaction become less valid. For the temperature region where the strain rate dependance of flow stress is small and the yield stress is not temperature dependant, the thermal stress is probably zero or very small i.e. yield is controlled by athermal interactions. Consequently the thermal stress determined from the flow stress temperature graph should give the most satisfactory value at the low values of τ^* since the other derivations assume $\tau_\mu = 0$ at zero strain i.e. yield is still a thermally activated process. Consequently, the thermal stress from flow stress measurements will be used in subsequent calculations. The temperature dependance of τ^* from different experimental techniques is similar to the agreement between m^* values: they are consistent at low temperatures only.

The components of the applied stress, τ^* and τ_μ are shown in Fig. 3.20.

(iii) Activation Volume.

For a particular type of thermal obstacle, V^* must be a unique function of τ^* and all results should lie

on this continuous curve. Activation volume can be determined from strain rate cycling experiments using equation (3.11) and etch pit studies from equation (3.12). It is independent of strain since $\Delta\tau$ is constant. The variation of activation volume with the thermal stress for each technique is given in Fig. 3.21. The values of V^* are large, approximately $100 b^3$ at 77°K , and increase rapidly with temperature. For the lower temperatures they lay on a continuous $V^* - \tau^*$ curve. The V^* from etch pit velocities do not lie on the curve and further suggests that the dislocation motion at higher temperature is limited by different types of obstacle.

(iv) Activation Enthalpy.

The determination of activation enthalpy requires the values of two terms for equation (3.13) at each temperature (thermal stress). The first $\left\{ \frac{\Delta \ln \dot{\epsilon}}{\Delta \tau} \right\}_T$ can be readily obtained from the strain rate cycling data, above. The second term $\left\{ \frac{\Delta \tau}{\Delta T} \right\}_{\dot{\epsilon}}$ can be found only by temperature cycling tests at constant strain rate. There must be no alteration of the athermal stress during the time taken for the equilibrium at the new temperature to be established (about 12 minutes). This is checked by deforming a specimen at each temperature to a particular strain, unloading (as for an actual temperature cycle, see section 3.2.1), but not changing the temperature, for 12 minutes, then compressing again at the same strain rate. The flow stress after unloading is equal to that before, so no measurable dislocation structure changes occur during this time interval. The

stress changes for a particular temperature increment are individually quite erratic, but show no consistent variation with the strain at which the cycle is undertaken, so an average value is taken. The results of these tests are shown in Fig. 3.22 for each temperature. The values of ΔH are plotted in Fig. 3.23 as a function of τ^* .

As τ^* decreases the value of ΔH slowly increases until suddenly ΔH increases much more rapidly at small values of the thermal stress (which correspond to the temperatures at which the flow stress becomes strain rate insensitive). The reason for this is clearer when the total enthalpy is considered (equation 3.15). Calculation of ΔH_0 requires the integral $\int V^* d\tau^*$ to be calculated numerically from Fig. 3.21. This gives a constant value of ΔH_0 for thermal stress larger than 30 gm/mm². Thus in the low temperature region of a yield stress temperature graph the strain rate cycling parameters are consistent with a single thermally activated obstacle of total enthalpy (0.5 ± 0.1) eV. (The error represents maximum and minimum values of the integration of $\int V^* d\tau^*$). For lower values of τ^* a different predominant dislocation obstacle limits dislocation motion: ΔH_0 increases rapidly as τ^* decreases. Ignoring the points for these lowest values of τ^* ΔH reasonably extrapolates to ΔH_0 for $\tau^* = 0$.

(d) Discussion.

These results show that the treatment of deformation can be divided into two temperature regions. This is demonstrated, for example, from the yield stress measurements; the flow stress temperature graph, like f.c.c. metals, has a high temperature region which is temperature and strain rate insensitive but at low temperature is very dependant on both these variables. Each region will now be considered separately.

At low temperatures below 200°K , there is a rapid increase of yield stress as temperature decreases. From similar observations in metals this suggests the main type of dislocation obstacle at yield is thermally activated. The strain rate cycling results must be shown to be consistent with the theoretical parameters of a thermally activated process before a comparison with particular models can be made.

Unfortunately, etch pit measurements of dislocation velocity are too erratic at these temperatures to give values of m^* (in all cases edge dislocations move further than screw ~~as~~ screw dislocation obstacles are rate controlling). Thus direct comparison with the m^* values from strain rate cycling was impossible but the values from the different equations that can be used to determine m^* from strain rate cycling tests give similar values. This can only occur if the boundary conditions are satisfied. The small difference in the values of m^* can be easily accounted for by the requirement that

$$\tau_y = 0 \text{ at } \epsilon = 0$$

This is probably nearly satisfied especially at the lowest temperatures but not completely. Extrapolation of the high temp region of the yield stress temperature graph show the athermal stress could be as high as 40 gm/mm^2 at yield.

Li 1967 has suggested that to satisfy the third law of thermodynamics m^*T is constant as $T \rightarrow 0^{\circ}\text{K}$ for a thermally activated process. The value of m^*T is plotted against temperature in Fig. 3.24. It can be seen that this relationship is reasonably satisfied below 200°K ; thus, this suggests further that these results apply to a thermally activated process. Within this region the $V^* - \tau^*$ curve is

continuous and ΔH_0 is constant as a function of τ^* , extrapolating to ΔH at zero effective stress. Thus all results are consistent with one type of thermally activated screw dislocation obstacle.

The particular type of thermal obstacle needs to be determined. Evans 1970 has listed the properties of possible thermal obstacles: this is given in Table 3.1: a comparison of the obstacle characteristics will eliminate most of them. The thermal stress is strain independent. Thus obstacles whose concentration or effect increases with strain can be excluded i.e. intersection of dislocation dipoles, dislocation intersection and conservative jog motion. The activation enthalpy, 0.5 eV, is much less than the self diffusion energy of ions, this excludes those mechanisms that depend on the diffusion of ions and vacancies i.e. point defect drag, non-conservative jog motion and dislocation climb.

The theoretical characteristics of a Peierls process have been described by Dorn & Rajnak and reviewed by Guyot and Dorn 1967. Two comparisons between theoretical and experimental parameters are given to decide whether a Peierls mechanism is operating, the variation of flow stress with temperature and of activation volume and enthalpy with stress. These two graphs are plotted in Fig. 3.25 and 3.26. Values of the Peierls stress at 0°K, τ_p , have to be assumed from a reasonable extrapolation of the flow stress temperature graph and, therefore, extrapolation from 77 to 0°K involves substantial error. Even for the smallest acceptable value of τ_p the experimental points for both graphs lie far from the theoretical curves at lower values of τ^* . For higher values of τ_p

discrepancy is even greater. Thus a Peierls process seems most unlikely. This leaves point defects as the most probable origin of the thermal interactions. The low density of these obstacles is the cause of the high value of the activation volume from the large spacing between obstacles.

Thus, this analysis, using the data of strain rate cycling tests to provide a comparison with the theory of a thermally activated process, is consistent with past work that has related the dependance of the low temperature region of the yield stress temperature graph to impurity content of the crystals.

For this work on KCl with multivalent impurity about 10 ppm, the low temperature impurity sensitive region ceases around 200°K : a similar temperature dependance of flow stress has been observed for NaCl and KCl with similar impurity. For greater impurity levels this temperature would be expected to be much higher so that the yield stress might be predominantly due to thermal interactions around room temperatures. The results of Evans and Pratt at 244°K can be considered consistent with this work on KCl: they reported that the yield stress was predominantly thermally activated at 244°K . This may arise from the larger total polyvalent impurity content of their NaCl crystal, estimated at about 40 ppm, which would raise the low temperature region above - 244°K

Further emphasis is given to this conclusion by the agreement between the activation enthalpies 0.5 eV for KCl and NaCl. They would be expected to be similar for the same type of dislocation obstacle.

At higher temperatures it is found that the dislocation etch pit velocities for edges and screws satisfy a relation with applied stress of

$$v = \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^{m_1^*}$$

between 196 & 295°K: m_1^* decreases slowly as the temperature increases.

Strain rate cycling shows the flow stresses are slightly strain rate dependant and this stress increment $\Delta\tau$ is constant with strain and temperature and increases for larger ratios of the strain rate increment. These results differ from those of Komnik on less pure KCl where no such strain rate sensitivity was observed, and of other ionic crystals e.g. MgO which shows flow stress drops on strain rate cycling in an athermal region.

Johnston & Nadeau have suggested values of m_2^* for KCl from extrapolation of m_2 values to zero strain at room temperature can be used in the dislocation velocity stress relation - no complementary dislocation etch pit velocity measurements were made. The large difference in the values of m_1^* and m_2^* obtained in this work show that the strain rate cycling data cannot be used in this way. In the derivation of equation (3.6) for values from the empirical dislocation velocity - stress, equation (3.2), the assumption that dislocation density remained unaltered during strain rate cycling can no longer be considered valid at these higher temperatures. The interpretation of the pressure cycling experiments by Davis and Gordon 1968 assumed that the dislocation density remains unaltered during a cycle of pressure: this must now be reconsidered since $\frac{(\Delta \ln N)}{(\Delta \ln \dot{\gamma})T}$ is not

zero at room temperature i.e. equation (3.5a) is not valid.

For the three stage work hardening curve of NaCl Hesse 1965 has suggested from etch pit observations that applied stress is directly related to the square root of the dislocation density, and yield and working hardening are predominantly caused by athermal stresses over a wide temperature range. This is the type of yield and work hardening curve observed for KCl in the high temperature region. Hesse suggests the limited mobility of jogs is responsible for the work hardening in Stage I. Matucha 1969 has reported a similar stress - dislocation density relation in Stage II. Evans & Pratt 1970 have extended the work of Hesse on the 3 stage work hardening curve. Although yield was a thermally activated process in their crystals, due to a larger impurity content, the work hardening was found to be identical: it was shown to be athermal from strain rate cycling tests and satisfy an athermal stress-root dislocation density relation. In Stage I slip lines were observed like those in Stage II of metals. Blocking obstacles may form on the active slip planes so that new parallel, active, slip planes operate in between the original planes. The obstacles suggested are sessile dislocation junctions which require slip on oblique slip planes for their formation. The process for forming these junctions starts with a cross-slipped screw dislocation. If subsequent dislocations have difficulty in passing this by themselves cross slipping because of adjacent slip bands, then local secondary dislocations on oblique planes may be generated to relieve any stress concentrations. These may interact forming dislocation junctions i.e. a sessile obstacle of a tangle of dislocations,

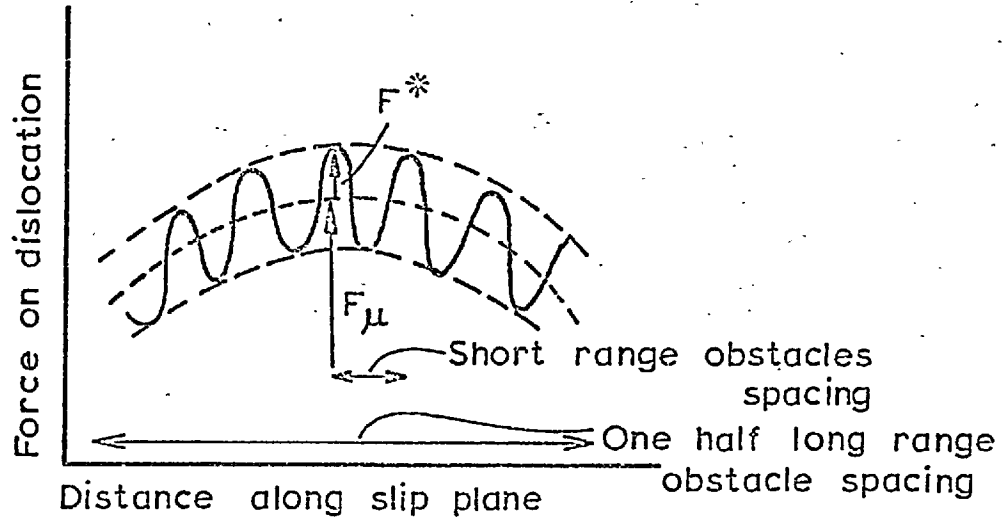


Fig. 3.1 FORCE DISLOCATION MOVING ALONG THE SLIP PLANE.

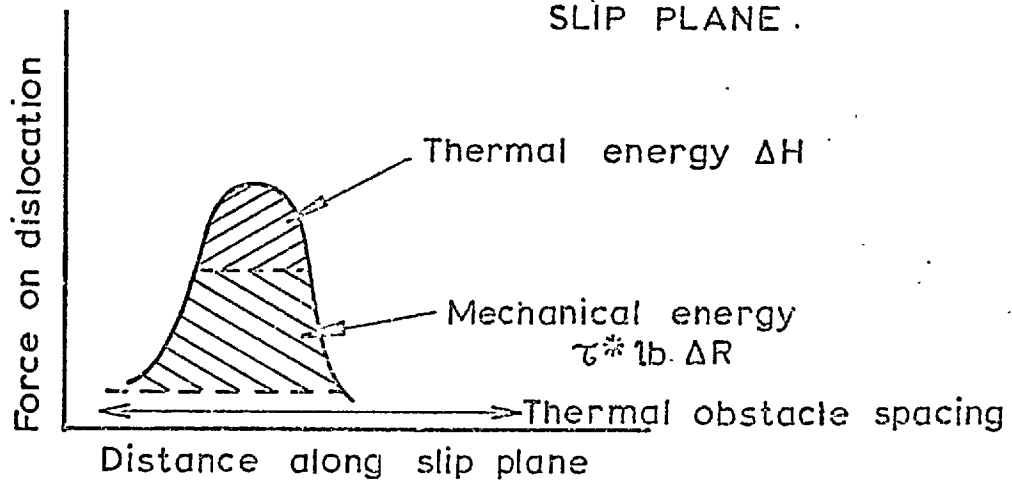


Fig32 THERMAL ACTIVATION OF SHORT RANGE OBSTACLES

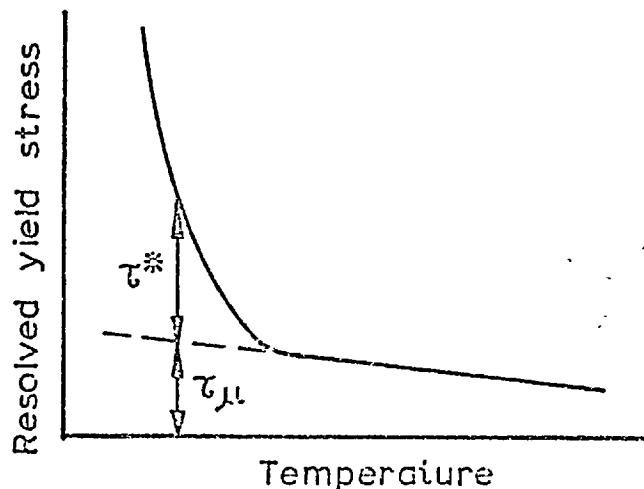


Fig33 CONTRIBUTION OF τ^* & τ_μ TO YIELD STRESS

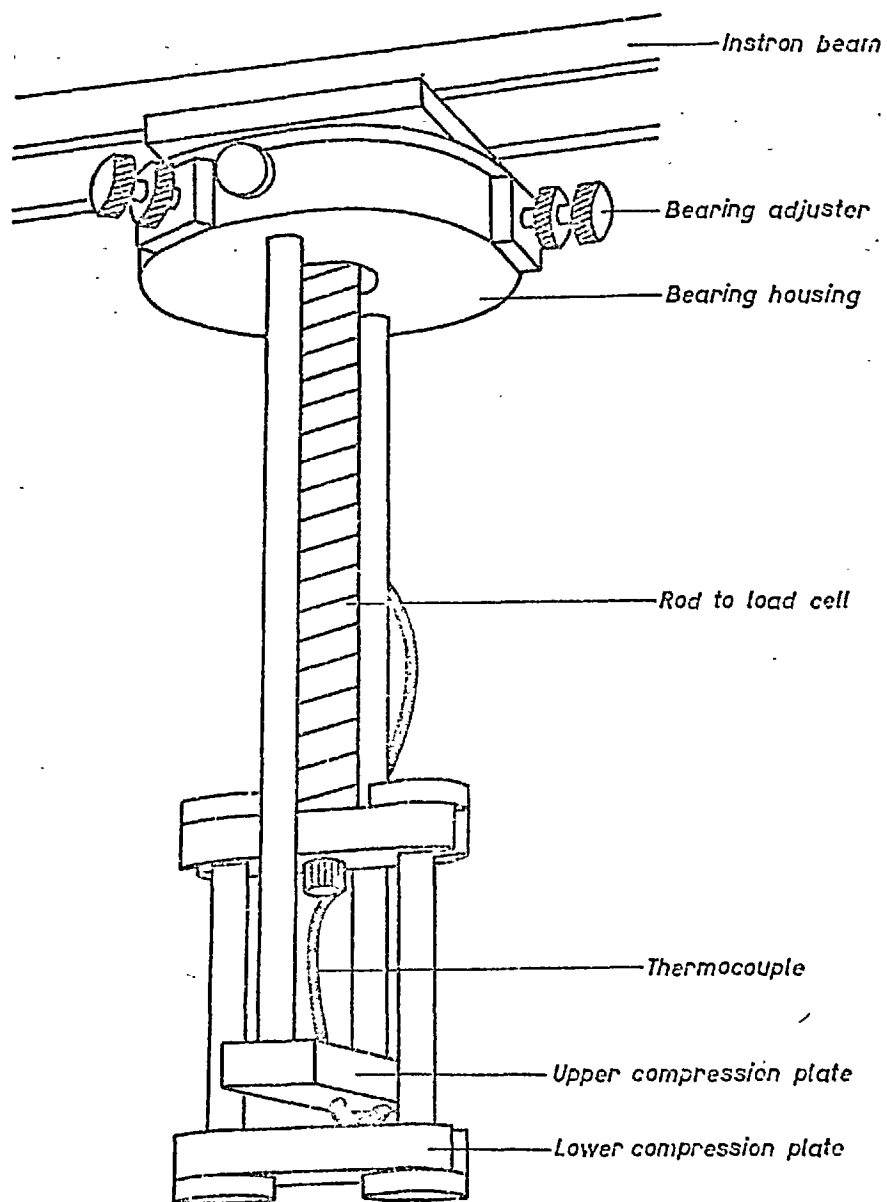


Fig.3.4. THE COMPRESSION JIG

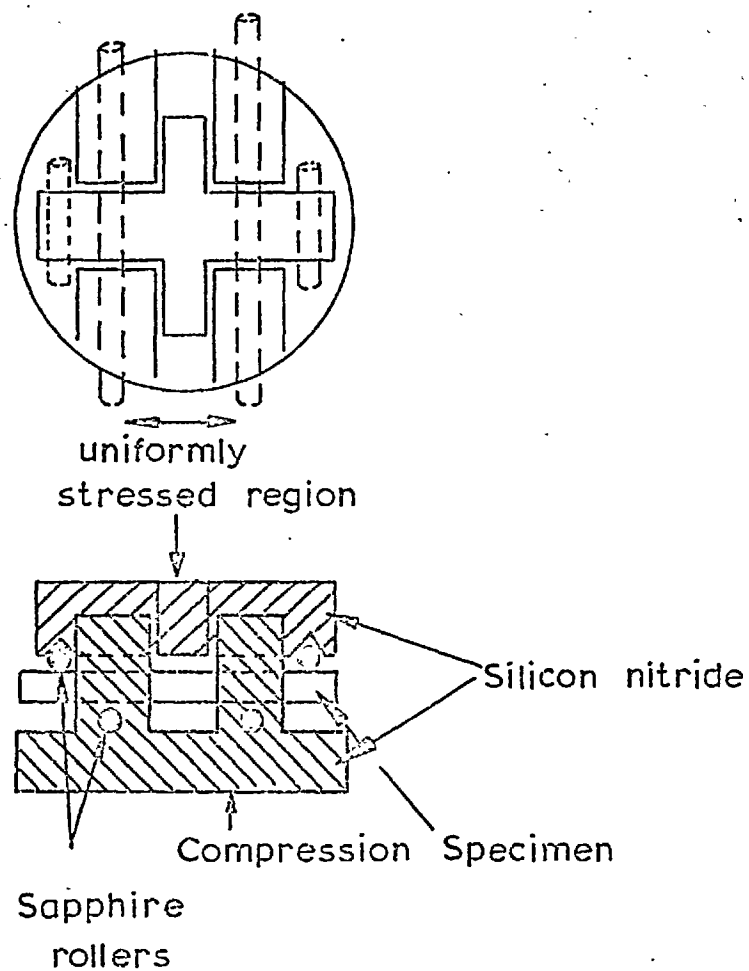


Fig. 3.5. FOUR POINT BENDING JIG

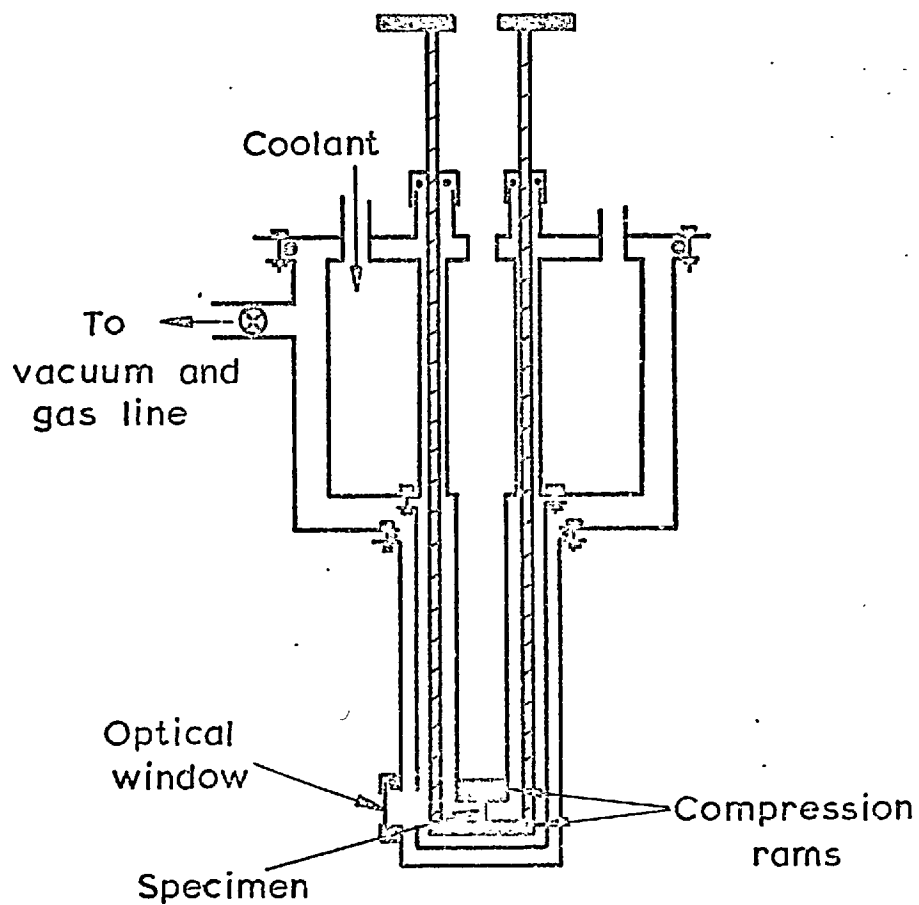


Fig.3.6 LOW TEMPERATURE COMPRESSION
JIG

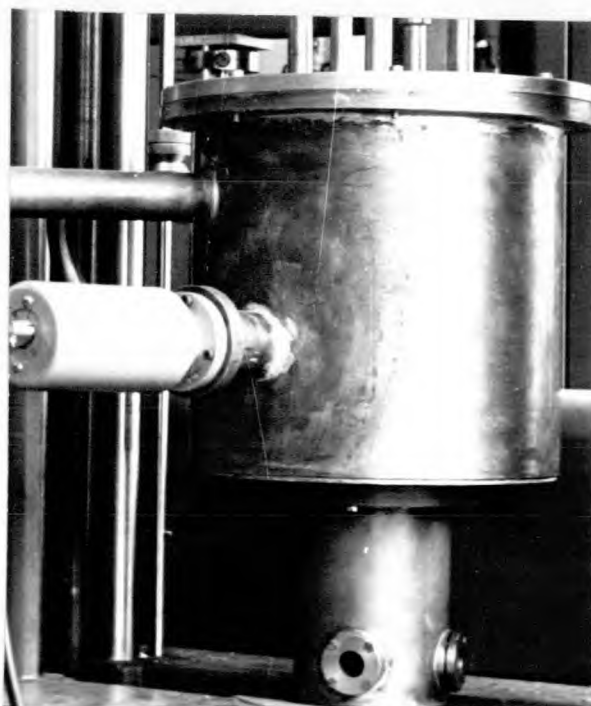


Fig. 3.7 Low temperature
compression jig on the Instron

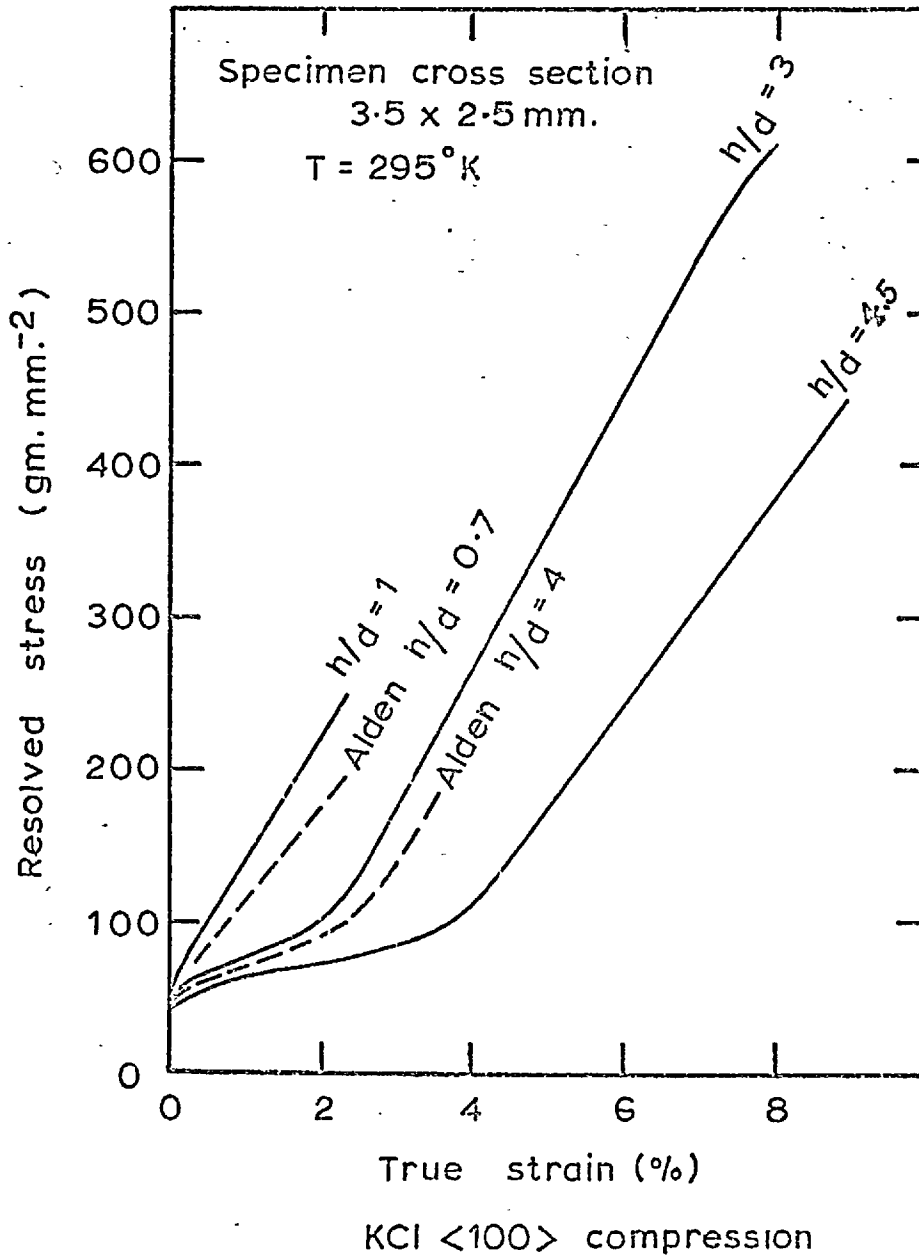
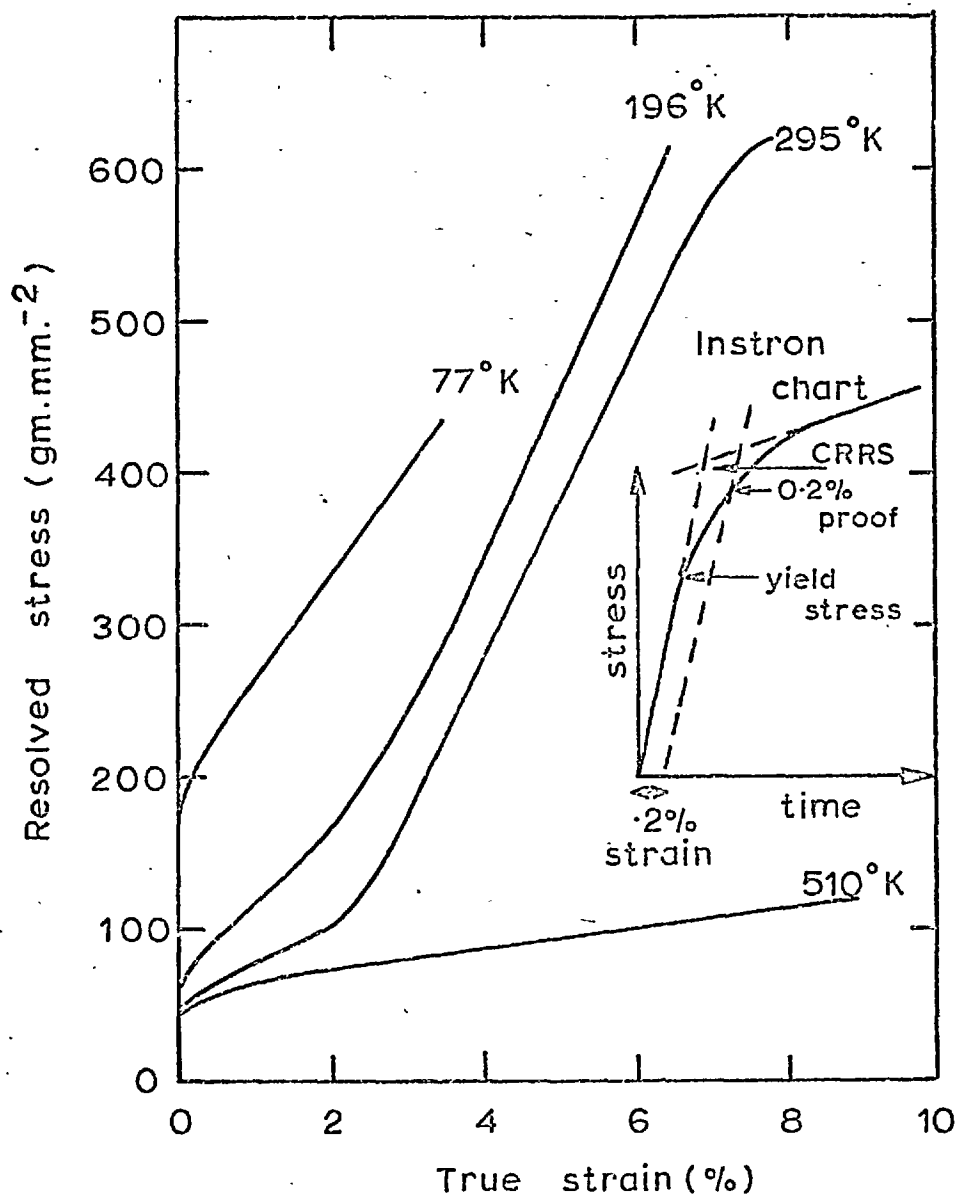
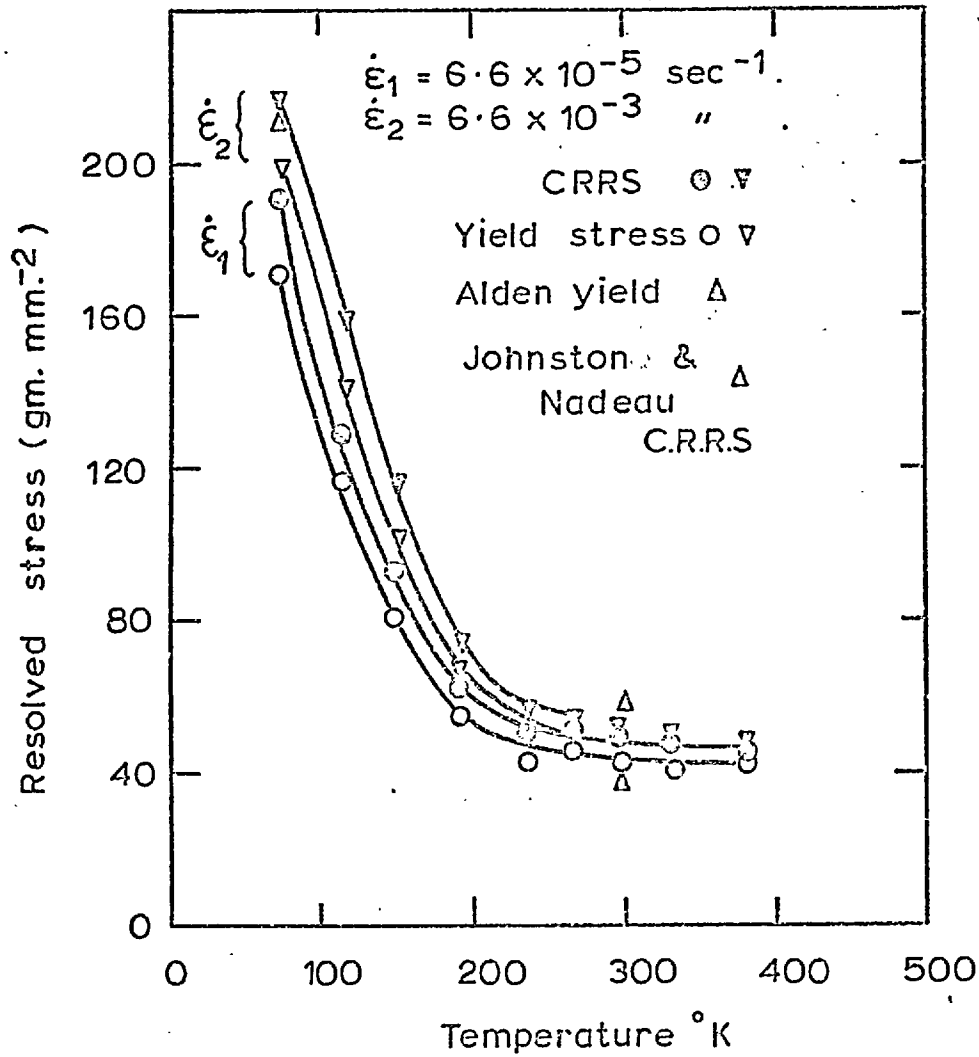


Fig.3.8 THE EFFECT OF h/d RATIO FOR CONSTANT CROSS SECTION SPECIMENS AT 295°K



KCl <100> Compression

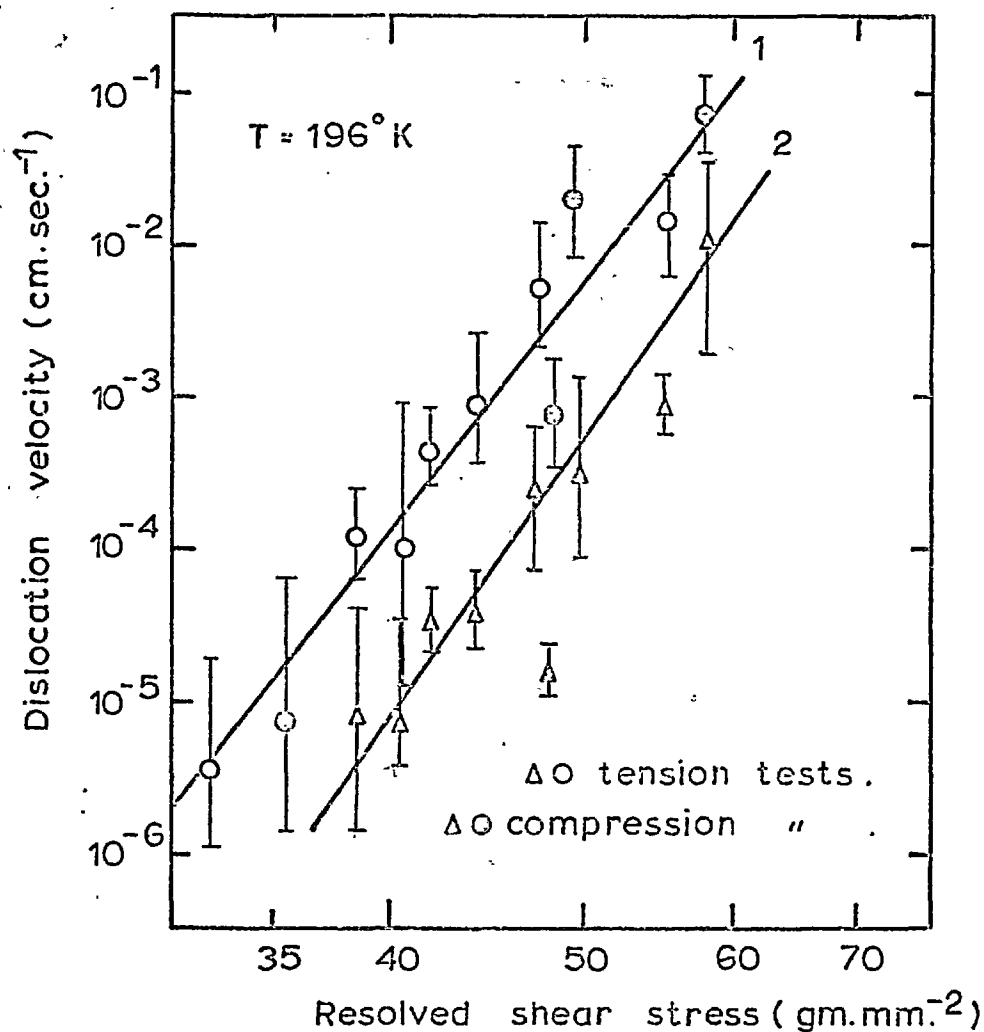
Fig.3.9 THE TEMPERATURE DEPENDANCE OF WORK HARDENING.



KCl <100> Compression

Fig. 3.10 THE VARIATION OF YIELD STRESS
WITH TEMPERATURE & STRAIN RATE.

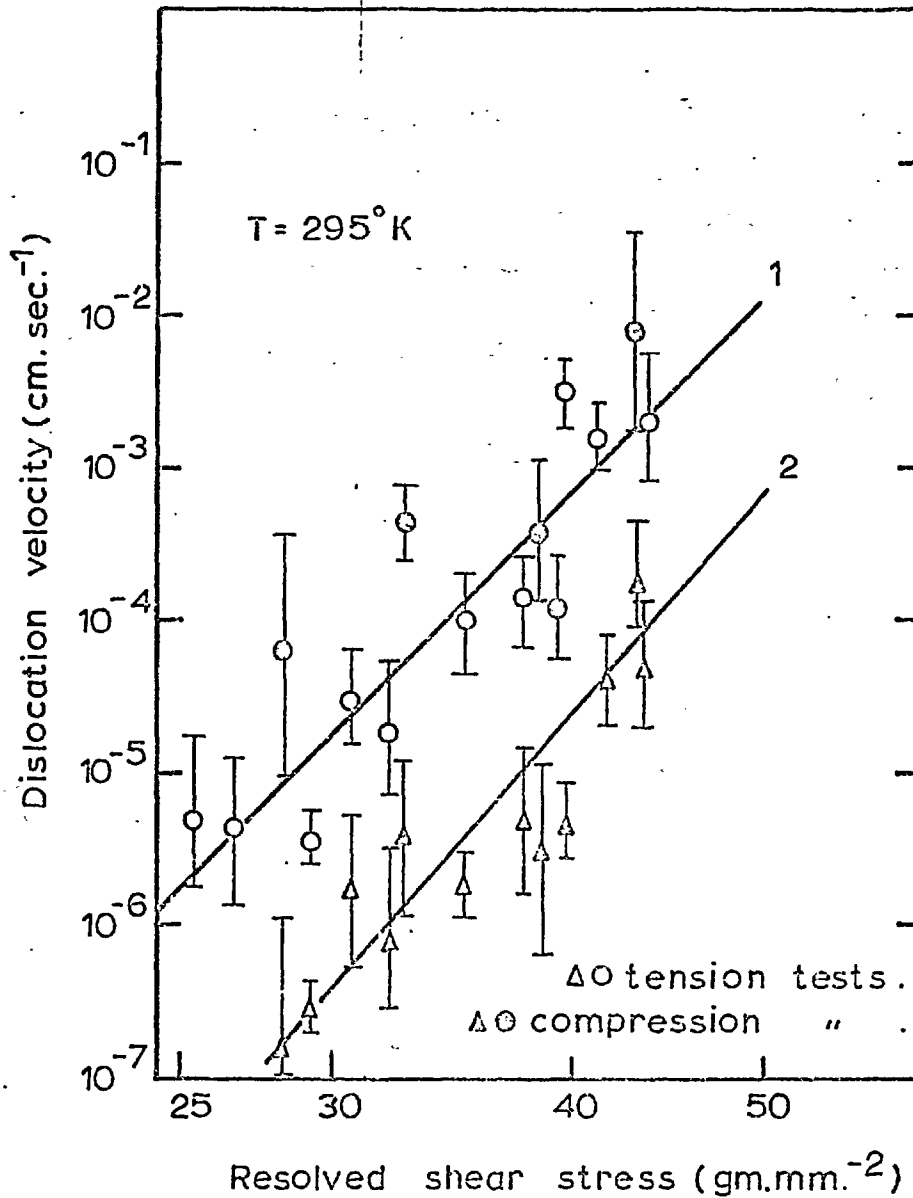
1. Edge dislocations 2. Screw dislocations.



KCl $\langle 100 \rangle$ Compression

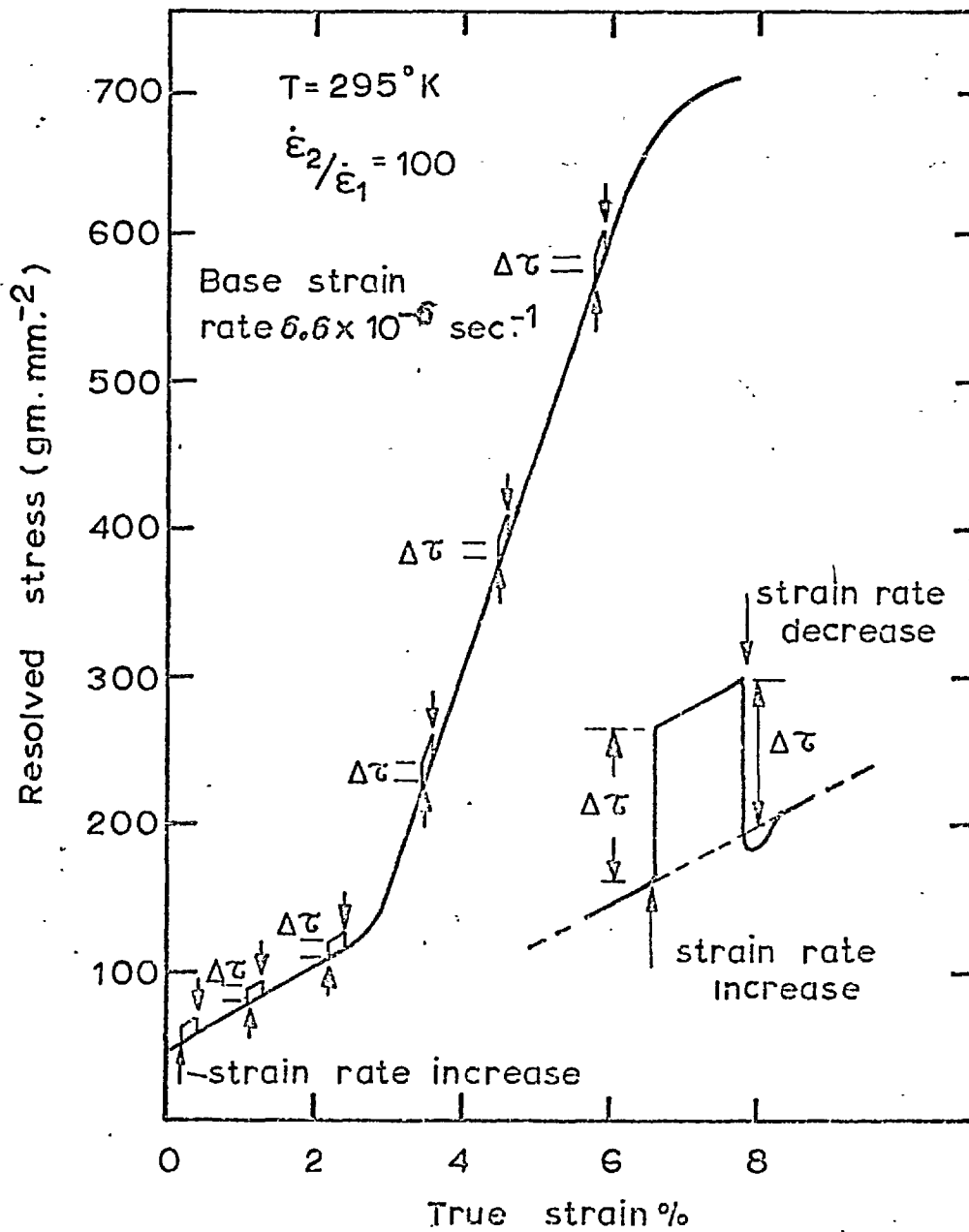
Fig. 3.11. EDGE & SCREW DISLOCATION VELOCITIES
AS A FUNCTION OF THE APPLIED STRESS

1. Edge dislocations. 2. Screw dislocations



KCl <100> Compression

Fig. 3.12. EDGE & SCREW DISLOCATION VELOCITIES
AS A FUNCTION OF THE APPLIED STRESS



KCl $\langle 100 \rangle$ Compression

Fig.3.13. TYPICAL CHANGE OF STRAIN RATE TEST

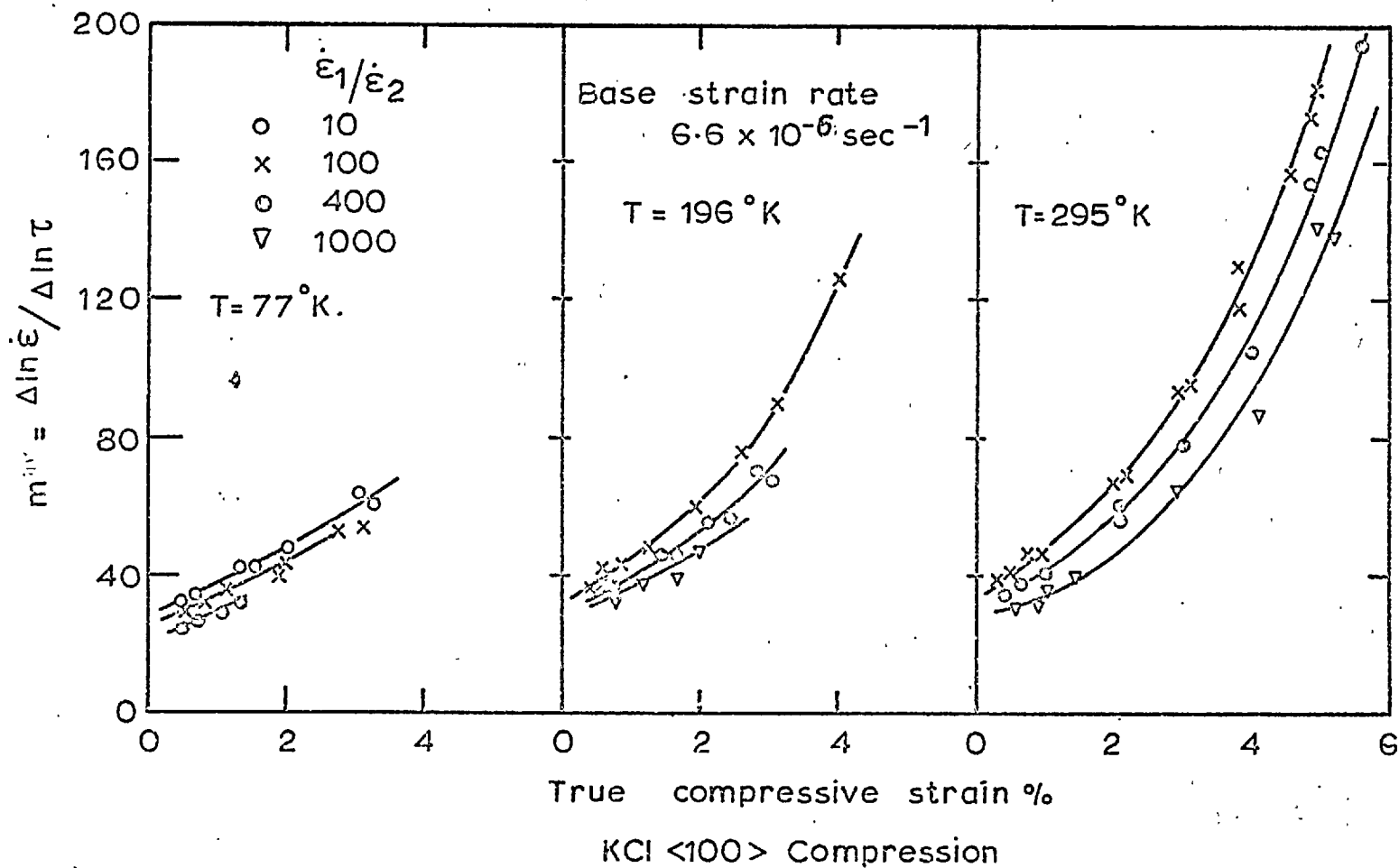


Fig.3.14 THE VARIATION OF $m = \left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \ln \tau} \right)$ WITH STRAIN FOR A RANGE OF STRAIN RATE INCREMENTS.

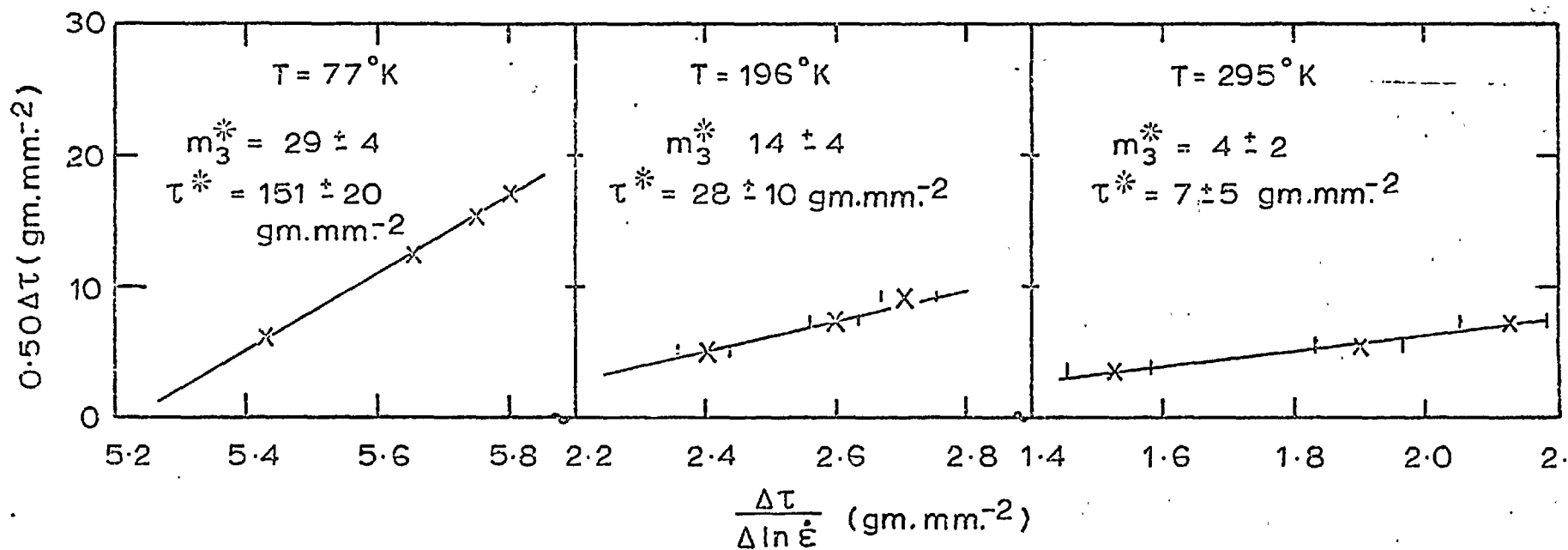
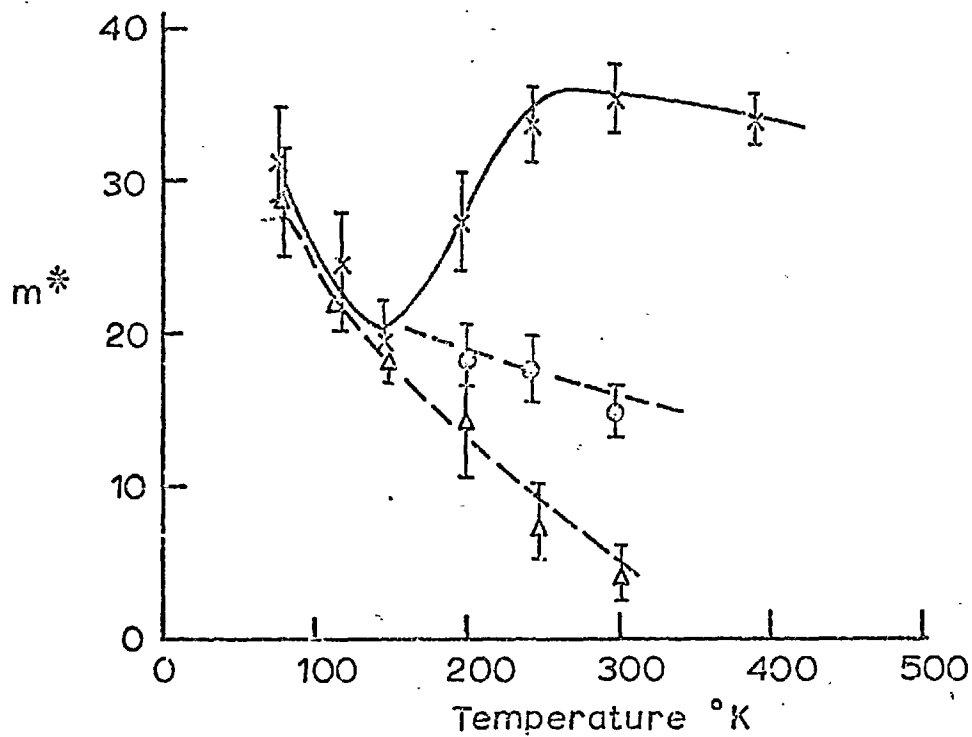


Fig.3.15. PLOT OF $\Delta\tau/2$ AGAINST $\Delta\tau/\Delta\ln\dot{\epsilon}$ TO DETERMINE m_3^* & τ^* FROM STRAIN RATE CYCLING TESTS.

- x extrapolation of m_2 values to $\varepsilon=0$
 o etch pit study m_1^*
 Δ $\Delta\tau$ plot (eqn. 3.7) m_3^*



KCl <100> Compression

Fig.3.16. VARIATION OF m^* WITH TEMPERATURE

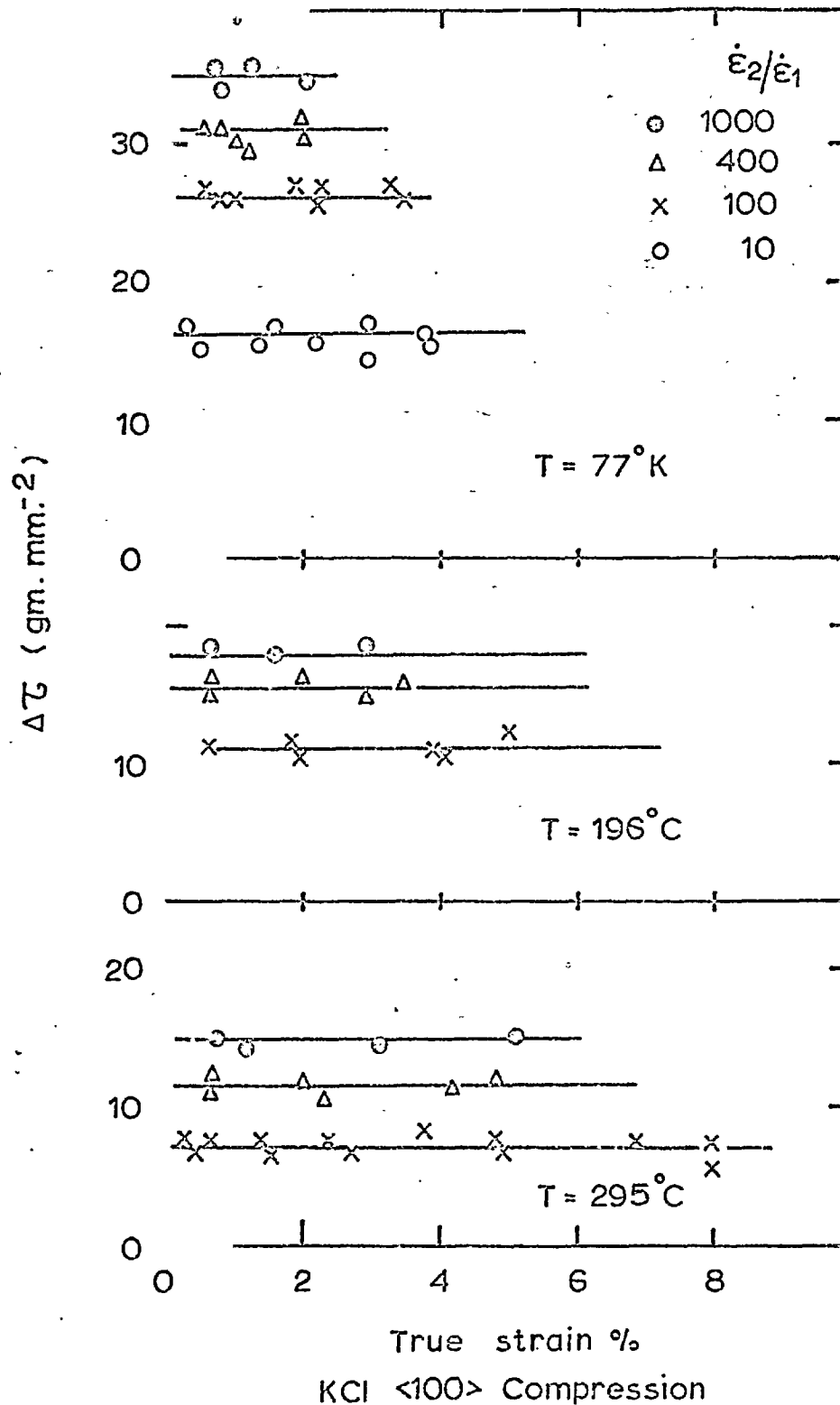
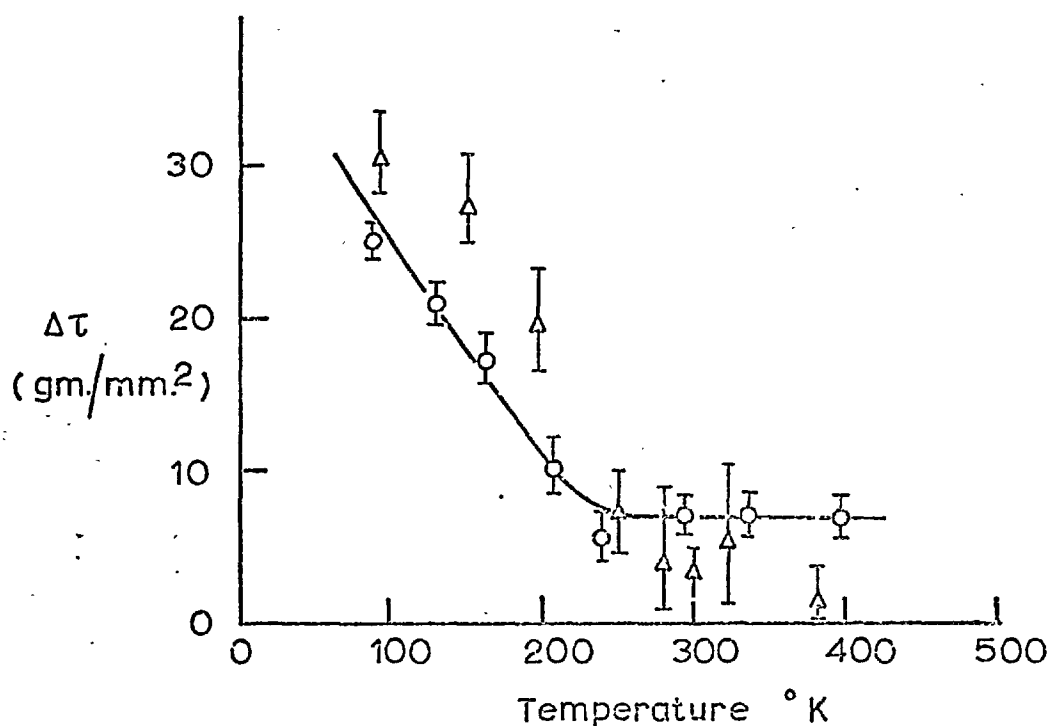


Fig. 3.17. STRESS INCREMENT AS A FUNCTION OF STRAIN FOR STRAIN RATE CYCLING EXPERIMENTS.

o strain rate cycling $\dot{\epsilon}_2/\dot{\epsilon}_1 = 100$
 Δ constant strain rate tests
 base strain rate $\dot{\epsilon} = 6.6 \times 10^{-6} \text{ sec.}^{-1}$



KCl <100> Compression

Fig. 3.18. $\Delta\tau$ VALUES FROM CHANGE OF
 STRAIN TESTS (i.e. STRAIN RATE
 CYCLING $\dot{\epsilon}_2/\dot{\epsilon}_1 = 100$), & FROM
 CONSTANT STRAIN RATE TESTS
 YIELD STRESSES

$$1. \tau^* = \Delta\tau / (\dot{\epsilon}_2/\epsilon_1)^{1/m^* - 1}$$

$$2. \tau^* \text{ from } \frac{\Delta\tau}{2} \text{ vs. } \Delta\tau/\Delta \ln \dot{\epsilon}$$

$$3. \tau^* \text{ from yield stress vs. Temp.,}$$

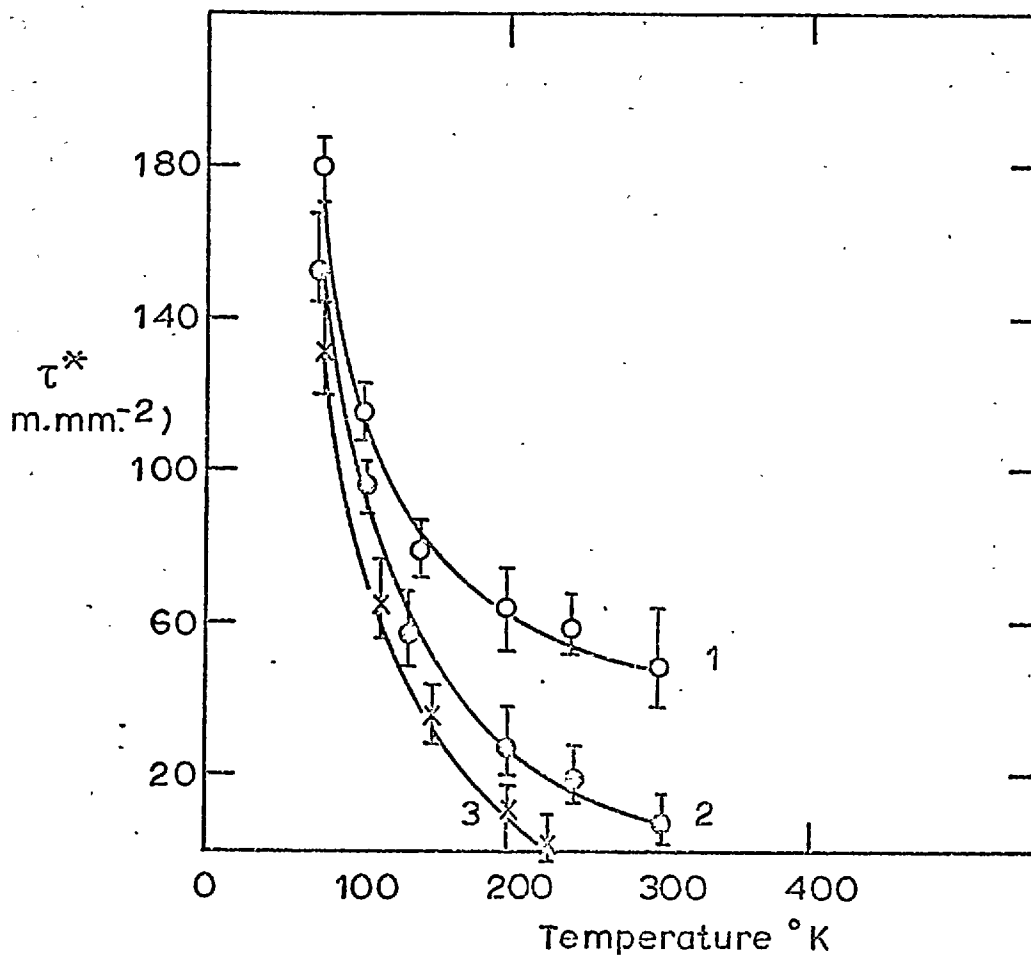
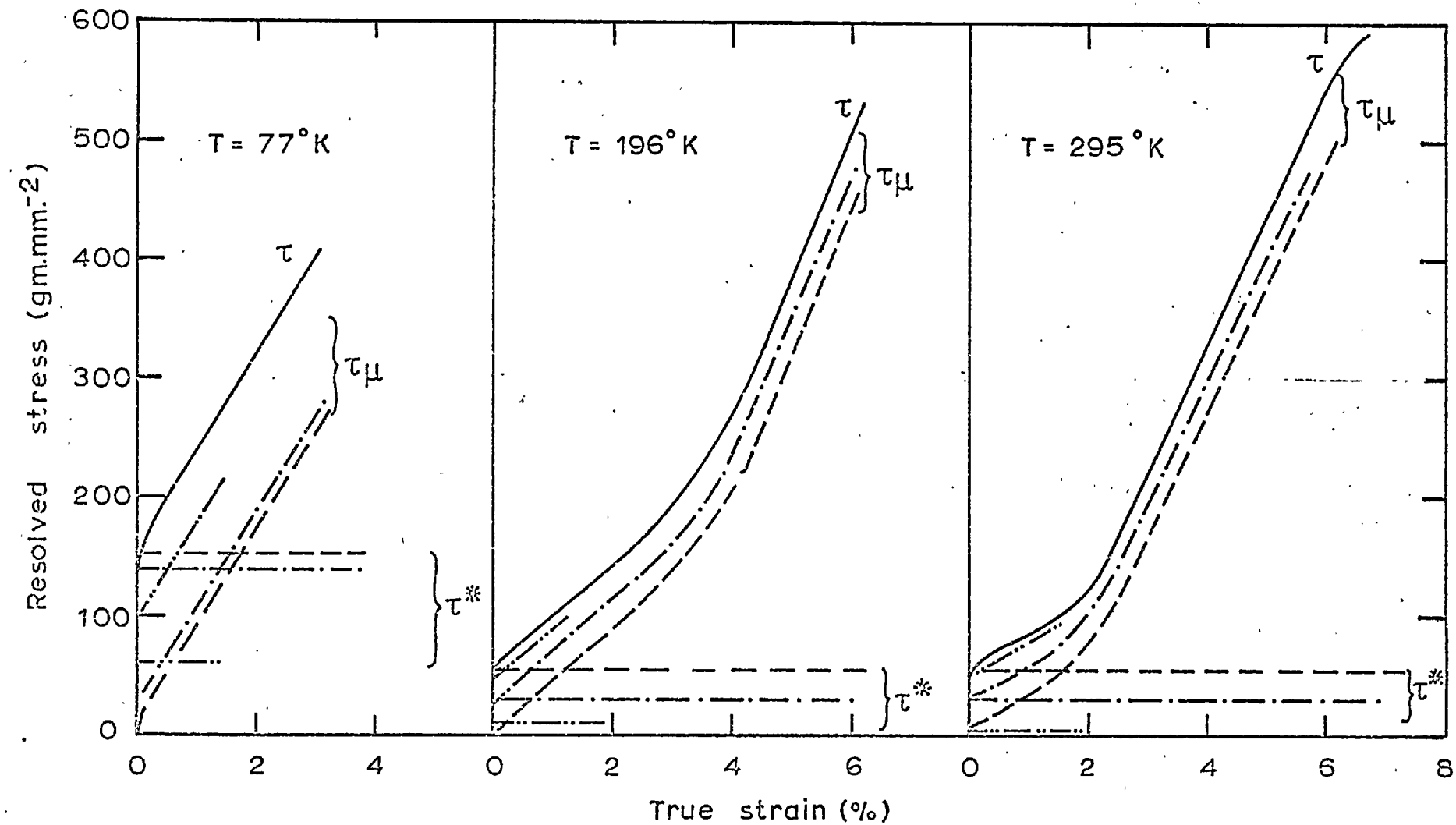


Fig.3.19. VARIATION OF THERMAL STRESS
WITH TEMPERATURE

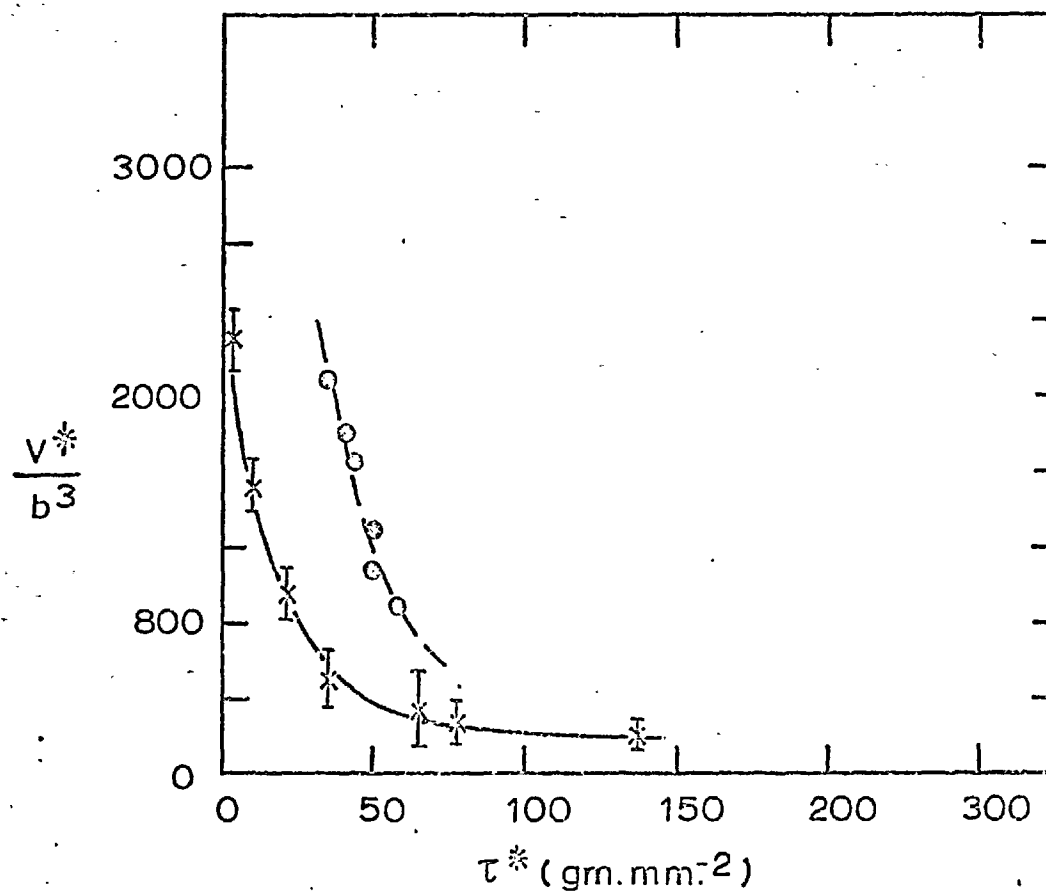


KCl $\langle 100 \rangle$ Compression

Fig.3.20. THE CONTRIBUTIONS OF τ^* & τ_μ TO THE APPLIED STRESS τ AS A FUNCTION OF STRAIN

— From yield stress vs. temp. --- from $\Delta\tau/2$ vs. $\Delta\tau/\Delta\ln\dot{\epsilon}$ - - - from $\tau^* = \Delta\tau/(\dot{\epsilon}_2/\dot{\epsilon}_1)^{1/m^*}$

x strain rate cycling
 o etch pit velocity ($\tau = \tau^*$)



KCl <100> Compression

Fig.3.21. THE VARIATION OF THE ACTIVATION VOLUME WITH THERMAL STRESS.

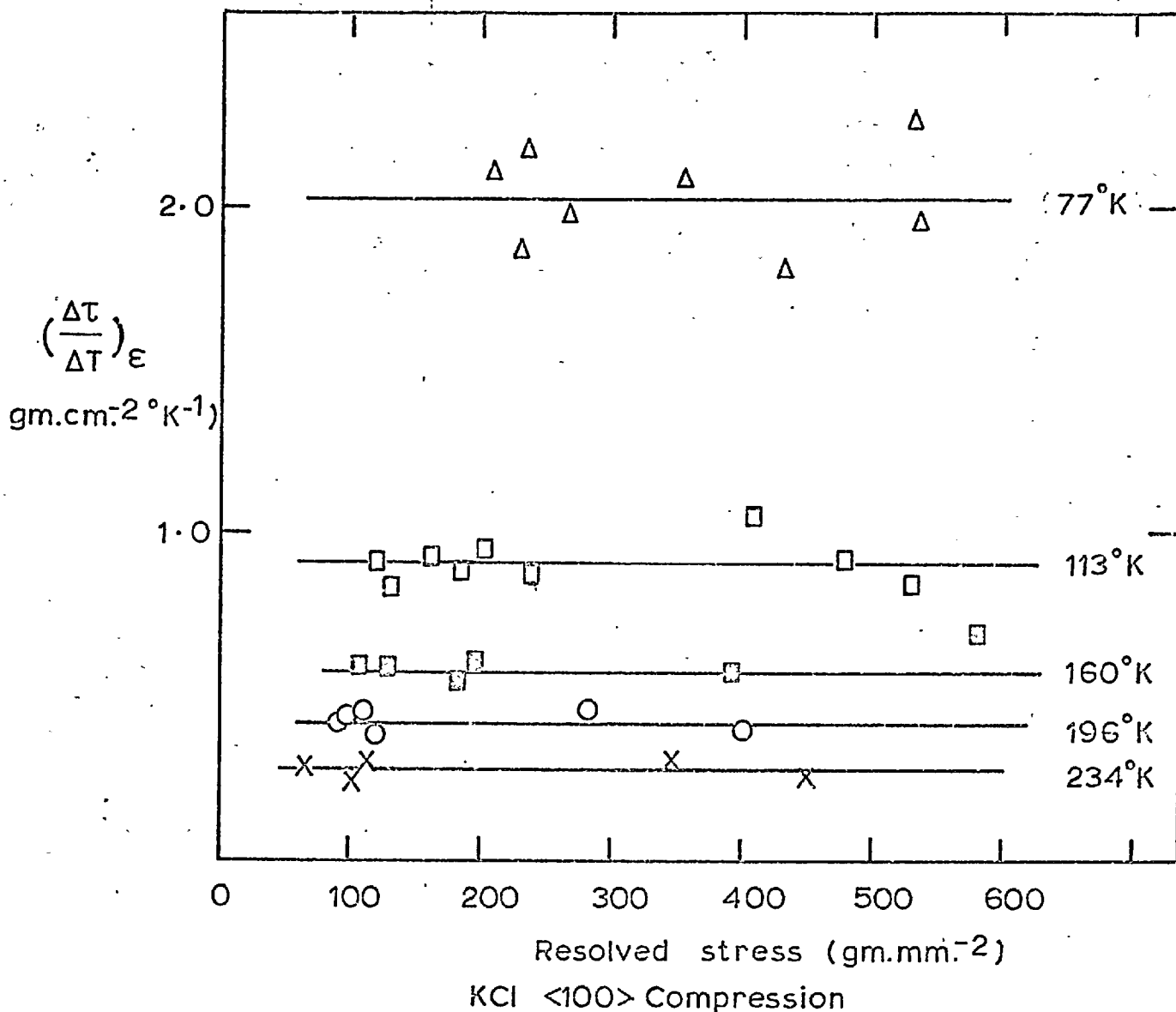
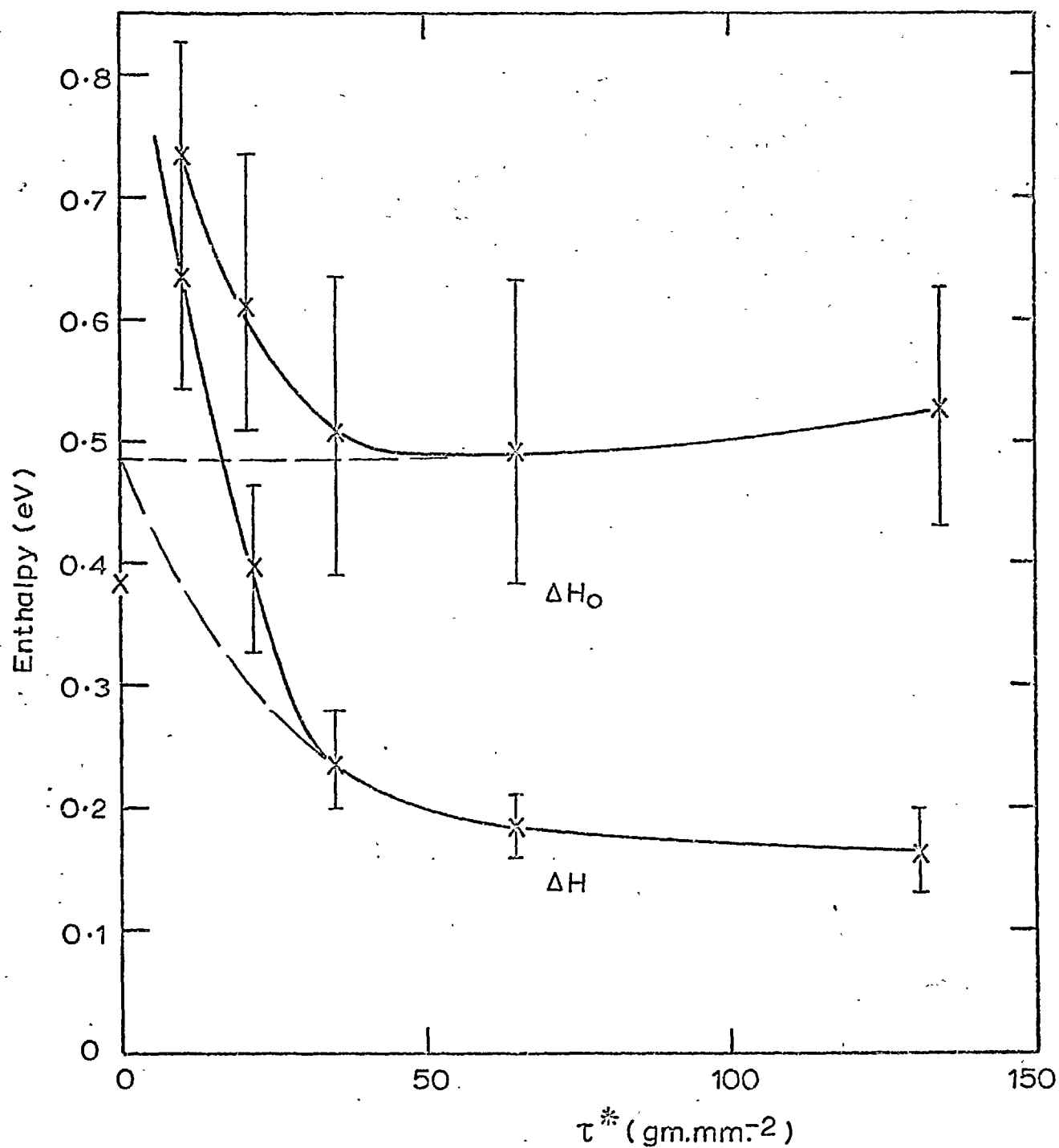
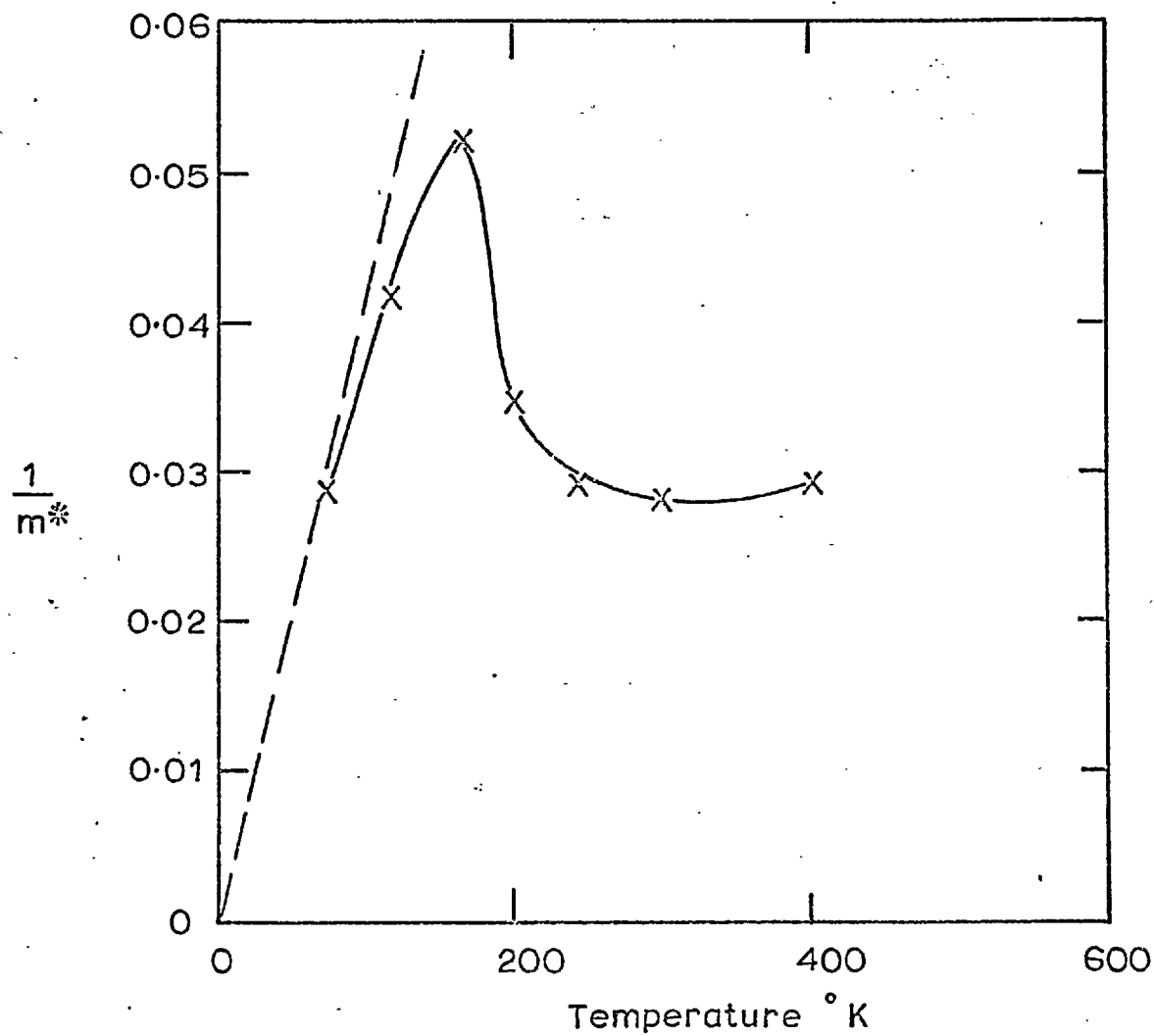


Fig.3.22 THE CHANGE OF STRESS ($\Delta\tau$) DURING TEMPERATURE (ΔT) CYCLING: TESTS AT CONSTANT STRAIN RATE



KCl <100> Compression

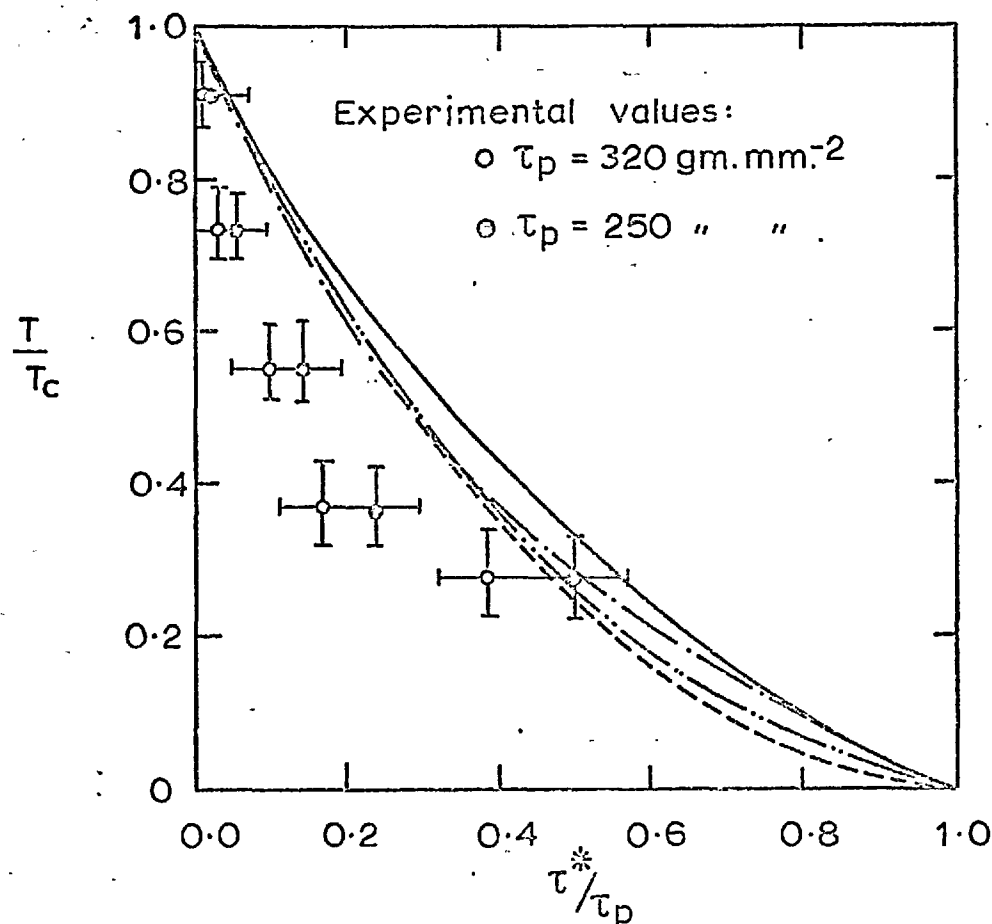
Fig.3.23. ENTHALPY AS A FUNCTION OF THERMAL STRESS



KCl <100> Compression

Fig. 3.24. THE VARIATION OF $1/m^*$ WITH TEMPERATURE

Peierls mechanism: $\alpha = -1$
 $\alpha = 0$
 $\alpha = +1$
 (Guyot & Dorn) quasi parabolic -----



KCl <100> Compression

Fig.3.25. VARIATION OF THE YIELD STRESS WITH TEMPERATURE. COMPARISON OF EXPERIMENTAL VALUES WITH THE THEORETICAL VALUES OF A PEIERLS MECHANISM.

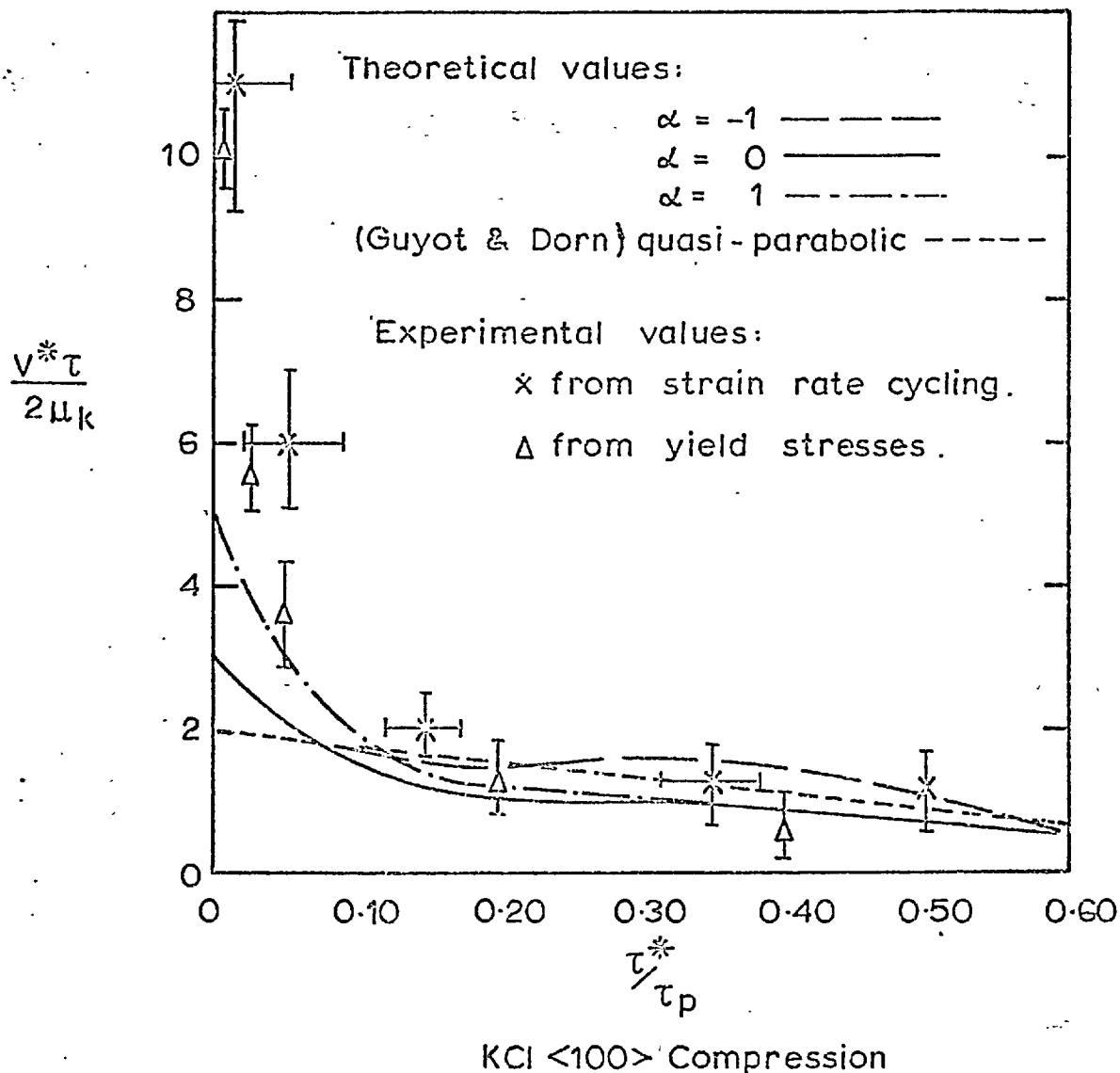


Fig.3.26. VARIATION OF THE ACTIVATION VOLUME WITH THERMAL STRESS. COMPARISON OF EXPERIMENTAL VALUES WITH THE THEORETICAL VALUES OF A PEIERLS MECHANISM.

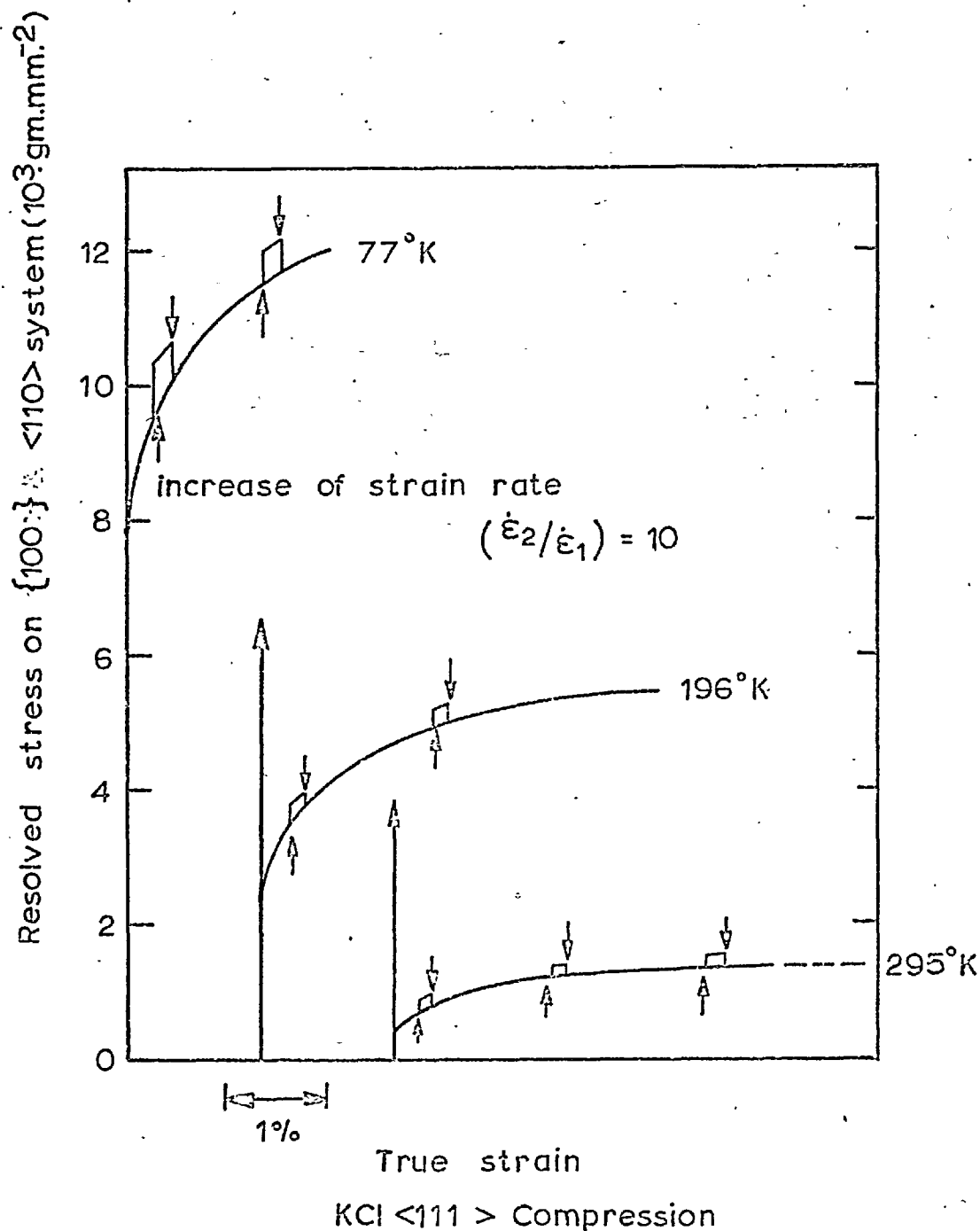


Fig.3.27. TEMPERATURE DEPENDENCE OF STRESS & STRAIN

junctions and dipoles. Thus in Stage I athermal stresses are expected to act on a subsequent dislocation from

- (1) Back stress from the obstacle
- (2) Intersection of forest dislocations around obstacles.
- (3) Limited mobility of thermal jogs in between obstacles.

In Stage II, in regions of favourable stress near the obstacles, there may be sufficient stress for the junction to dissociate and dislocations on oblique systems move. Such a dislocation moving would give much debris inclined to the active slip system which would interact strongly with the majority of the dislocations moving on the active system giving rise to greater rate of debris production and consequently a higher rate of work hardening. Thus athermal stresses acting on a dislocation in Stage II occur from

- (1) All the stresses acting in Stage I
- plus (2) Increased number of jogs
 - (a) On planes parallel to the active system
 - (b) On planes inclined to the active system.

The authors suggest the greatest stresses are caused by forest dislocations, blocking obstacles and debris on planes inclined to the active slip system.

The thermal activation in the lower temperature region of KCl deformation is similar to that observed by Evans and Pratt at 244°K for NaCl. The work hardening curves obtained for KCl over the whole temperature range are similar to those for NaCl. Thus it may be reasonably suggested that similar athermal work hardening interactions apply.

3.2.3. Deformation on the secondary slip system.

Specimens for compression in the $\langle 111 \rangle$ direction are prepared by the method outlined in Chapter 2.

Particular care needs to be taken to ensure that the end faces of the specimen are the $\langle 111 \rangle$ planes to the nearest half a degree. Weaver 1964 has demonstrated for similar experiments on MgO that if misalignment is greater than a few degrees there is sufficient resolved stress on the primary slip systems for dislocations to move, despite the highly unfavourable Schmid factor, instead of the secondary slip systems being activated. Thus from each batch of samples the compression faces of one specimen are rechecked using the Laue back reflection X-ray technique after cutting and polishing.

Compression in the $\langle 111 \rangle$ direction has been reviewed in Chapter 1. The $\{100\}\langle 110 \rangle$ are shown in Chapter 2 to be the activated slip systems for this deformation; resolved stresses in this section refer to these systems.

(a) Constant strain rate tests.

(1) Effect of specimen dimensions.

The specimen faces parallel to the compression axis need to be reproducible and give a rectangular specimen cross section to be comparable to the $\langle 100 \rangle$ compression results, and be rational planes preferably of low indices for easier slip trace analysis. The standard (111) projection of a cubic crystal, Fig. 1.13, indicates the most suitable faces that satisfy these conditions are $(10\bar{1})$ and close to a $(1\bar{2}1)$ plane. Changing the height to diameter ratio for the specimens does not alter the yield nor the work hardening below 3% strain. At higher strains, the stress strain curve becomes increasingly dependant on the h/d ratio: this is probably a result of the varying lattice rotation that occurs and the beginning of dislocation motion on the

primary slip planes. Thus providing only small strains are used, valid results are obtained using the specimen dimensions of the $\langle 100 \rangle$ compression tests.

(ii) Variation of the stress strain curve with temperature.

Typical stress strain curves for $\langle 111 \rangle$ compression are shown in Fig. 3.27 for a range of temperatures. At each temperature the stress strain curve is parabolic. Thus the shape of these curves for the alkali halides are similar to those obtained by Hulse, Copley and Pask 1963 for MgO deformed in $\langle 111 \rangle$ at much higher temperatures, by Evans 1967 for the deformation of CaF_2 on its secondary slip system and similar to those obtained for b.c.c. metals. The rate of work hardening at a particular strain decreases with temperature. The variation of yield stress with temperature is drawn in Fig. 3.28.

Above 330°K the yield stress is neither sensitively dependant on temperature nor strain rate. Below this temperature there is a rapid increase in the yield stress and strain rate dependance suggesting thermally activated dislocation motion. Strain rate cycling tests should confirm this. The change from thermal to athermal interaction occurs at a much higher temperature than for the $\{110\} \langle 110 \rangle$ slip system as determined in the previous section, thus different slip mechanism are responsible. This is a lower temperature than the 600°K observed by Stepanov & Bobrikov 1963 for similar observations on natural rock salt. This suggests that impurities may effect this temperature of the transition from one mechanism to another.

(b) Thermally activated dislocation motion.

(i) Stress change during strain rate cycling tests.

The stress changes during strain rate cycling are independent of strain at all temperatures tested.

Thus, if strain rate cycling data are valid for these tests, within experimental error there is no production of thermal obstacles during deformation: any thermal obstacles must be present at yield and consequently the work hardening is athermal. The variation of $\Delta\tau$ with temperature for a particular strain rate increment is shown in Fig. 3.29. There is little temperature dependance above 350°K . (350°K is the temperature for the transition of the yield stress from being temperature dependant to temperature independant, Fig. 3.28.) Below 350°K there is a rapid increase in $\Delta\tau$, below 200°K a slow decrease. Thus at low temperatures the flow stress is strain rate sensitive, probably from thermal obstacles, but the strain rate dependance decreases as the temperature is reduced: this is similar to the theoretical operation of a Peierls stress which tends to become strain rate independant as the temperature approaches 0°K .

(ii) m_2^* values.

The variation of m_2 values with strain, determined from strain rate cycling using equation (3.6) is plotted in Fig. 3.30. For a range of strain rate increments these extrapolate to the same value, m_2^* , at zero strain. The variation of these m_2 values with strain can be easily understood from equation (3.6).

$$m_2 = \frac{\Delta \ln \dot{\epsilon}}{\Delta \ln \tau}$$

If $\Delta\tau \ll \tau$, this equation approximates to

$$m_2 = \frac{\ln \frac{\dot{\epsilon}_2}{\dot{\epsilon}_1}}{\Delta \tau / \tau}$$

Since both the strain rate increments and $\Delta\tau$ are constant during strain rate cycling, m_2 will rapidly increase as a function of strain from the similar

increase of $\dot{\epsilon}$ i.e. m_2 value-strain curves are similar to the stress strain curves.

The m_3^* values are determined at finite strains from equation (3.7) for a range of strain rate increments. m_3^* is the gradient of the graph of $\frac{\Delta \sigma}{2}$ plotted against $\frac{\Delta \dot{\epsilon}}{\Delta \ln \dot{\epsilon}}$ see Fig. 3.31.

The number of points is limited by the suitable strain rates obtainable from the Instron, strain rates that are too fast lead to premature cracking of the specimen.

Within the low temperature region of the yield stress-temperature, these experimental points give straight lines of gradient m_3^* which are only just below the values of m_2^* , see Fig. 3.32. This suggests the boundary conditions for the validity of strain rate cycling data may be satisfied (see section 3.1.2). Where the yield stress temperature graph indicates an athermal region these values no longer give m_3^* values consistent with m_2^* values. Thus at higher temperatures the yield stress being athermal suggests a non zero athermal stress at zero strain, so the boundary conditions for strain rate cycling are no longer satisfied, equation (3.3a).

The variation of the m^* values with temperature is shown in Fig. 3.32. At the lowest temperature the strain rate sensitivity decreases as the temperature rises and the yield stress decreases, hence m_2^* (from (3.6)) decreases rapidly. Between 200 and 300°K. m_2^* decreases rapidly and yield stress is nearly athermal so m^* increases. Finally, yield stress and m^* values are both approximately constant above 300°K.

Further confirmations of the validity of these m^* values at low temperatures can be obtained from a plot of $\frac{1}{m^*}$ against temperature, see Fig. 3.33.

The plot is linear and may pass through the origin within experimental error for low temperatures below 200°K . This relationship is consistent with the work of Li 1967 that suggests the product m^*T tends to a constant value as the temperature approaches 0°K . The determination of dislocation velocity as a function of stress to calculate m_1^* from etch pit observations of dislocations around indents, as outlined in Chapter 2, is not possible for slip on the $\{100\}\langle 110 \rangle$ system. Four point bending in the $\langle 111 \rangle$ direction fractures the specimens before deformation takes place. Compression tests do not yield consistent results: the distance moved by the edge and screw dislocations varies over a wide range for the several indents in one specimen and between specimens. However, these indents do show the important result that the screw dislocations move consistently further than the edge dislocations. Consequently the rate controlling obstacle for dislocations moving on the $\{100\}\langle 110 \rangle$ system must be effective for edge dislocations and not screw dislocations.

(iii) The Thermal Stress

The thermal stress at yield can be estimated from the yield stress - temperature graph by subtraction of an extrapolation of the high temperature athermal region. To be valid, this requires that the structure at yield is similar over the whole temperature range.

Strain rate cycling data provide two alternative derivations of τ^* at finite strains from equations (3.8) & (3.9). Since A is constant as a function of strain both these equations give τ^* also constant. Agreement between these three different derivations at low temperatures suggest the boundary conditions (3.3a) (3.5a) and (3.7a). of the equations are satisfied

and predominantly thermally activated obstacles control dislocation motion at yield. In the athermal region of the yield stress temperature graph no consistency is obtained for τ^* values; probably the athermal stresses predominantly control yield and so parameters of a thermally activated process are not relevant. This variation of τ^* with temperature is shown in Fig. 3.34. The values from the yield stress measurements are probably closest to the true values since they are consistent with those from strain rate cycling at low temperature and are zero in the athermal region where there is no temperature dependence.

The relative contributions of thermal and athermal stresses to the observed applied stress is presented in Fig. 3.35.

(iv) Activation Volume

For the thermally activated, low temperature region the activation volumes Fig. 3.36 are much lower than for slip on the primary system suggesting the obstacle interaction distance extends over a shorter distance or the spacing between obstacles is much less. When plotted against τ^* the experimental values of V^* from strain rate cycling lie on a smooth curve, consistent with the same thermal obstacle being rate controlling throughout the temperature range.

(v) The activation enthalpy.

Temperature cycling tests are required at constant strain rate to calculate the activation enthalpy. To be valid they must be carried out at constant dislocation structure. To ensure no measurable structure change occurred, specimens were deformed to a particular strain, unloaded for

a period of time equal to the duration of a temperature cycling test and then reloaded. No changes in flow stress are observed before and after unloading for temperatures up to 400°K. The measurements of temperature cycling are given in Fig. 3.37 and are approximately independent of strain. This confirms that no large thermal obstacles form during deformation.

Values of the activation enthalpy ΔH can now be calculated, combining the results of temperature and strain rate cycling, and the total enthalpy of the thermal obstacles ΔH_0 can be estimated by the addition of $\int V d\tau^*$ from the numerical integration of Fig. 3.36. These enthalpies are plotted in Fig. 3.38 and as a function of τ^* . Except for the lowest value of τ^* , ΔH_0 is independent of τ^* and equal to 1.04 ± 0.17 eV. The error quoted in the value of total activation enthalpy represents the uncertainties in the calculation of the $\int V d\tau^*$ and the temperature cycling tests. The activation enthalpy should extrapolate to this value at zero stress (when the barrier would be completely thermally activated): ΔH_0 is an acceptable value for this extrapolation provided that the result for the lowest value of τ^* is again ignored. This point may be excluded since it corresponds to the beginning of the athermal region of lower strain rate sensitivity where the boundary conditions are not completely satisfied.

(c) Discussion.

The observations in Chapter 2 confirm previous observations that deformation takes place on $\{100\}$ $\langle 110 \rangle$ secondary slip systems for compression in a $\langle 111 \rangle$ direction.

The results of yield stress, and temperature and strain rate cycling experiments indicate that there are two distinct temperature regions. Below 300°K the yield stress is controlled mainly by thermal obstacles which are then equally effective at all strains. Above this temperature there is no evidence to suggest that thermal obstacles predominantly slow dislocation motion and yield is probably controlled mainly by athermal interactions. The mechanism of work hardening seems to be similar at all temperatures and due to athermal obstacles.

Comparisons will now be made between the experimental results and possible types of obstacle. Since the total activation enthalpy was independent of stress in the low temperature region, the $V^* - \tau^*$ curve is continuous and the m^* and τ^* values are consistent for different derivations, this suggests that one type of thermally activated dislocation process may control the yield stress, and then the boundary conditions, upon which the validity of the strain rate cycling equations depend, must be satisfied.

The strain rate sensitivity is independent of strain, thus the obstacles may be excluded whose density increases with strain (see Table 3.I). Fontaine 1968, 1969 has calculated that the stacking fault energy is too high for partial dislocations to form during slip on the $\{100\}$ planes.

Huntington, Dickey & Thompson 1956 have calculated the theoretical formation energies of dislocations on both the primary $\{110\} \langle 110 \rangle$ slip systems and secondary $\{100\} \langle 110 \rangle$ slip systems of NaCl. They concluded the difference between the formation energies of these two systems is not

nearly large enough to cause the large experimental variation of yield stress. Thus the difference between them must be a result of their relative resistance to the movement of dislocations rather than the energy of formation. Both Huntingdon and Gilman 1959 have suggested that the large repulsion between the chlorine ions as they closely approach one another during edge dislocation motion on the $\{100\}\langle 110 \rangle$ system may be the limiting process. This type of interaction should satisfy the kinetics of a Peierls mechanism. Evans 1970 has observed that the deformation of CaF_2 along its secondary slip system requires a similar close approach of fluorine ions and has found a reasonable comparison of the experimental and theoretical Peierls parameters for this structure.

Thus, this data for KCl will be compared to the theoretical requisites for this type of mechanism. Dorn & Rajnak 1964 and Guyot & Dorn 1967 have reported the comparisons that are most satisfactory. The activation volume should be small, about $20b^3$, and independent of strain: these are satisfied, Fig. 3.36. The theory predicts a particular variation between temperature, and activation volume and thermal stress. A comparison of experimental and theoretical values is made in Figs. 3.39 and 3.40. They both agree within experimental error except at the lowest value of τ^* (this point has already been considered and can be excluded). The strain rate dependence becomes less as the temperature decreases.

If a Peierls mechanism is operating, the experimental value of the dislocation line energy should agree with theoretical calculations from lattice constants. For a Peierls mechanism the line energy per unit distance of the dislocation has

been given by Guyot and Dorn as

$$U_k = \frac{2ab}{\pi} \left(\frac{2ab\tau_p}{\pi b_0} \right)^{\frac{1}{2}}$$

for a sinusoidal Peierls hill where a = lattice spacing (the distance between the Peierls hills), b the burgers vector, τ_p the Peierls stress at 0°K and $2U_k$ is the energy required to nucleate the pair of kinks to surmount the Peierls hill at 0°K . Substituting ΔH_0 gives the experimental value 1.2×10^8 eV/cm for b_0 . Huntington, Dickey and Thompson calculated this line energy for NaCl as 0.6×10^8 eV/cm. The order of magnitude agreement reflects the similarity between KCl and NaCl and the reliability of the theoretical and experimental calculations.

Li 1967 has shown that m^*T is a constant as the temperature approaches 0°K and for a Peierls mechanism

$$m^*T \longrightarrow \frac{2U_k}{2.303K}$$

where K = Boltzmann's constant. Fig. 3.33 shows that there is a linear relation between $1/m^*$ and T for low temperatures and this gives a value of $2U_k = 0.7 \pm 0.1$ eV. This is just below the experimental value for the total enthalpy of the obstacle (1.04 ± 0.17) eV and is sufficiently close to show the consistency between the experimental observations and the theoretical values for a Peierls process.

Thus, although all the other possible thermally activated obstacles cannot be systematically eliminated, the agreement between the experimental and theoretical parameters strongly indicates that a Peierls interaction provides the predominate thermal obstacles that limit dislocation velocity. A theoretical model exists that is consistent with this interaction: this involves the close approach of chlorine ions during dislocation motion.

The characteristics of the athermal work hardening are now considered. Particularly significant is the decreasing rate of work hardening as deformation proceeds i.e. the interactions become increasingly less effective the greater the strain.

There are 3 possible $\{100\}$ slip planes equally orientated to the stress axis but only one active $\langle 110 \rangle$ slip direction in each plane for $\langle 111 \rangle$ compression. (See fig. 3.41.) Consider the interaction of dislocations on any two of these planes. The intersection of b_1 and b_4 is given by

$$\frac{a_0}{2} [011] + \frac{a_0}{2} [10\bar{1}] \rightarrow \frac{a_0}{2} [110]$$

The junction dislocation is a pure edge dislocation on the primary $\{110\} \langle 110 \rangle$ system. Energetically this is likely to be a stable junction but it lies on a plane of zero resolved shear stress. Since this is the primary slip system the junction may move conservatively from local stresses especially if small lattice rotations occur.

The interaction of b_1 and b_3 is given by

$$\frac{a_0}{2} [011] + \frac{a_0}{2} [101] \rightarrow \frac{a_0}{2} [112]$$

The product is an immobile junction of a $\{110\} \langle 112 \rangle$ system. However, the energy of this junction is unlikely to be much less than that of its constituents so it may be expected to be easily dissociated by a small pile up. A similar conclusion applies to the combination of an edge and screw dislocation, b_1 and b_2 , on the same plane. (Evans 1967)

Intersection of an edge dislocation b_1 by a forest dislocation b_3 or b_4 simply forms a jog on the edge dislocation and is unlikely to be impeded.

A similar jog on a screw dislocation is of same type as the junction of b_1 and b_4 . Multiple cross glide produces probably larger jogs of the same type. Thus the rapid work hardening may be explained by the initial formation of weak obstacles which dissociate at higher stress, and small lattice rotations lead to slip on the primary system.

The decrease of work hardening rate as the temperature is increased is consistent with increased cross slip at obstacles reducing the effectiveness of obstacles and the rate of debris production at a particular strain. Transmission electron microscopy may elucidate further these dislocation interactions.

3.2.4 Comparison of Primary and Secondary slip systems.

For the plastic deformation of polycrystalline material there must be at least five independent slip systems - Von Mises criterion. Failure to satisfy this means that high internal stresses cannot be relieved at grain boundaries and eventually voids and cracks form to relax these stresses and fracture occurs. Groves and Kelly 1963 and Kocks 1967 have calculated that only two of the six $\{110\} \langle 110 \rangle$ slip systems of rock salt structure are independent. Thus deformation on these primary systems alone is not sufficient for the plastic deformation of polycrystals: this will only occur if slip takes place on a secondary set of slip systems. For the $\{100\} \langle 110 \rangle$ slip systems there are three independent systems. Slip on the secondary system requires much higher stress than on the primary system at a given temperature, thus the stress temperature graph for polycrystals may have a similar temperature variation to that of the secondary slip system. This suggests from the results for the yield stress of KCl on the $\{100\} \langle 110 \rangle$ system that poly-crystals might

become ductile around room temperature since yield stress of the secondary system decreases rapidly up to this temperature and is then approximately constant.

Stoloff, Lezius and Johnston 1963 have shown that their KCl polycrystals deformed plastically about 523°K . . Stokes found significant plastic deformation of NaCl polycrystals at 428°K at a slower strain rate ($5 \times 10^{-5} \text{sec}^{-1}$). Clearly these temperatures are both higher than the expected transition temperature from the secondary slip system. This discrepancy may depend on the relative purities of the single and polycrystals, particularly from contamination during the preparation of polycrystals. This extra impurity may have produced an athermal stress which raises the yield stress transition from thermal to athermal mechanisms for secondary slip to a higher temperature. Crack formation occurs mainly at grain boundaries thus this impurity effect may be enhanced by the segregation of impurities to these boundaries.

Aladag et al 1970, has suggested that the onset of macroscopic thermally activated cross slip may correspond to the beginning of plasticity in polycrystals rather than slip on $\{100\} \langle 110 \rangle$ system. From the temperature dependence of the start of stage III work hardening, which Hesse 1965 and Aladag suggest corresponds to thermal activated cross slip, an extrapolation indicates that cross slip will be completely thermally activated at around 900°K . This is consistent with the $\langle 111 \rangle$ compression result which show that slip on the secondary system does not directly control the onset of plasticity.

Alternatively, the ductile-brittle transition may be controlled by deformation on the $\{111\} \langle 110 \rangle$ secondary slip system. A similar set of experiments on single and polycrystal KCl doped with controlled impurity concentration may distinguish between these alternatives.

Gilman 1959 using torsional tests to deform single KCl crystals on the secondary $\{100\} \langle 110 \rangle$ system found at room temperature

$$\frac{\text{Yield Stress } \{100\} \langle 110 \rangle}{\text{Yield Stress } \{110\} \langle 110 \rangle} = 10.5.$$

$$\text{Yield Stress } \{110\} \langle 110 \rangle$$

In this work the ratio is 12.2 using compression tests.

Johnston and Nadeau 1964 have reported microhardness measurements on KCl from 273 to 673°K. They suggest that for bulk deformation around the indent, rather than cracking, Von Mises criterion must be satisfied. Thus hardness may be a measure of the ease of slip on the secondary slip systems. No sudden change in microhardness was observed in this temperature range. Thus these results are consistent with the athermal region of yield temperature plot of $\{100\} \langle 110 \rangle$ system obtained from the $\langle 111 \rangle$ compression tests. A more rapid increase of micro hardness would be expected below room temperature if the Peierls mechanism restricts dislocation motion.

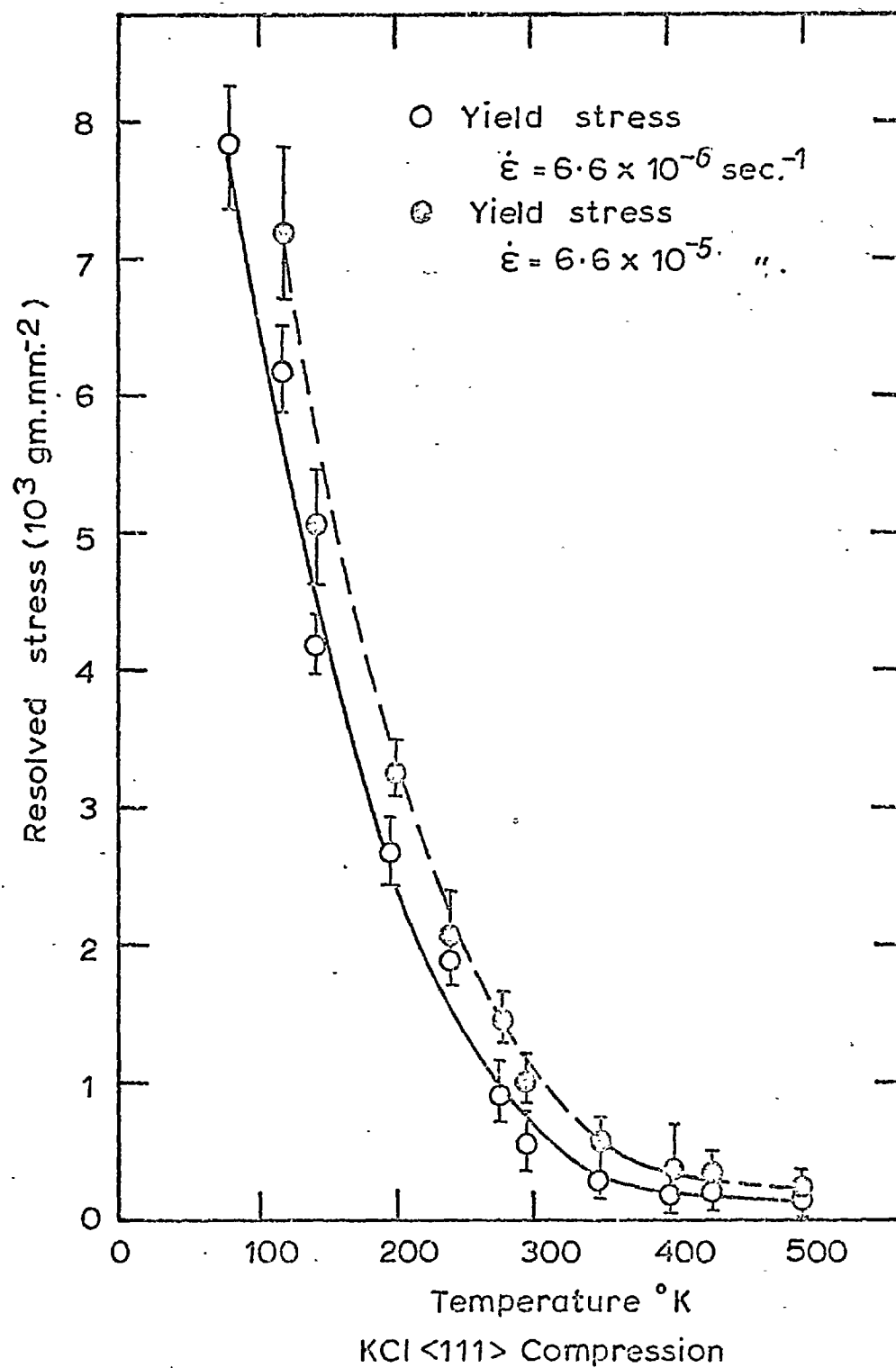


Fig.3.28. VARIATION OF YIELD STRESS WITH TEMPERATURE AND STRAIN RATE

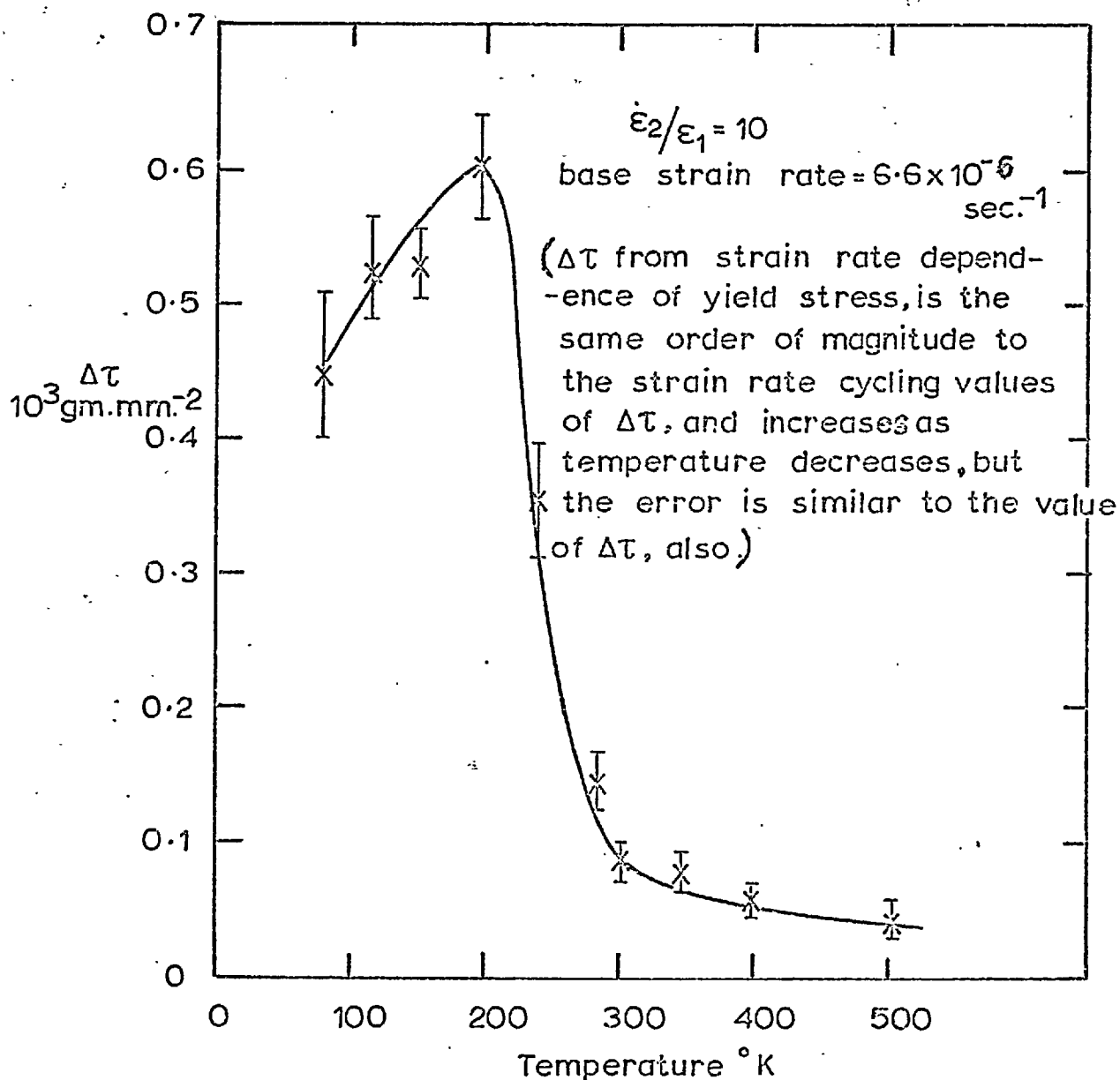
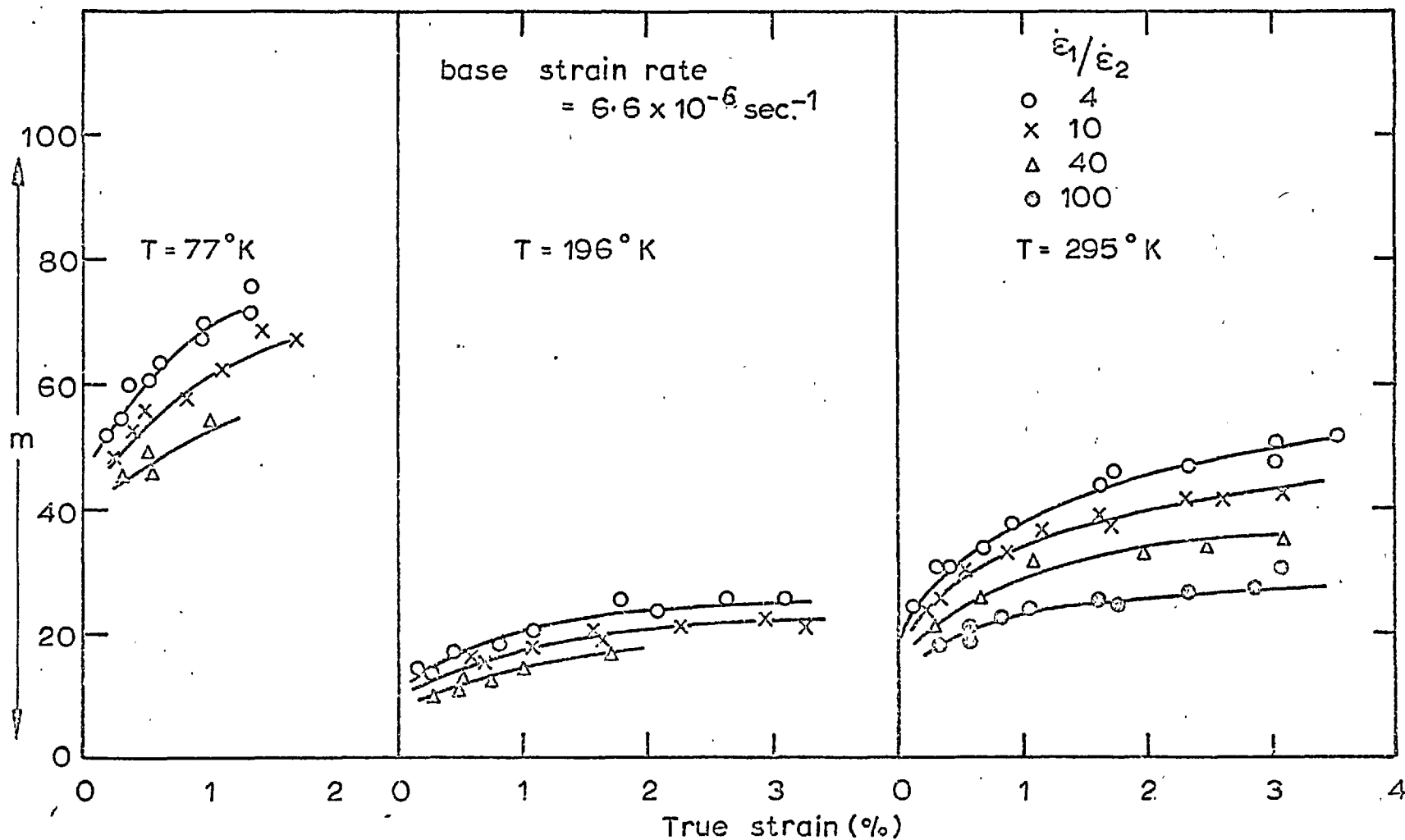
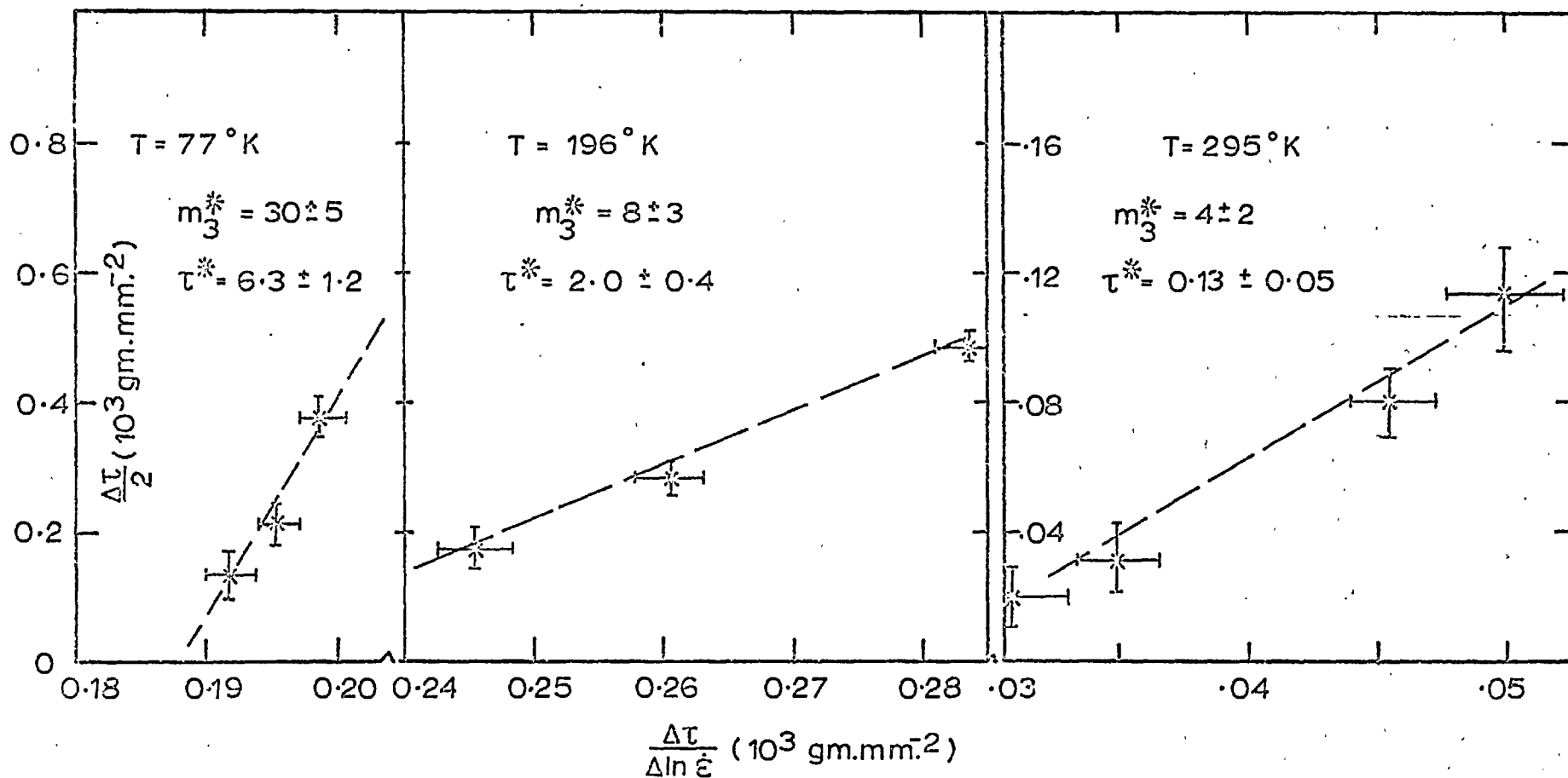


Fig. 3.29. TEMPERATURE VARIATION OF $\Delta\tau$ VALUES
 FROM STRAIN RATE CYCLING
 KCl $\langle 111 \rangle$ Compression



KCl <111> Compression

Fig.3.30. THE VARIATION OF $m = \left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \ln \tau} \right)_T$ WITH STRAIN FOR A RANGE OF STRAIN RATE INCREMENTS

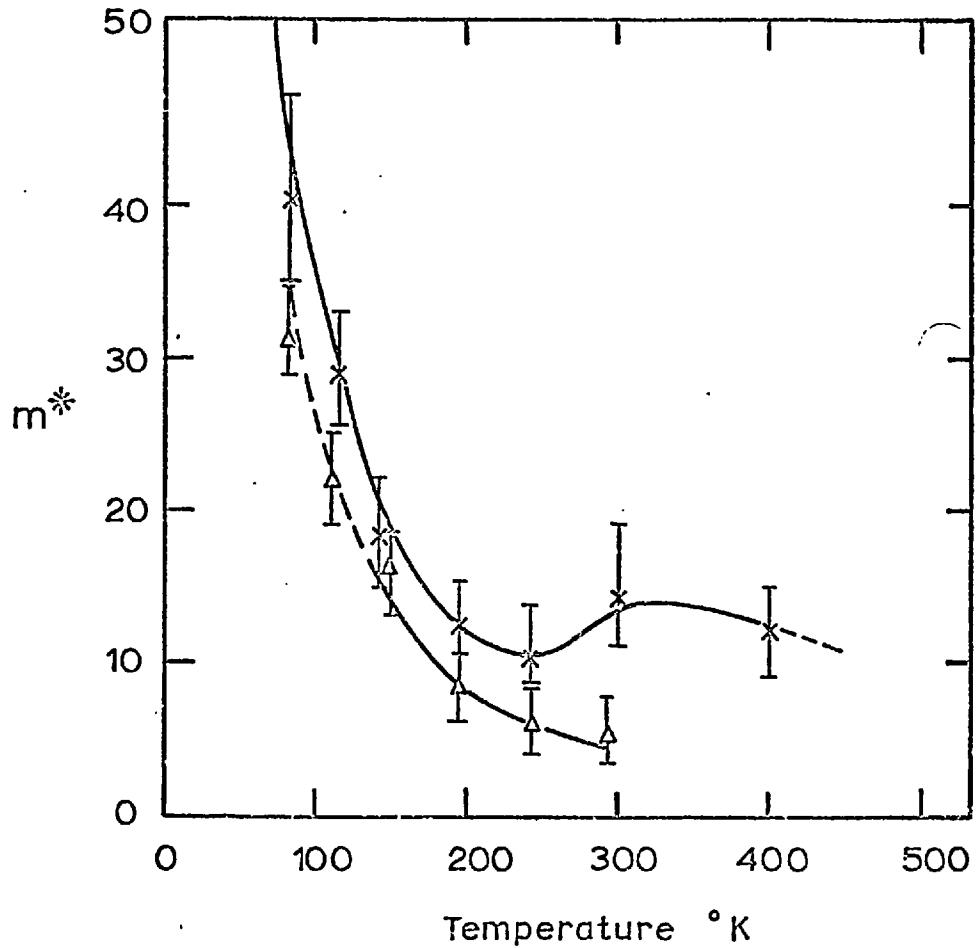


KCl $\langle 111 \rangle$ Compression

Fig. 3.31. PLOT OF $\Delta\tau/2$ AGAINST $\Delta\tau/\Delta \ln \dot{\epsilon}$ TO DETERMINE m_3^* AND τ^* FROM STRAIN RATE CYCLING TESTS.

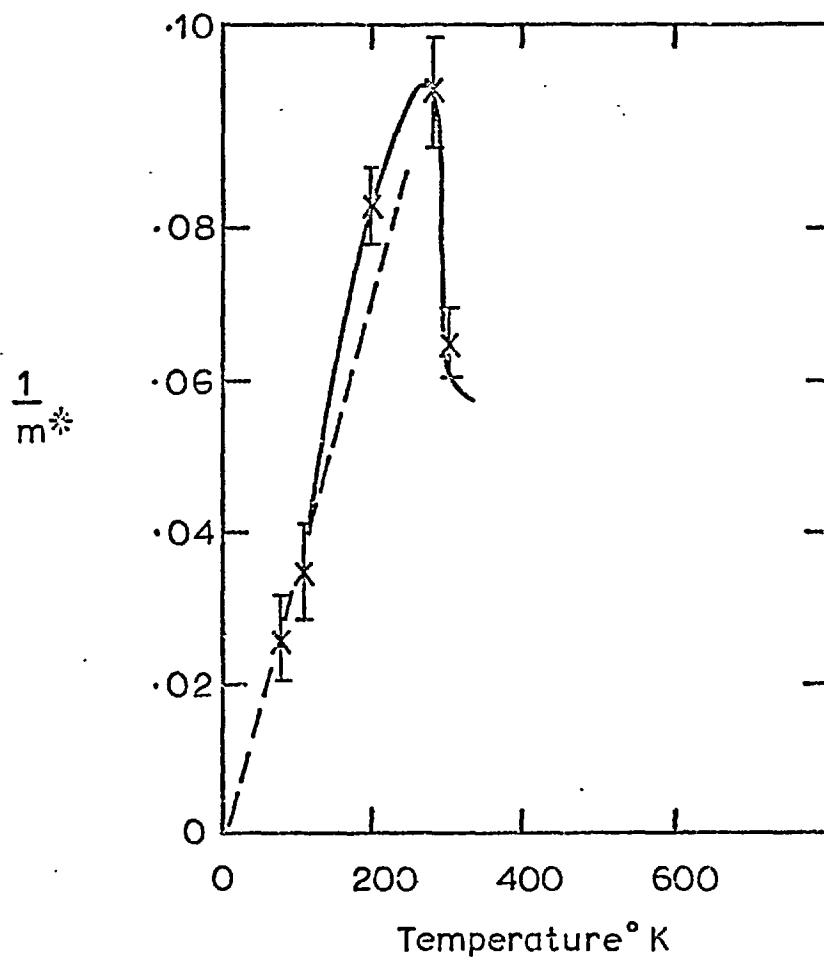
x extrapolation of m_2 values to $\varepsilon = 0, m_2^*$

Δ ΔT plot (eqn 3.7) m_3^*



KCl <111> Compression

Fig.3.32. VARIATION OF m^* WITH TEMPERATURE.



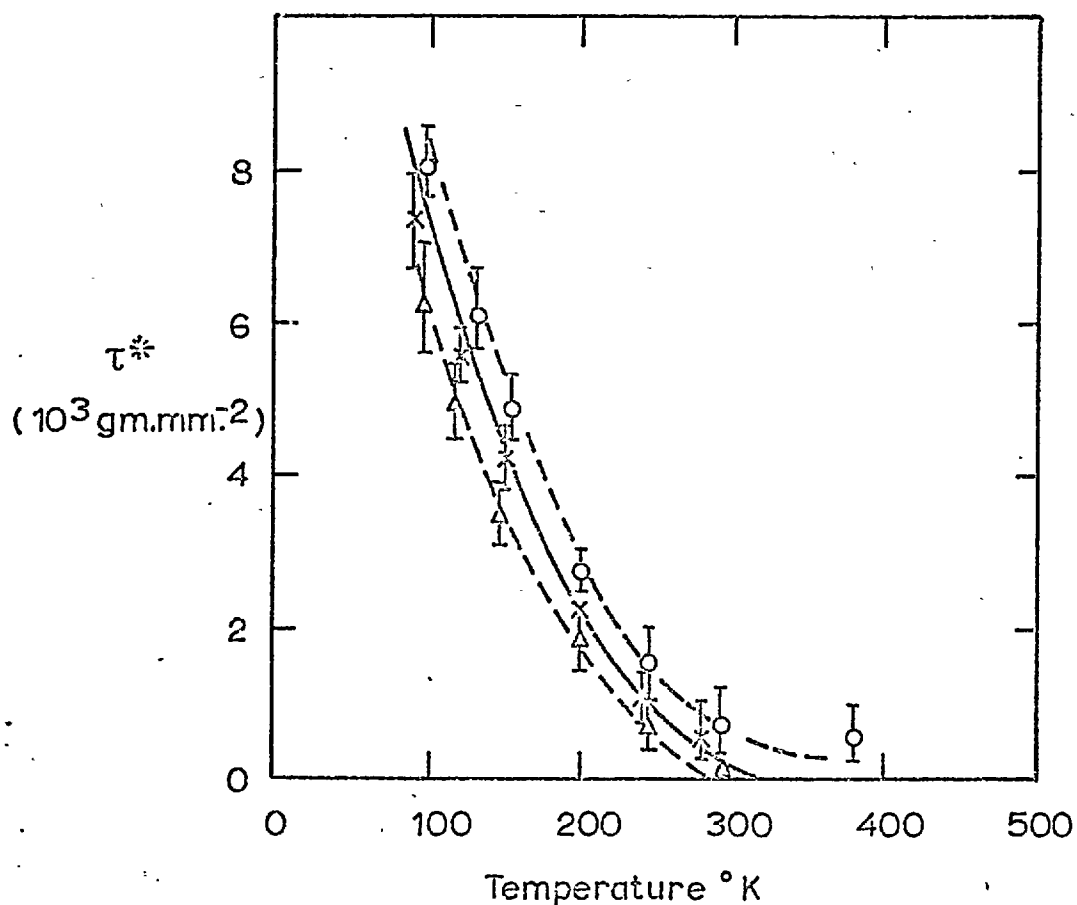
KCl $\langle 111 \rangle$ Compression

Fig. 3.33 THE VARIATION OF $1/m^*$
WITH TEMPERATURE
Below 200°K , $m^*T \approx 3500 \pm 500^\circ\text{K}$

$\Delta \tau^*$ from $\frac{\Delta \tau}{2}$ vs. $\frac{\Delta \tau}{\Delta \ln \dot{\epsilon}}$ graphs.

$\times \tau^*$ from yield stress vs. temp.

$\circ \tau^*$ from $\tau^* = \frac{\Delta \tau}{(\dot{\epsilon}_2/\dot{\epsilon}_1)^{1/m^*} - 1}$



KCl. $\langle 111 \rangle$ Compression

Fig.3.34. THE VARIATION OF THERMAL STRESS WITH TEMPERATURE

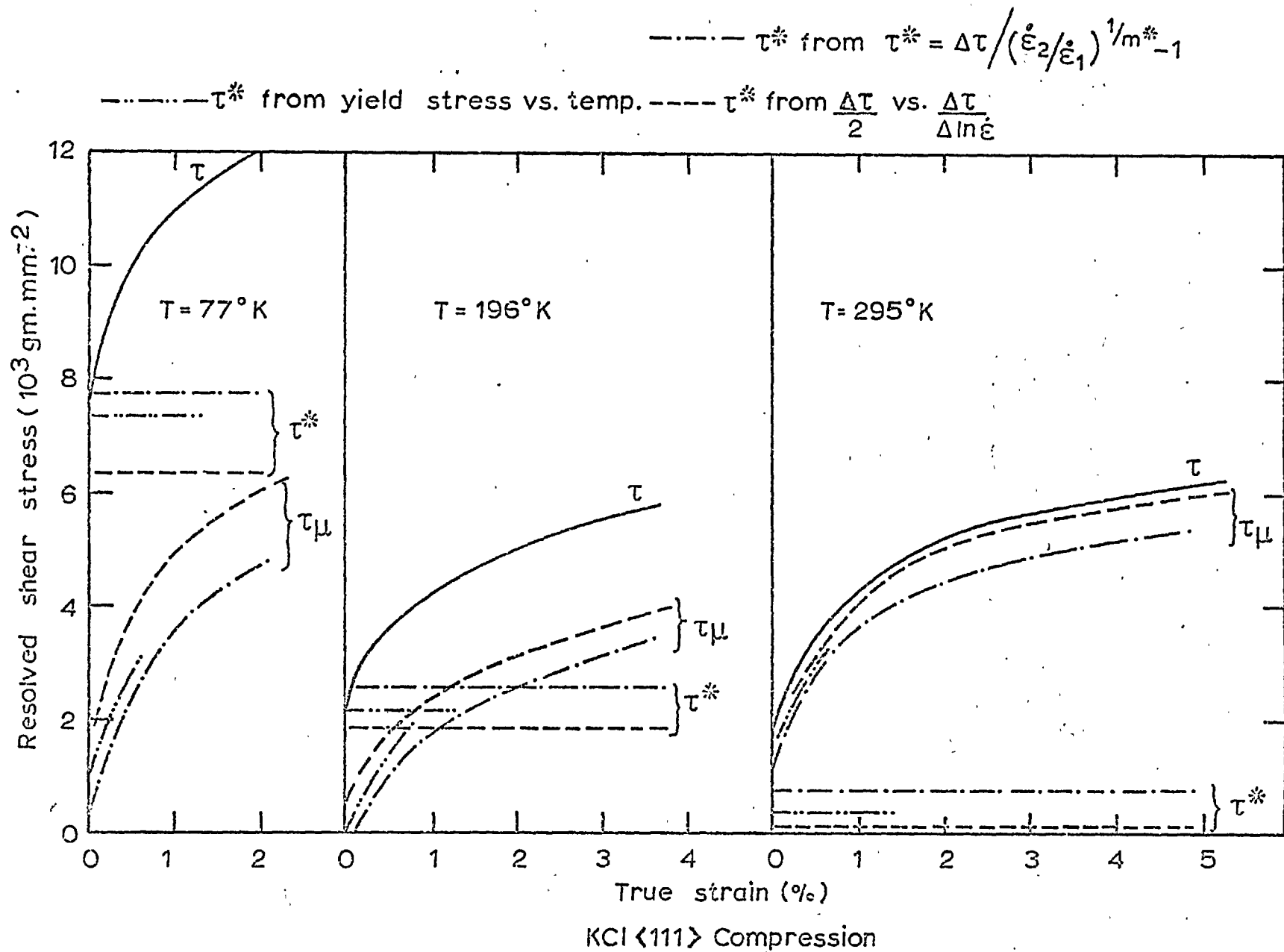
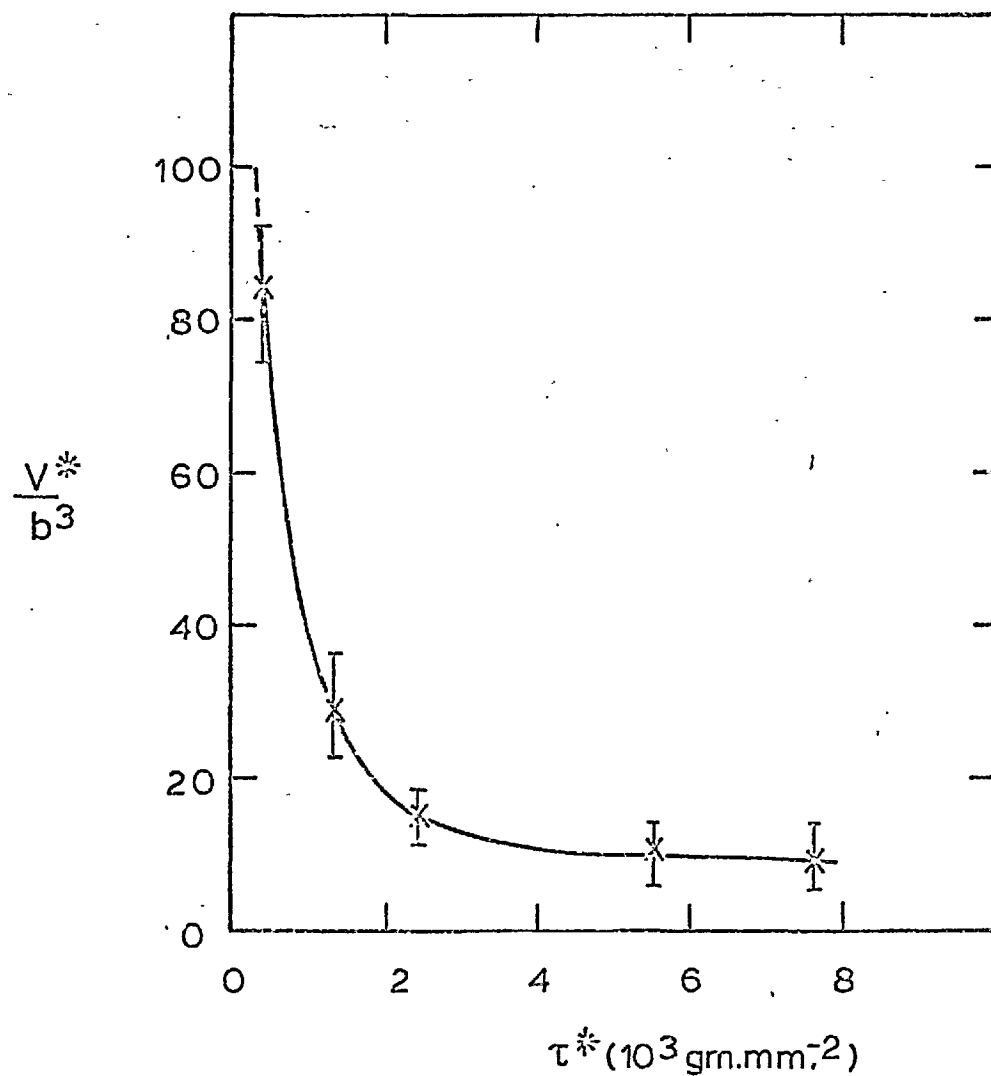


Fig.3.35. THE CONTRIBUTION OF τ^* AND τ_μ TO THE APPLIED STRESS τ AS A FUNCTION OF STRAIN



KCl <111> Compression

Fig.3.36 THE VARIATION OF ACTIVATION VOLUME
WITH THERMAL STRESS

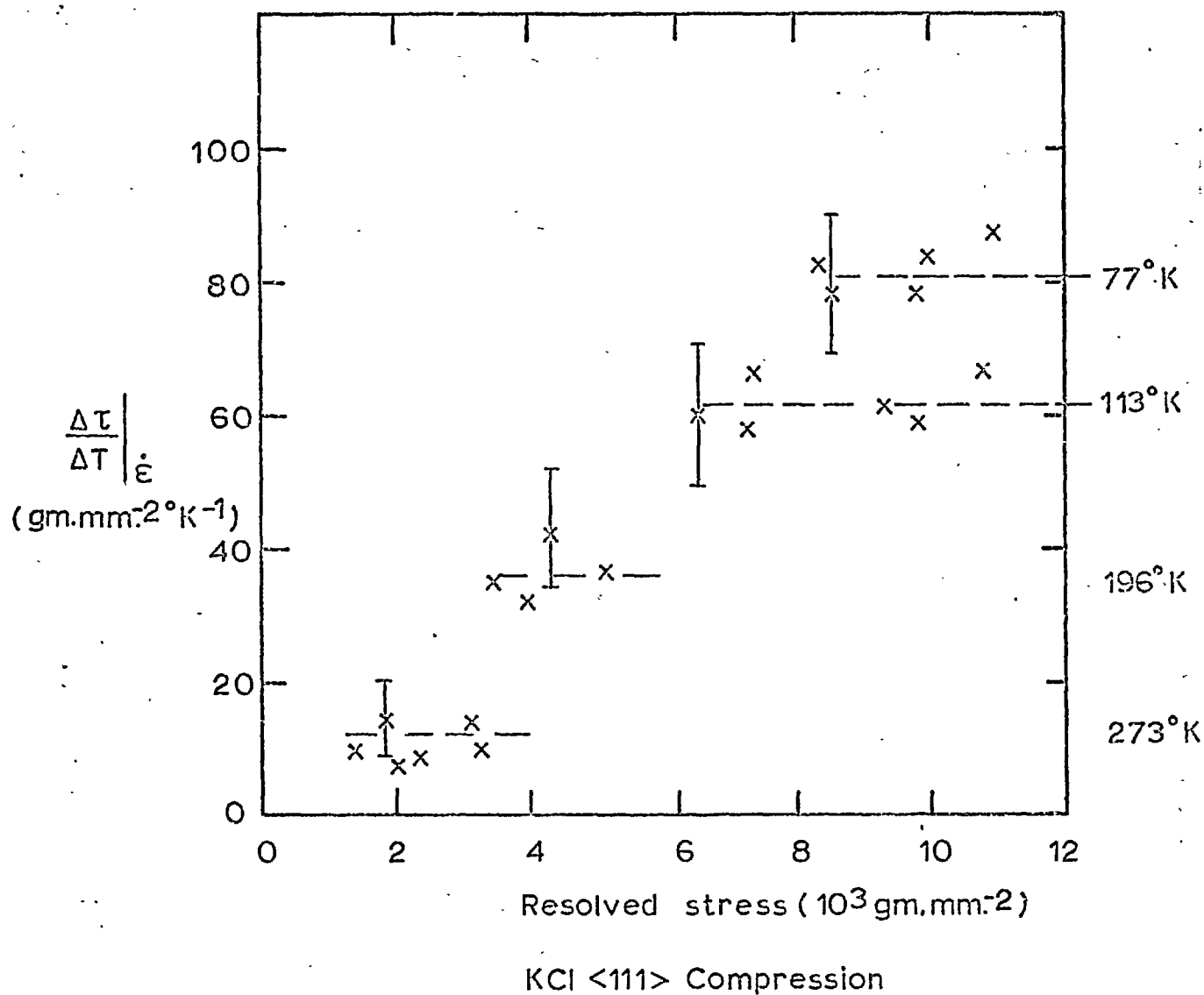


Fig.3.37 THE CHANGE OF STRESS DURING TEMPERATURE CYCLING TESTS AT CONSTANT STRAIN RATE

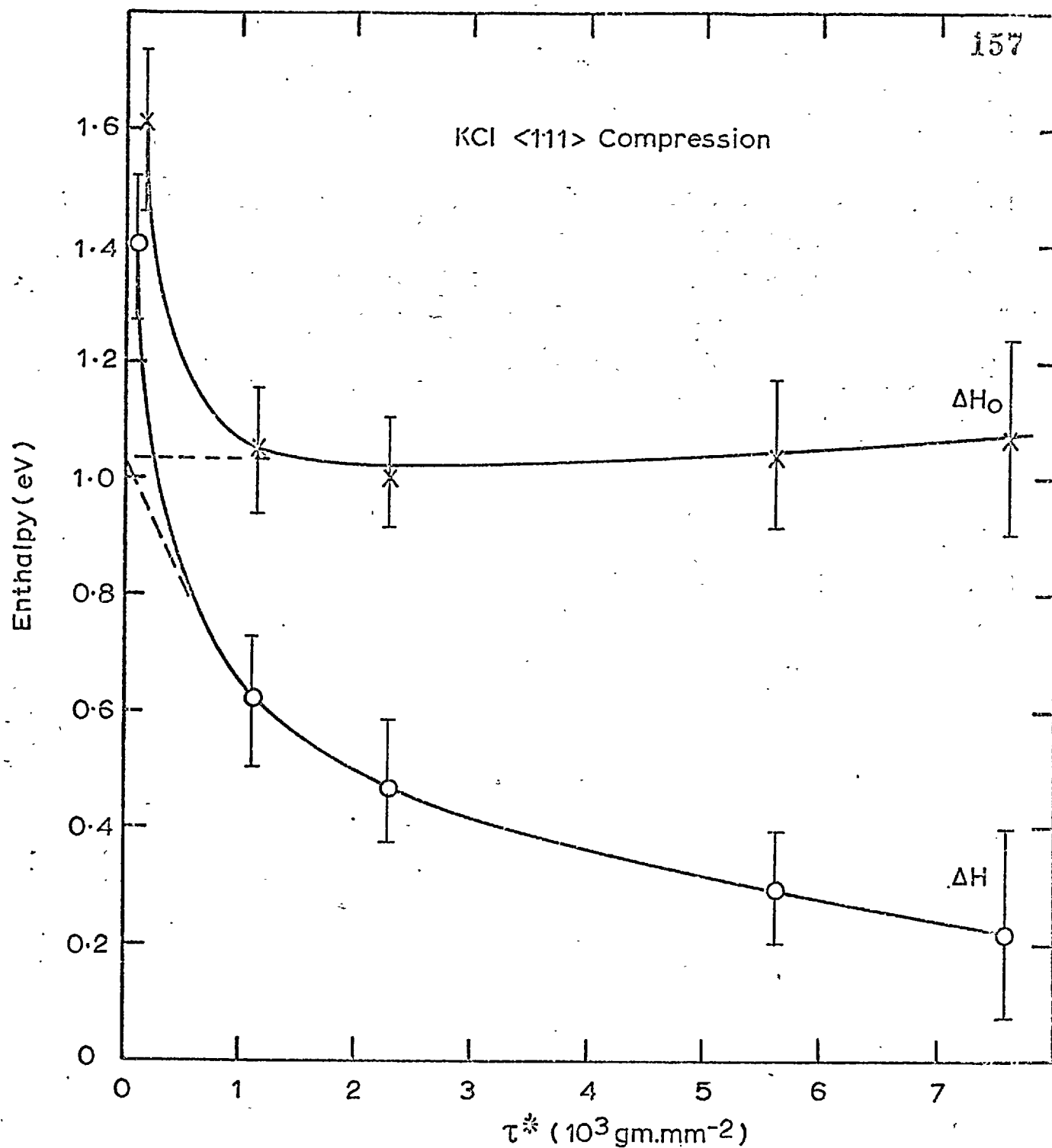
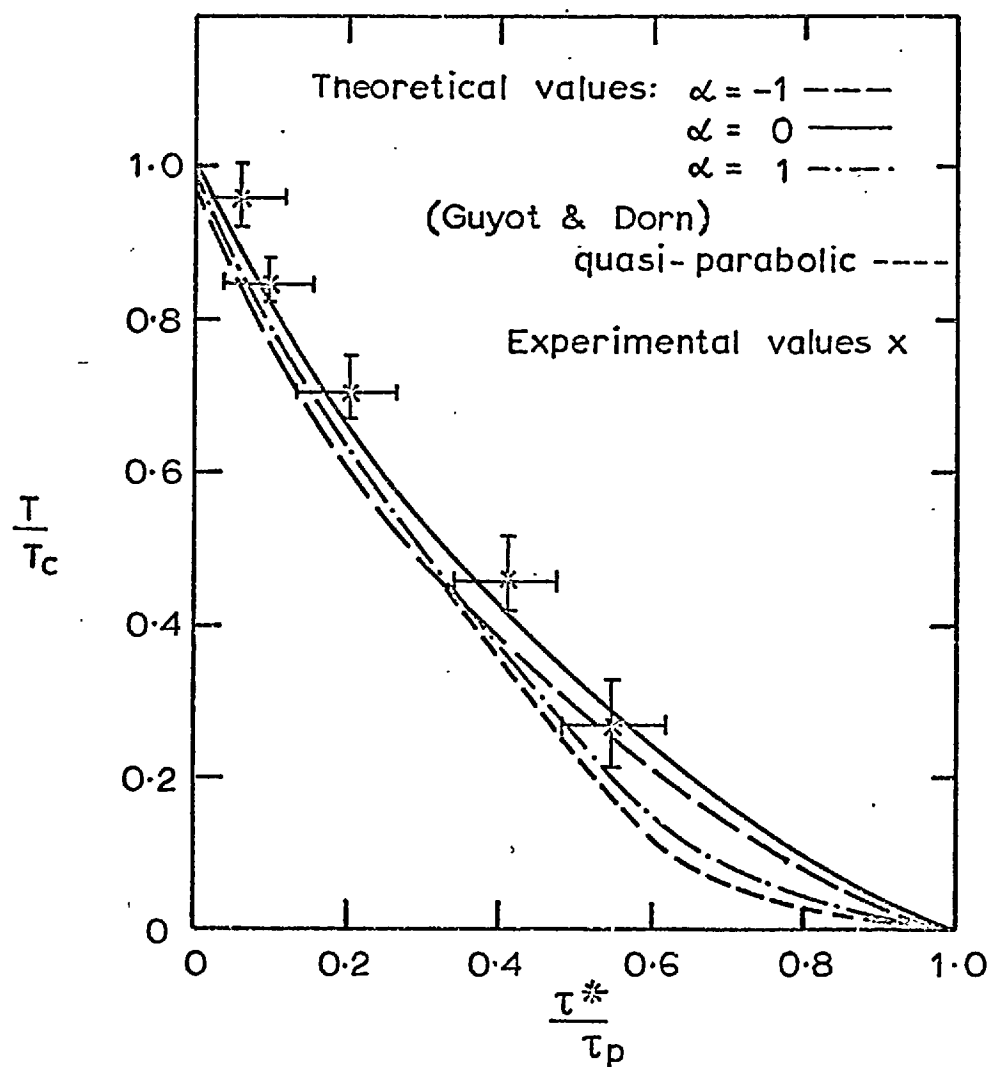


Fig.3.38. ENTHALPY AS A FUNCTION OF THERMAL STRESS



KCl <111> Compression

Fig.3.39. VARIATION OF THE YIELD STRESS WITH TEMPERATURE. COMPARISON OF EXPERIMENTAL VALUES WITH THE THEORETICAL VALUES OF A PEIERLS MECHANISM.

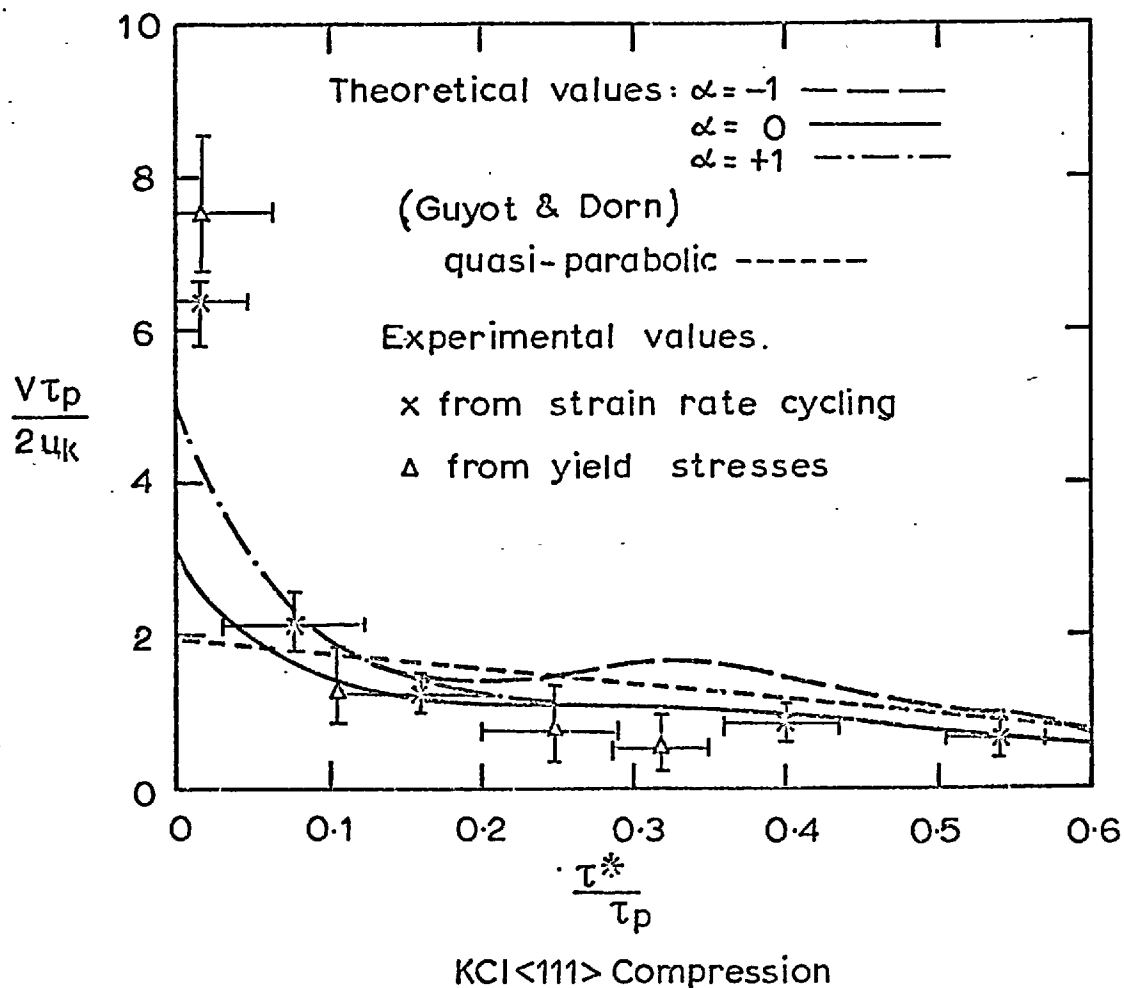


Fig.3.40. VARIATION OF THE ACTIVATION VOLUME WITH THERMAL STRESS. COMPARISON OF EXPERIMENTAL VALUES WITH THE THEORETICAL VALUES OF A PEIERLS MECHANISM

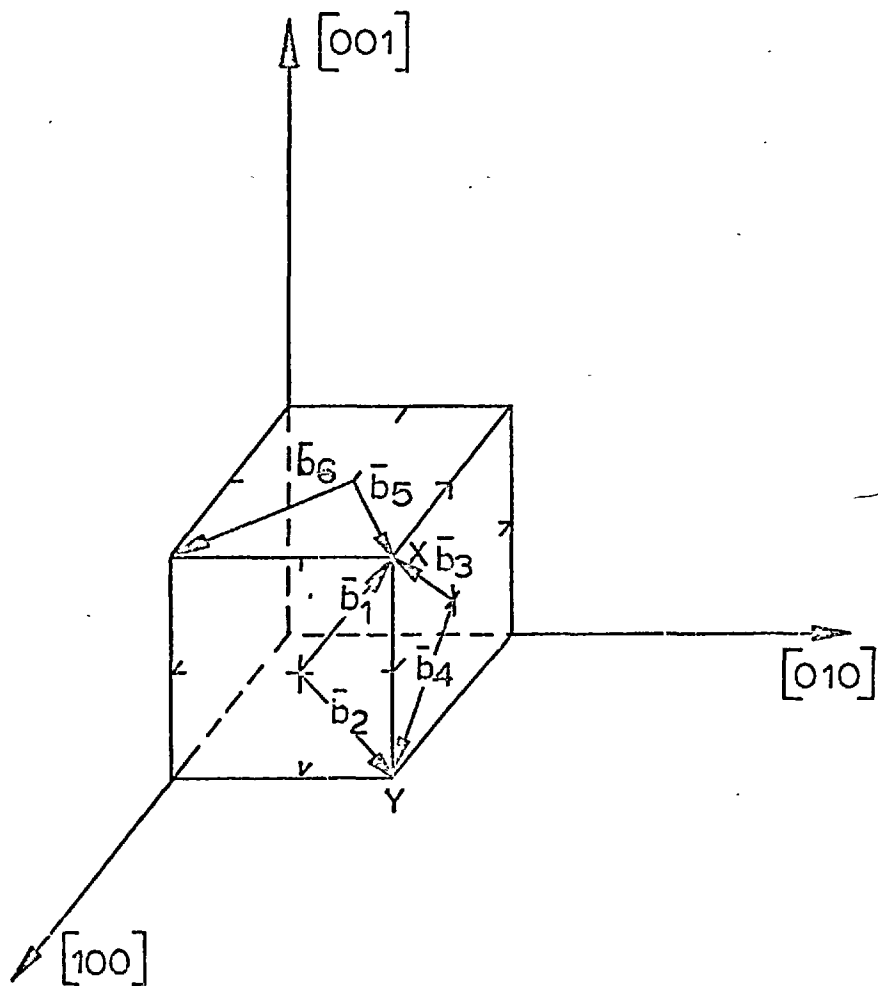


Fig.3.4 1 BURGERS VECTORS OF THE $\{100\} \langle 110 \rangle$ SLIP SYSTEM

TABLE 3H - Characteristics of various
activation processes

Mechanism	R(b)	l(b)	Comments
Peierls-Nabarro	1	1 - 20	V* independent of strain; various theoretical models for the stress dependence of activation volume are available; Ho related to the line energy of the dislocation.
Point defect drag	1	1 - 10 ³	Ho given by the migration energy of the point defect; usually applies preferentially to edge dislocation where binding energy is larger.
Point defect Interaction	10	1 - 10 ² *	V* must be related to the concentration of the point defect type controlling the deformation, it may depend upon strain if deformation alters the point defect concentration or distribution.
Dislocation Intersection	10	10 ³	V* must decrease (and ρ^* increase) as the forest density increases, i.e. it depends upon strain.
Non-conservative jog motion.	1	10 - 10 ³	Ho given by the self diffusion energy. Applies exclusively to the screw dislocation. V* may depend upon strain as the thermal jog spacing increases & intersection jog spacing decreases.
Climb	1	1	Ho given by self diffusion energy; operates exclusively at the edge dislocation.
Conservative jog motion	1	10 - 10 ³	Applies to the screw dislocation only; V* may depend on strain as for non-conservative motion.
Cross slip	1	10 - 10 ²	Applies to the screw dislocation only; often rate controlling when the dislocations are extended so that it includes a constriction term.
Intersection of Dislocation	1 10	10 ³	V* decreases as the dipole density increases with strain.

* Point defect concentration in required form 1 p.p.m.
Forest density 10⁹ cm⁻²
Dipole density 10⁹ cm⁻²

The Influence of Defect Structure on F Centre Production.

The analysis of deformation in Chapter 3 has studied the thermal stress. It is found to be independent of strain for both slip systems at all temperatures tested. Thus, work hardening is due to athermal obstacles. The stages of work hardening are similar to NaCl and the dislocation obstacles probably are of the same type, dislocation - dislocation & debris interactions.

There are few techniques available to measure the dislocation debris production. The total vacancy concentration can be measured as a function of strain by density measurements. F centre formation by ionising radiations is particularly sensitive to prior deformation of the crystal: the F enhancement has been suggested to be due to dislocation dipoles.

The aim of this chapter is to develop a new technique to be able to relate simple irradiation and F centre absorption measurements to strain and the athermal stages of work hardening determined in Chapter 3, through models that relate F enhancement to the presence of dislocation dipoles. These results can be compared to density measurements that indicate a higher rate of vacancy production during Stage II than Stage I work hardening.

If vacancy concentration can be related to F centre enhancement then irradiation of bicrystals may provide a useful technique to study the vacancy structure of grain boundaries.

4.1. F centre colouration enhanced by deformation.

4.1.1. General

Past work to investigate the effect of deformation on F colouration used strain, not stress, and deformed specimens with one cross section dimension much less than the other, typically 1 to 6 or 8.

This deformation must have occurred by plastic buckling with an anomalously long Stage I of low work hardening and debris production rate.

this shape of specimen this mechanism of deformation remains unknown due to the formation and action of stress concentrations, and the transition from Stage I to II occurs at high strains about 10% when the crystals are appreciably bent. If crystals are deformed to these high strains, the enhancement of colouration by the strain cannot be consistently measured. Consequently the changes of work hardening at these high strains are unlikely to be accurately monitored by the F colouration.

The aim of this section is to deform specimens of the dimensions used in Chapter 3: for these the deformation mode is reasonably understood and the transition from Stage I to II work hardening, with the corresponding increase of dislocation debris, is observed at strain of a few per cent. A comparison can then be made with longer specimens. Thus, it should be possible to correlate the F centre enhancement with the stress strain curve and also compare debris production rates for Stages I and II work hardening which is difficult using other methods.

If this correlation is obtained it provides valuable confirmation of the proposed mechanisms of dislocation motion and F centre enhancement.

4.1.2. F centre enhancement.

Dislocation debris has been recognised as the source of deformation enhanced Stage I colouration. The modification of this enhancement by certain electronic processes is still not clearly understood.

Seitz 1954 proposed that dislocations provide easy sites for vacancy and F centre formation. This model was ruled out mainly by Crawford and Young 1960 and Geudeke and Burgers 1963 they observed that the etch pits of dislocations failed to move after heavy irradiation. Nowick 1958 suggested that

plastic deformation dispersed precipitated impurity: 164
 it is this redissolved impurity which then gives an added impurity colouration. But if it was a Nowick type of mechanism giving F enhancement, then after deformation re-aggregation of impurity would be expected, causing a decrease of colouration with time after deformation. This has not been observed. Sibley & Russel 1967 Mitchell et al 1961 developed an equation to fit their experimental growth curves. They divided the initial vacancy concentration into two types: those vacancies initially present that are randomly distributed through the crystal would give a bulk colouration when irradiated: the other vacancies are concentrated in particular regions of the crystal. The numbers of the latter type are found to increase with plastic deformation of the crystal (in agreement with later work e.g. Chang 1965 F centres produced near dislocation dipoles). This approach is also confirmed by bleaching experiments by Schneider which require two rate constants for the decay of the F band suggesting there are two types of F centre. A similar approach has been made by Alvarez, Rivas and Levy 1969 who analysed the F colouration curve, $F(t)$, as a series of three saturating experimental processes which constitute Stage I of the curve (i.e. F centres formed by 3 different mechanisms) plus a linear term corresponding to F centre production during Stage II colouration

$$\text{i.e. } F(t) = a t + A_1 (1 - e^{-a_1 t})$$

where t is time and A and a are constants.

On deformation the F centre enhancement changed the saturation level of only one of these exponential processes. They suggested that this analysis was valid, not just fortuitous, and indicated that the variation

of the exponential with deformation was due to F centres formed in the region of dislocation structure. Their analysis could not explain the variation of the saturation level with strain.

Davidge and Pratt (1964) found that the deformation enhancement was no longer present after the crystal was annealed at 450°C : they concluded this temperature would anneal dislocation dipoles but not dislocations, so the deformation colouration was due to dislocation dipoles rather than the dislocations themselves. Agullo-Lopez 1967 irradiated a crystal at room temperature into Stage II coloration, then deformed the crystal. When it was re-irradiated the coloration has a new Stages I & II with the same shape as the previous colouration curve. These results were repeated by Sibley 1965. He found the enhancement of the new Stage I process was proportional to the plastic deformation and this enhancement then saturated as the dose was further increased. This suggests a finite number of vacancies has been introduced as debris by the dislocation interaction during deformation. These extra vacancies are gradually used up. If the debris had not caused enhancement, but was due to dislocations as Bauer & Gordon had concluded, it would have been harder to understand why such dislocations became used up and caused saturation. Thus Sibley proposed that deformation enhancement is caused by such vacancy pairs and clusters rather than isolated vacancies or dislocations. The deformation enhanced colourability also depends in magnitude on trace impurities. (This is not surprising, since Stage II colouration in undeformed crystals also depends on trace impurities).

If an F centre is close to a dislocation dipole in deformed crystal, the stress field of the dipole will

influence the energy levels of the F centre electron, causing the characteristic wavelength of the F band to change by a very small amount. Chang (1965) has observed this change. Using the Drickamer (1960) calculation of the wavelength variation with applied stress to give the stress field from the dipole at the F centre site, Chang determined the position of the dipole with respect to the F centre for a dipole of particular width. Such a treatment gives the F centre situated a few Burgers vectors away from the dislocation core, slightly above the slip plane, in the compression region of one of the dislocation pairs that constitute a dipole. Chang also found that crystals deformed at liquid nitrogen coloured twice as fast as crystals deformed at room temperatures. The critical shear stress for such deformation at 77°K is a factor of two higher than deformation at room temperature. He reasons that dislocation theory gives the average dipole spacing proportional to the inverse of the resolved shear stress, so the crystal with twice the resolved shear stress contains twice the dipoles, i.e. colouration is well related to dipole influence.

Sibley & Russel 1964 have considered the possibility of a purely electronic process to account for the deformation enhanced F centre concentration by the dislocation jogs trapping holes. The radiation is believed to produce halide vacancy-interstitial pairs; trapping holes at jogs increases the density of free electrons, increasing the number of vacancies that traps electrons and reducing recombination of vacancy and interstitial. Results from flow stress measurements to detect the extra hardening of more interstitials were inconclusive.

Bauer and Gordon (1962) showed the deformation enhanced colouration is temperature dependant. Neither they nor Rabin & Klick (1960) could measure any enhancement at 77°K but both Royce and Smoluchowski (1964) and Sibley and Russell (1964) have subsequently been able to measure small enhancements at lower doses and a suppression of late stage colouration.

Sibley, Nelson & Crawford (1965) showed that deformation colouration is impurity dependant. Their Stage I F colouration of pure crystal was 4×10^6 per cm^{-3} which was half the 8×10^{16} vacancies per cm^3 estimated to be introduced by 1% strain in the crystals of Davidge & Pratt (1964) i.e. all the enhancement might be caused by vacancies introduced by the deformation. However, calcium doped crystal has a much larger deformation enhanced colouration than lead doped crystal. An increase of deformation might be expected from doped over pure crystals since the impurities may form obstacles which raise the dipole formation and flow stress. It was found that for similar impurity content and flow stresses, the calcium doped crystal gave a much greater deformation enhancement than lead. Thus, there is probably an electronic influence from the impurity on part of the colouration process.

Summarising, dislocation debris is probably the main cause of deformation enhanced colouration, acting as vacancy sources or easy regions for vacancy production. This may then be modified by electronic traps.

4.1.3. Experimental

(a) Experimental technique.

The specimen preparation and compression . . .

jig have already been described in Chapters 2 & 3. Colouration at $295 \pm 3^\circ \text{C}$ is obtained using γ -rays from a Co^{60} source (see Fig. 4.1) γ -rays have low absorption coefficient in crystals giving a uniform colouration and have almost monochromatic energy about 1.2 MeV (low energy X-rays, 0.8 MeV, have higher absorption which results in a greater colouration in the surface regions of the crystal than the bulk).

The Co^{60} source is divided into six vertical rods: specimens are placed in holders giving reproducible positions along the axis of these six rods. Here there is maximum intensity from the source 1×10^6 Rads/hr (Siddiqui 1969) and is approximately uniform, so that intensity is not so dependant on specimen position as it would be outside of the circle of six rods, where the intensity is proportional to the square of the distance away from the source. During irradiation specimens are contained in thin walled glass tubes with plastic caps: these prevent surface contamination and the outside of the tubes is coated with photographic black paint to prevent bleaching of the crystal. The spectrophotometer specimen holders are designed so that the specimen can slide from the glass tubes directly into place without handling the optical surfaces.

After deformation the surfaces of the specimen are no longer planar due to slip steps and the crystal becomes bowed or barrel shaped at higher strains. Consequently the thickness needs to be measured with a travelling microscope parallel to the direction of absorption making measurements at different points along the length of specimens; the use of a micrometer does not give an accurate measurement of thickness after deformation and damages the specimen surface.

Before irradiation the absorption coefficient of a deformed crystal is the same as that of an undeformed specimen, thus the large number of slip steps on the surface do not cause significant absorption and need not be removed by polishing.

Optical absorption is measured as a function of wavelength using a Perkin Elmer 450 Spectrophotometer. It was necessary to have greater resolution of the spectrophotometer for absorbance levels above 2. This was achieved by using a Wayne Kerr frequency voltmeter. The spectrophotometer incorporates a constant velocity 60 cycles per sec beam chopper in the light that passes through the specimen to the photomultiplier. The voltmeter can be adjusted to this frequency and acts as a very sensitive pulsed amplifier to measure the output from the photomultiplier tubes. This modification is calibrated with a series of filters of high known absorbances. Specimen absorbance readings are made six minutes after irradiation. This is sufficient time to allow for any F' centre decay but still one quarter of the time period that elapses before thermal decay of the F band can be noticed. Part of the M centre band, from two bound F centres, lays partly under the F band; although much smaller than the F band, its height also varies with strain. A suitable correction is the subtraction of the height of the M centre at 825 $m\mu$ from the F band peak height. (e.g. Sibley et al 1965).

(b) Results.

The effect of deformation for different strains on the F band growth curve is shown in Fig. 4.2. Stage I is enhanced by the deformation but not Stage II which has a linear dependance on dose similar to the undeformed crystal.

The late stage colouration is extrapolated to zero dose to determine the magnitude of Stage I colouration. The increase of these intercepts with strain is plotted in Fig. 4.3 for specimens with different dimensions. None of these curves extrapolates exactly to zero enhancement at zero strain. A specimen compressed to its yield stress also shows a small F centre enhancement. This effect is probably due to localised dislocation motion and debris production prior to macroscopic yield.

The deformed crystals with one cross section dimension much less than the other (e.g. specimen size $8 \times 8 \times 1$ mm) or with high h/d ratio (e.g. specimen size $30 \times 5 \times 2$ mm, $h/d = 6$) have an F band enhancement that increases with strain up to 8 % at a decreasing rate. Inconsistent results are obtained at higher strains. Specimens with one cross section dimension much less than the other is typical of the specimen shapes reported by previous authors who have investigated the influence of deformation on F colouration. As indicated in Chapter 3, the stress strain curve for this type of specimen has a long single stage of low work hardening rate: plastic buckling of the specimen takes place above 3% strain.

For crystals with the specimen dimension used for the majority of compression tests in Chapter 3, $h/d = 3$, the F centre enhancement is larger for the same strain than for the thinner specimens. At small strains less than 2% the strain dependence is similar to the thinner crystals but by 3% the rate of enhancement is considerably greater for the specimens with $h/d = 3$. Above 6% strain for these specimens the absorption is beyond the sensitivity of the spectrophotometer. Specimens with the same cross section as the $h/d = 3$ specimens, but longer length, $h/d = 4$,

have an F centre enhancement consistently below that for specimens of $h/d = 3$ and above that for the thinner specimens. The strain dependence increases more rapidly than the thinner specimens only above 4% strain.

The enhancement of Stage I F centre formation by compression in $\langle 111 \rangle$ direction for a similar set of deformation specimens with $h/d = 3$ is given in Fig. 4.4. as a function of strain. The enhancement increases rapidly at low strains but then has a decreasing strain dependence.

(c) Discussion.

For compression specimens with $h/d = 3$ there are three stages of work hardening with a transition between Stages I and II at 3% strain (Chapter 3). The second stage is of much higher rate than the first probably due to the increasing rate of debris production. If dislocation debris enhances F centre formation, then the increasing rate of debris production at 3% strain accounts for the observed increasing rate of F centre enhancement at this strain. The F enhancement graph has a similar strain dependence to that reported by Davidge 1964 for bulk density changes (e.g. for 6% strain, bulk density gives a vacancy pair concentration of 5×10^{17} per cm^3 , whereas Stage I F enhancement is $(5 \pm 2) \times 10^{16}$ per cm^3). Thus these results confirm that the enhancement by deformation of F centre production is caused by dislocation dipole and debris and there is an increased rate of dislocation debris during Stage II of the stress strain curve. Longer specimens of the same cross section i.e. $h/d = 4$ have stress strain curves with a lower rate of work hardening at all strains than for $h/d = 3$ specimens and a Stage I that extends to higher strains (Chapter 3). A comparison of the F centre enhancement as a function of strain between the specimens with $h/d = 3$ and 4, Fig. 4.3, corresponds to the differences between the stress strain curves. For the longer specimen both

the F centre density and the stress - strain curve remains consistently lower than that for the $h/d=3$ specimens. If F enhancement is due to dislocation dipoles, this result suggests that the rate of dislocation debris production is less for crystals with a higher ratio of h/d . The stress strain curves of thin specimens and those with dimensions $h/d=6$ have only a single stage of work hardening below 10% strain, the work hardening rates are lower than for the specimens with $h/d = 3$ as above. Thin specimens also have lowest F centre enhancement as a function of strain without a more rapid increase of the F enhancement at higher strains comparable to that observed for the specimen with $h/d = 3$. This indicates that this increase in enhancement for the specimen with $h/d = 3$ is the result of the increase of dislocation dipole production in Stage II.

Thus the F centre enhancement for $\langle 100 \rangle$ compression tests follows qualitatively the work hardening stages of the stress strain curves for the specimens of different dimensions, giving strong support to models that relate (a) work hardening to dislocation debris and dipole production and (b) F centre enhancement by deformation to the debris and dipoles produced in the crystal.

The steep increase of the F centre enhancement for specimens strained in the $\langle 111 \rangle$ direction Fig. 4.4 suggests the rapid production of dislocation debris at low strains, if a similar process is responsible for F centre enhancement. The deformation tests in Chapter 3 show that there is a steep athermal work hardening rate at low strains; this is also consistent with the rapid production of dislocation debris during deformation at low strains. However, the unequivocal

correlation of F centre enhancement to dislocation debris and athermal work hardening cannot be made for the secondary slip system until the work hardening mechanisms have been more conclusively determined.

4.2. F centre colouration enhanced by boundaries in NaCl

4.2.1. General

The use of alkali halide crystals for radiation dosimeters has been a field of considerable research recently. Radiation produces electrons and holes. The stable trapping of these by point defects can be used to record quantitatively the radiation received. Subsequent heating of the irradiated specimen releases the electron or holes from their traps and recombination can take place with the radiative emission of visible light. The intensity of this thermoluminescence is found to be directly proportional to the dose of irradiation.

This technique has not been successfully applied to pure single crystals of LiF. Thus the existence of traps has been associated with the influence of certain impurities. However, recently the Harshaw Chemical Company has marketed as TLD material, very pure LiF powder hot pressed in billets. This has been found to give much more reproducible results for dosimetry since it does not depend sensitively on impurity concentration. The polycrystalline structure must provide sufficient trapping centres to stabilise electrons, holes or interstitials, since single crystals themselves give no traps.

The type of trapping centre and the structure of grain boundaries are not well known. This section will use bicrystals of NaCl to investigate the effect of F colouration of these interfaces.

4.2.2. Experimental

(a) Experimental Technique

The growth and preparation of bicrystal NaCl specimens with the boundary at right angles to the direction of absorption measurements is explained in Chapter 2 and the method of irradiation and absorption measurements is given in the previous section.

(b) Results

The bicrystals used are pure tilt boundaries i.e. zero twist. No twist of the cleavage plane is observable when a bicrystal is cleaved through a plane at right angles to the boundary. Such boundaries are characterised solely by the angle of tilt.

The F centre colouration curves for irradiated bicrystals are given in Fig. 4.5. The curves are plotted for different angles of tilt. Stage I colouration is increasingly enhanced as tilt angle increases while Stage II remains similar to the single crystal rate. If the linear colouration of Stage II is extrapolated to zero dose for each crystal, the enhancement of Stage I from the tilt boundary can be obtained by subtracting the single crystal intercept. The boundary region used is taken from the top of the boule near the seed for each angle of tilt so that impurity concentration should be identical. To determine this enhancement due to the grain boundary region two single crystal specimens, of the same thickness as those containing the boundary, are taken from the adjacent single crystal on both sides of the boundary. This enhancement due to the boundary is plotted in Fig. 4.6 as a function of the angle of tilt of the boundary. Absorbance is used instead of absorption coefficient due to the problems associated with determining an effective thickness of the grain

boundary region consequently specimens are polished to the same thickness (Chapter 2). Fig. 4.6. shows that the F enhancement is not so sensitive to tilt angle below 20° as above this angle.

At low doses the tilt boundary can be seen as a darker region of the crystal when viewed end on, so the increase of colouration is due to the boundary rather than some change in bulk colouration.

(c) Discussion.

The F colouration enhancement of bicrystal boundaries may be due to the structure of the tilt boundary or an impurity effect.

During the preparation of polycrystalline specimens from powder, water vapour may contaminate the surface of the grains. It has been suggested by Gibbon 1966 that F centre enhancement of polycrystals is due to these hydroxyl ions at the grain boundaries. By growing bicrystals from the melt this possibility can no longer arise. Segregation of cation impurity to grain boundaries is unlikely to cause the observed F centre enhancement since Sibley 1967 has shown that levels above 50 ppm are necessary to give impurity enhancement. Thus F enhancement by impurities is most unlikely.

The increase of F enhancement with the angle of the tilt boundary is given in Fig. 4.6. There is a slow increase of F enhancement at low angles of tilt. This is consistent with electron microscope observations which show low angle boundaries consist of a dislocation array only (Mott & Gordon 1964). At larger tilt angles diffusion experiments (McQuhrie 1969) indicate an increasing vacancy concentration, suggesting an island model of grain boundary structure i.e. islands of good atomic matching surrounded by areas of mismatch proposed by Mott 1948 and modified by Gifkins 1967.

These vacancies may lead to F centre enhancement in a manner similar to the influence of the vacancy sheets of dislocation dipoles.

The unexpected feature of the F enhancement is the continuing increase of enhancement for tilt angles above 45° . Since a 60° tilt boundary, for instance, should be equivalent to a 30° boundary, the F enhancement should be the same at both these angles. Thus, bicrystal growth by this technique may be introducing an increasing vacancy concentration. No bubbles or cloudiness are visible in these high angle boundaries. Thus further investigation by electron microscopy may determine more precisely the grain boundary structure.

4.3. Conclusions

This chapter has well related the rate of dislocation dipole production during the athermal work hardening stages observed in Chapter 3 to corresponding increases in F centre enhancement of deformed crystals as a function of strain. This gives support to the models that (a) relate work hardening leading to dislocation dipole production, particularly confirming an increased rate of dislocation intersection during Stage II work hardening, and (b) F centre enhancement by deformation is due to the debris and dipoles. This confirms previous observations measuring crystal density as a function of strain. (Davidge & Pratt 1964) which is a more sensitive technique for measuring absolute vacancy concentrations particularly at higher strains.

Irradiation of grain boundaries is shown to be a useful technique to study grain boundary structure. It is suggested that F enhancement from boundaries is due to the vacancy concentration within the boundary. The F centre enhancement can then be related to the existing models of grain boundaries, dislocation arrays at low angles and an island model at high

angles. The results indicate that further investigation is needed to understand the anomalous structure of high angle boundaries grown by the twin seed method.

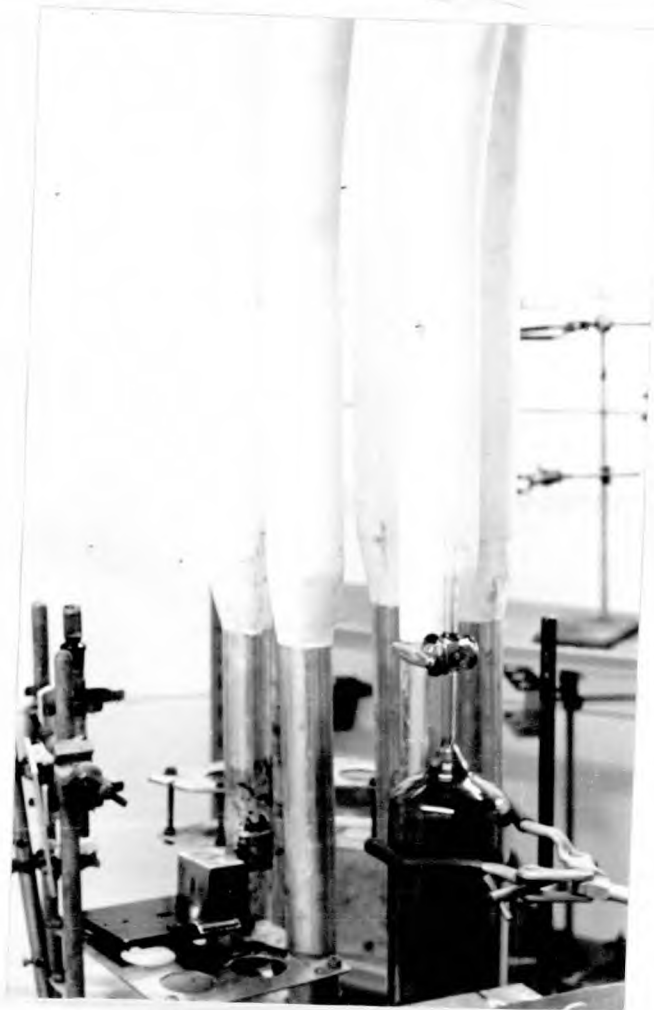
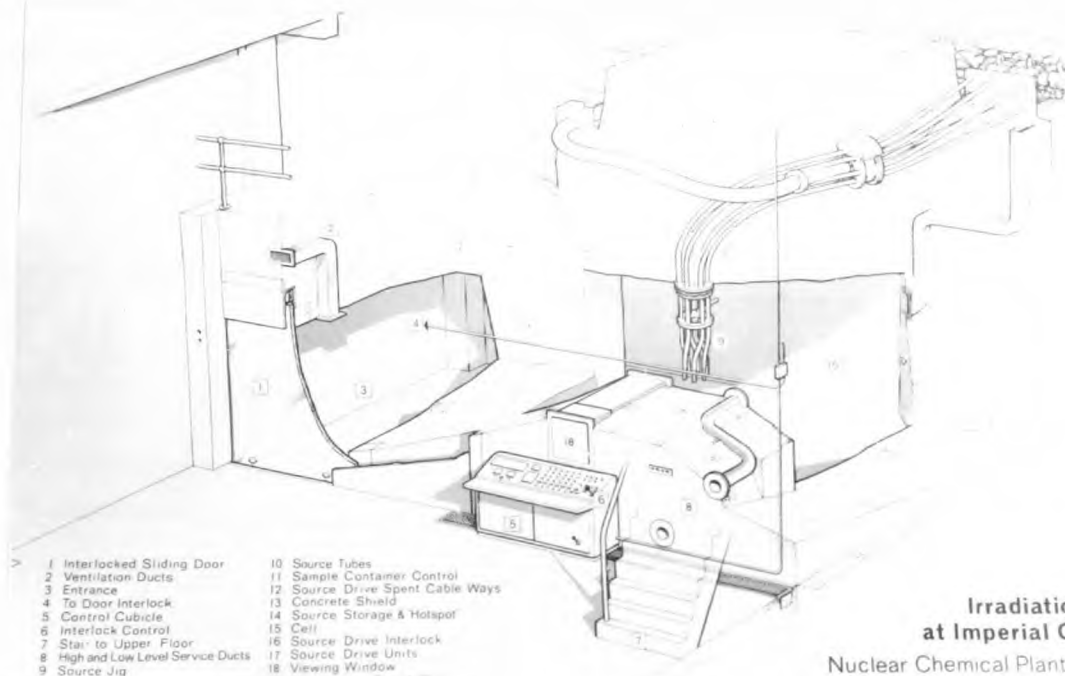


Fig 4.1
 γ -irradiation unit.

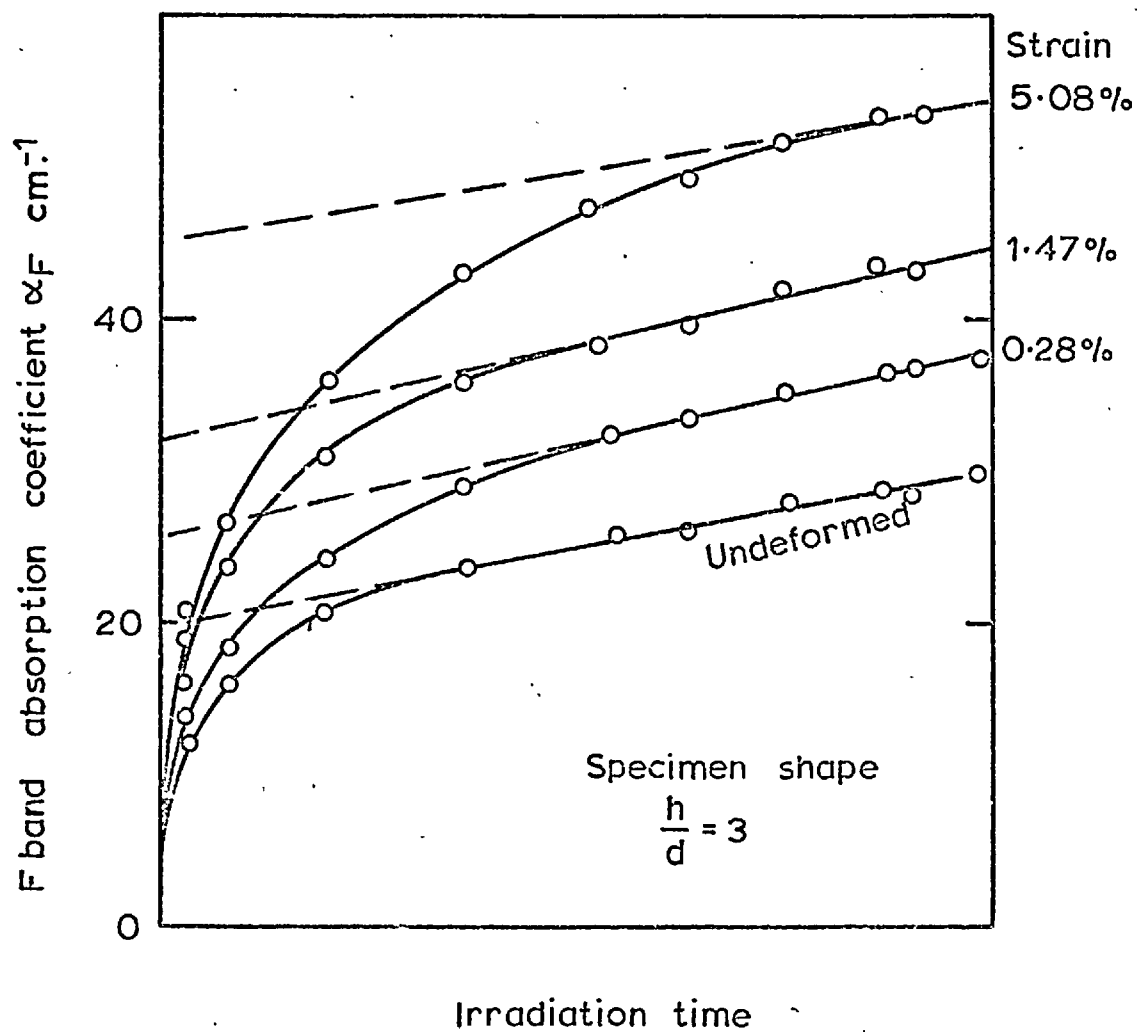


Fig.4.2. F CENTRE CONCENTRATION AS A FUNCTION OF γ -RADIATION DOSE FOR KCl CRYSTALS COMPRESSED $\langle 100 \rangle$

Specimen shape $h/d = 3$.

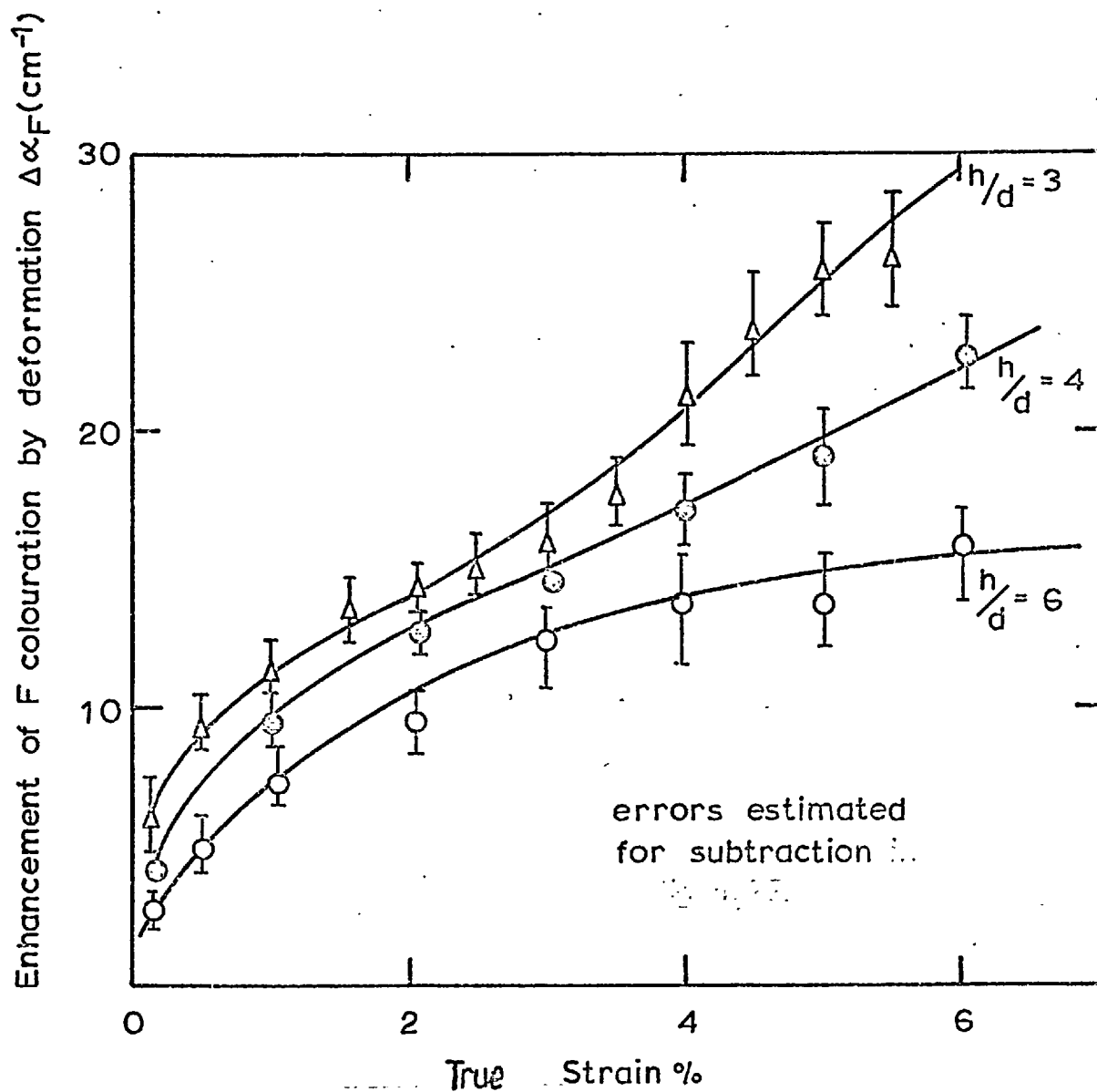


Fig.4.3. INCREASE OF STAGE 1 F COLOURATION BY COMPRESSION IN $\langle 100 \rangle$ FOR KCl

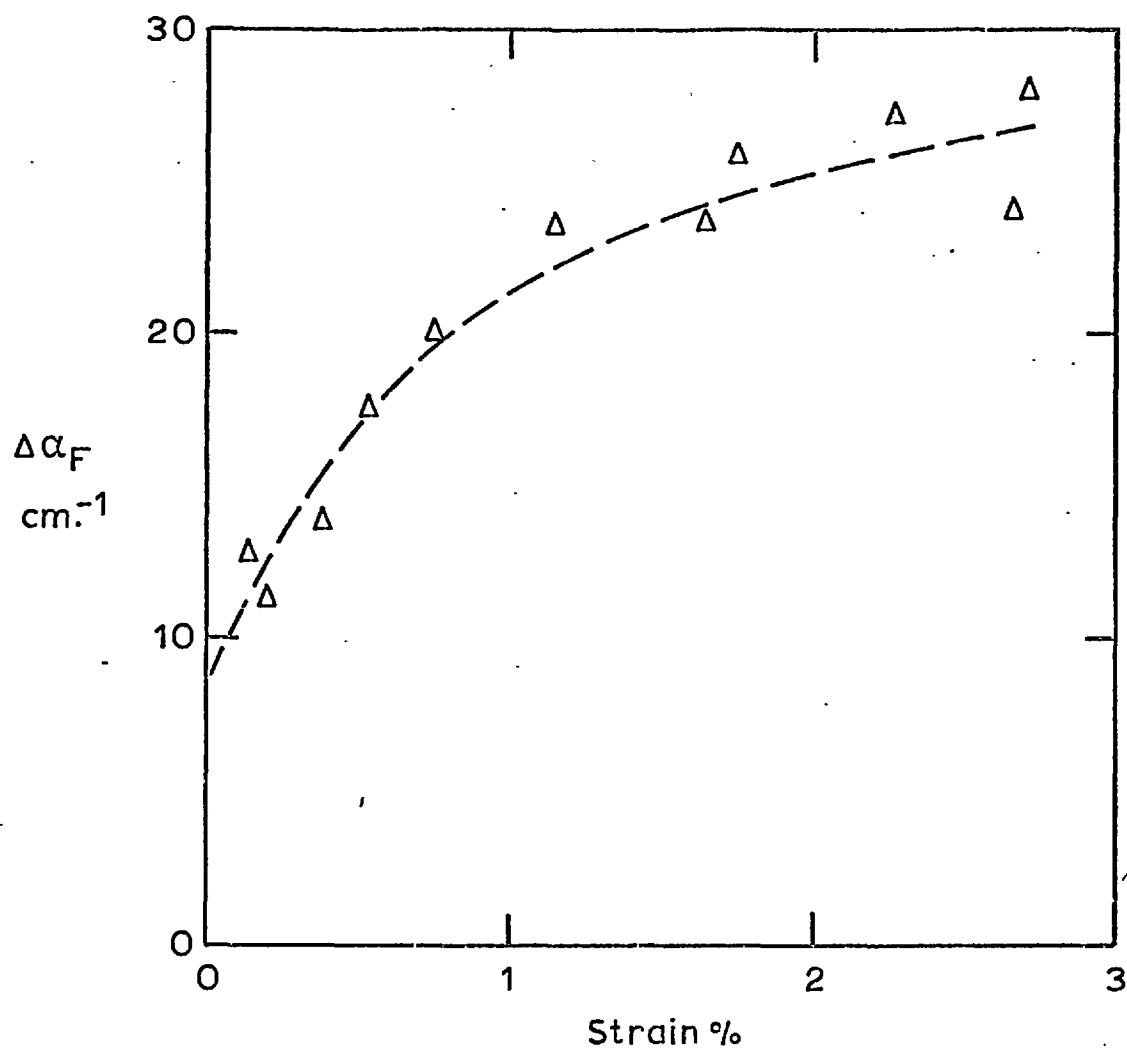


Fig. 4.4 THE INCREASE IN STAGE I F COLOURATION
FOR KCl BY COMPRESSION IN $\langle 111 \rangle$ DIRECTION

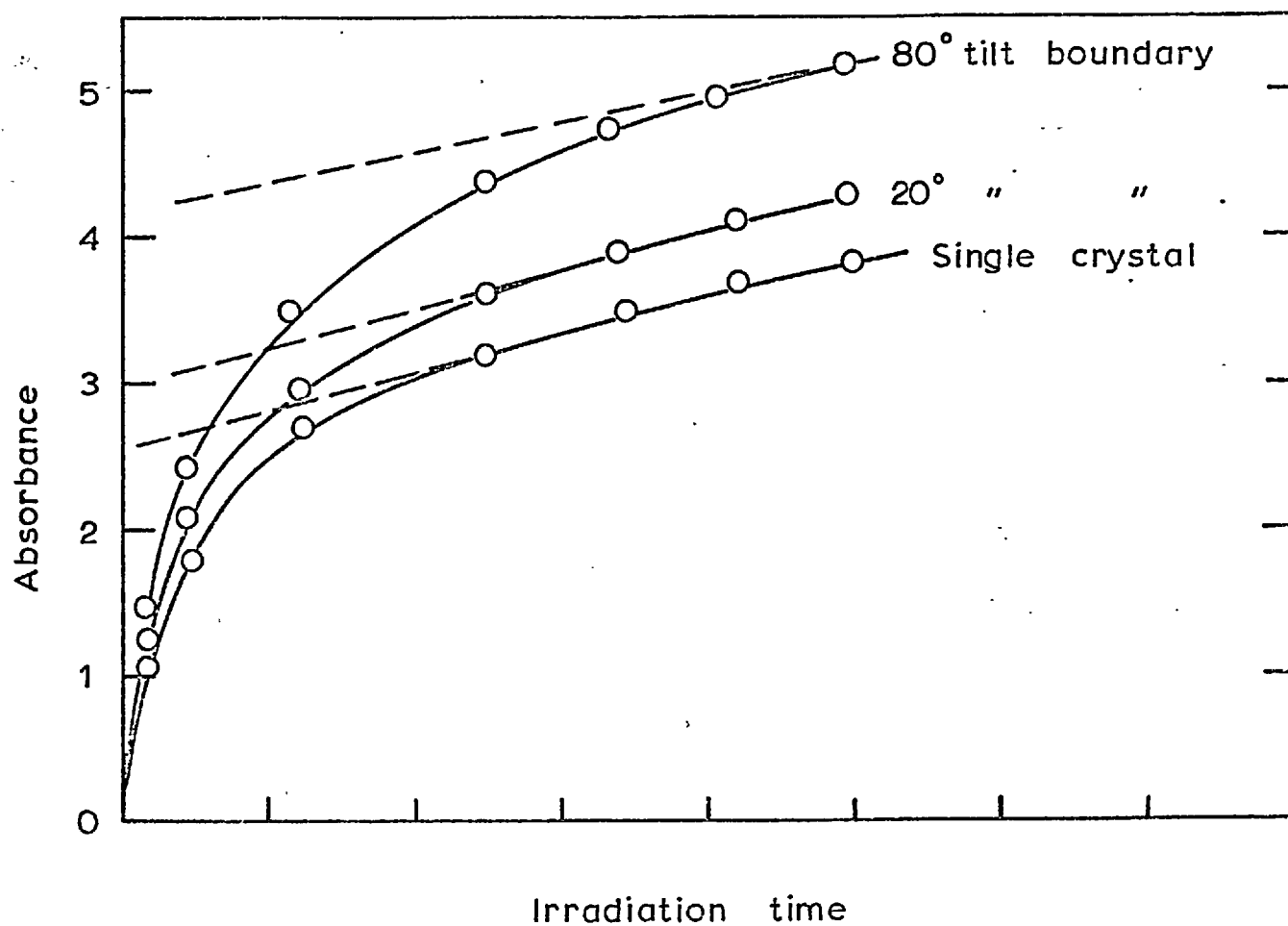


Fig.4.5 THE F CENTRE PEAK ABSORBANCE AS A FUNCTION OF γ -IRRADIATION DOSE FOR NaCl BICRYSTALS

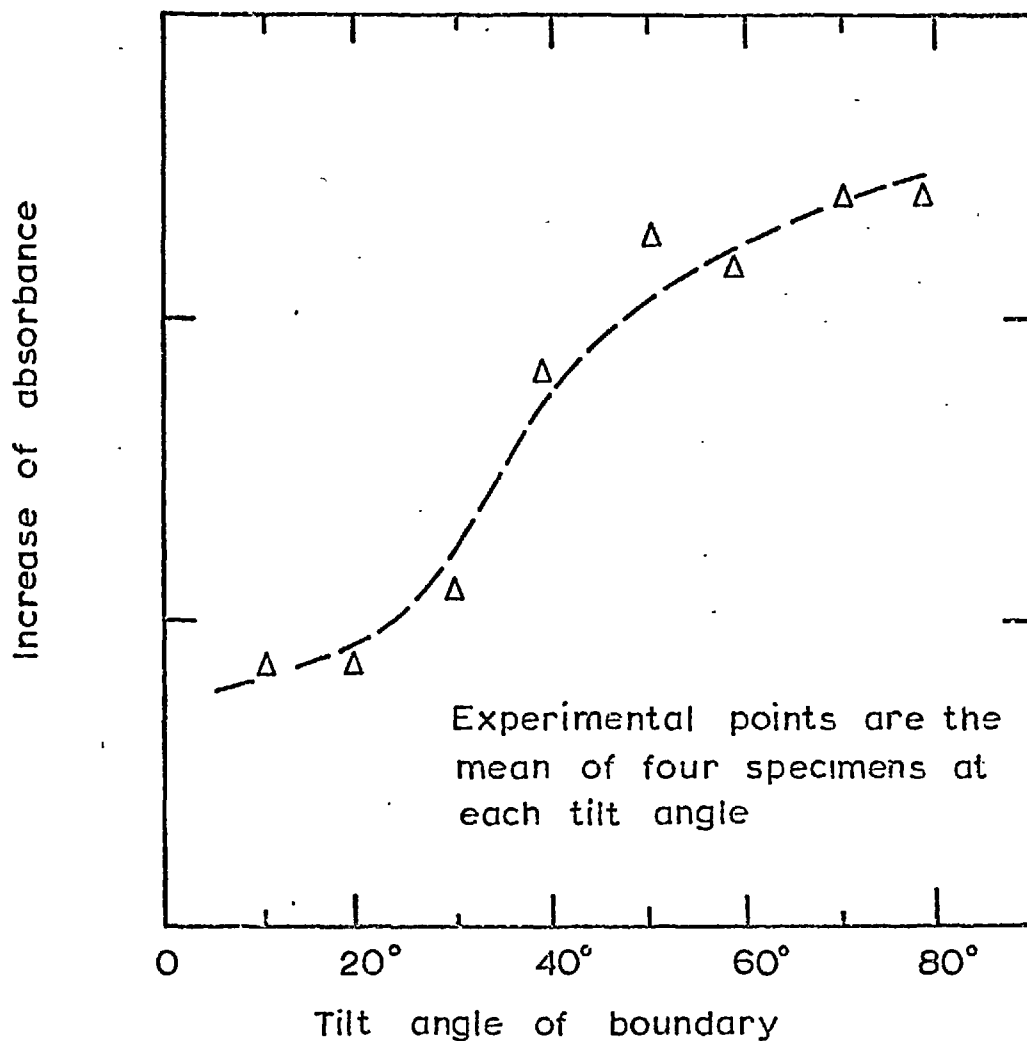


Fig.4.6 THE ENHANCED F CENTRE COLOURATION FROM BICRYSTAL TILT BOUNDARY IN NaCl.

5.1. Conclusions

This study introduces some information about dislocation motion in potassium chloride single crystals and the effect of this deformation and of grain boundaries on F centre formation by radiation. The principle conclusions are summarised in this chapter.

Stress strain curves and the results of strain rate and temperature cycling tests are reported over a wide temperature range for both primary $\{110\}\langle 110 \rangle$ and secondary $\{100\}\langle 110 \rangle$ slip systems. The temperature dependance of the dislocation motion on each system is separated into two distinct temperature ranges: yield at low temperatures is sensitively temperature dependant but nearly temperature independant at higher temperatures.

The strain rate sensitivity of the flow stress is independant of strain under all conditions tested. Thus, the observations are consistent with the predominantly athermal work hardening interactions recently proposed by Evans & Pratt 1970.

For the primary $\{110\}\langle 110 \rangle$ slip system in the high temperature region, the dislocation velocity is found to be proportional to the m^* power of the applied shear stress obtained from measurements of the velocity of edge and screw dislocations observed using etch pits e.g. $m^* = 14.3 \pm 2.1$ at 295°K and $m^* = 18.2 \pm 2.9$ at 196°K . Edge dislocations move faster than the screw components but both have the same value of m^* within experimental error. Determination of values of m^* by strain rate cycling, e.g. $m^* = 36 \pm 3$ at 295°K , assumes that the dislocation density does not change during the cycle. Since these values of m^* by the different

experimental techniques are not the same, the assumptions made cannot be considered as valid and the values of m^* 135 determined from strain rate cycling experiments at room temperature, and previously reported, do not have the significance that their authors suggest, and may be explained as a combination of both changes of dislocation density and dislocation velocity during strain rate cycling in this temperature region.

At low temperatures the yield stress becomes increasingly temperature and strain rate sensitive. Application of the analysis of a thermally activated dislocation motion to the strain rate and temperature cycling data gives point defect interactions as the most probable screw dislocation obstacle. This is consistent with the impurity dependence of the low temperature yield stress. By loading the crystal

specimens in the $\langle 111 \rangle$ direction slip is obtained on the $\{100\} \langle 110 \rangle$ system: for low strains slip step traces are consistent with deformation occurring predominantly on a single slip system. Yield-stress temperature graphs satisfy the dependence predicted for a Peierls mechanism controlling dislocation motion. Strain rate and temperature cycling tests give activation parameters which are consistent with this type of thermally activated dislocation interaction, although all the other dislocation interactions cannot be unequivocally eliminated. The large anion outer electron shells are believed to be responsible for the Peierls potential hill which restricts dislocation motion. The strain rate sensitivity is independent of strain thus the parabolic work hardening is probably due to athermal obstacles which have decreasing effectiveness as deformation proceeds. At higher strains for this compression direction slip steps are observed for slip on the primary

slip systems: this is the result of lattice rotation as deformation proceeds so that the resolved shear stresses on these planes is no longer zero.

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A comparison between the temperature dependance of the yield stress for the secondary $\{100\}\langle 110\rangle$ systems and similar deformation tests that have been reported for KCl polycrystals suggests that the onset of the high temperature region of low yield stress for the secondary system about 300°K does not correspond to the beginning of the plasticity of polycrystals between 420 and 520°K . Consequently, the operation of five independant slip systems - Von Mises criterion - does not in itself completely control the plasticity of polycrystals: grain boundaries or dislocation interactions must also be responsible to a large extent.

Increased rates of F centre enhancement by deformation as a function of strain are observed for crystals deformed into Stage II of the stress strain curve. Early stage colouration is believed to be enhanced by dislocation dipoles. Work hardening models predict greater dislocation production during Stage II of the stress strain curve then during Stage I. This confirms the enhancement of F colouration by dislocation debris formed during deformation and that the rate of debris production is greater during Stage II work hardening.

The early stage F colouration of NaCl is found to be enhanced by the presence of pure tilt boundaries in the test specimens. The enhancement increases with the angle of misorientation between the single crystal regions. Conductivity experiments previously reported for tilt boundaries, are consistent with increased vacancy concentrations at higher angles of tilt and at low angles the boundary contains dislocation arrays. Past work has established that F centre colouration by radiation is not

enhanced by isolated dislocations, thus little enhancement
may be expected from the dislocation array. The higher
vacancy concentrations at larger tilt angles may behave
in a similar manner to dislocation dipoles in the method
by which the F colouration is enhanced since the structure
of dislocation dipoles may be considered also as vacancy
sheets. 137

5.2. Suggestions for further work.

The deformation studies now require comprehensive tests on crystals doped with low concentrations of polyvalent impurity ions in order to determine the impurity dependance of the dislocation interactions on both slip systems. This would give a much more complete understanding of the processes controlling the plastic deformation of polycrystals and its impurity dependance. A parallel study should be made for polycrystalline material of different grain sizes prepared from the same doped crystals.

These deformation experiments may then be similarly repeated on other ionic crystals, particularly NaCl and MgO to build a more complete study of dislocation motion on the primary and secondary slip systems to interpret the influence of these factors on polycrystalline deformation.

An extensive study using high energy transmission electron microscopy on crystals immediately after deformation may give valuable confirmation of the dislocation interaction and debris production mechanisms. Currently these have to be inferred from macroscopic observations of the electron microscopy studies of MgO which is considerably stronger than the alkali halide crystals.

Experiments are currently being undertaken on the creep of irradiated KCl and NaCl single crystals to measure the hardening of the crystals by the colour centres produced by the radiation, thus combined creep tests and optical absorption studies may give information about the structure of the radiation damage, Pooley 1970. Strain rate cycling tests would be equally suitable for a parallel study of the radiation hardening centres.

An examination of grain boundaries of bicrystals with controlled angles of tilt and twist and polycrystals of varying grain sizes using combined F colouration and conductivity may lead to a better understanding of vacancies in the grain boundary structure.

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