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SOME TRANSPORT PROPERTIES OF SINGLE AND
POLYCRYSTALLINE SODIUM CHLORIDE

A Thesis submitted in supplication for the

Diploma of Imperial College

by

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Abstract

The conductivity of pure and manganese doped single crystals has been measured from 620°K to 920°K. The enthalpies of formation of Schottky defects and motion of cation vacancies, 2.36 ± 0.02 eV and 0.69 ± 0.02 eV respectively, have been calculated. The entropy of formation of Schottky defects is found to be $5.40 (\pm 0.10) \times 10^{-4} \text{ eV}^\circ\text{K}^{-1}$.

The polarisation of pure and doped crystals in the temperature range 620°K to 920°K has been interpreted in terms of blocking of both anion and cation vacancies at the electrode-crystal interface. The failure of the models of Friauf (117) and MacDonald (116) has been described in the light of the more recent model of Raleigh (114).

The conductivity of polycrystalline sodium chloride has shown that there is a considerable enhancement of conduction compared with single crystals, in the extrinsic region. This is interpreted as being due to the diffusion of segregated impurities in the grain boundaries. The absence of any enhanced conduction at high temperatures indicates that anion vacancies are not more mobile in grain boundaries. No polarisation appears to arise from the grain boundaries. The results indicate a boundary structure containing a high vacancy density with continuity of the lattice between each grain. The 'island' or coincident site models appear to be appropriate.

A microhardness technique has been developed to measure grain boundary segregation in bicrystals of sodium chloride. The technique appears to be capable of detecting small changes in hardness over small distances. Preliminary tests on high angled boundaries show that hardening is apparent over a region about $75\mu m$ from the boundary.

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CHAPTER 1.

Introduction and Literature Review.

1 - 1 General Introduction.

The movement of ions in ionic crystals has been largely studied by the use of diffusion, electrical conductivity and nuclear magnetic resonance techniques. It has long been recognised that ionic crystals generally behave in an intrinsic manner at high temperatures and in an extrinsic manner at lower temperatures. It has been established that transport in alkali halides is due to the motion of point defects, and it has been found that generally cation vacancies contribute to the majority of the current, whilst anion vacancies only become significant at temperatures near the melting point. Electrons play a minor role in the conduction processes.

Much attention has been paid to the ionic conductivity in pure and doped alkali halides. The enthalpies of formation and motion of Schottky defects are well documented, although the values are somewhat uncertain, this being mainly due to differences in the experimental techniques employed.

Until recently the transport of matter in grain boundary regions has been neglected. Recent diffusion⁽¹⁻³⁾ and ionic conductivity⁽⁴⁻⁶⁾ studies have shown that grain boundary regions contain a high vacancy density and that impurity ions can move more easily in boundaries than in the bulk. There are, however, doubts⁽³⁾ whether the motion of anion vacancies is enhanced in grain boundary regions, as suggested by some previous work.^(1,2,5)

Conduction in surface regions has recently been

investigated^(7,8) and in some ceramics, such as alumina, it was found to be significant. In alkali halides however, surface conduction is not considered to be very important because the bulk conduction is relatively larger.

The presence of impurity ions in ionic crystals gives rise to several important effects. They result in a modification of the conduction in the extrinsic region and at low temperatures they will form vacancy-impurity complexes and precipitates. If grain boundaries are present the impurities will tend to segregate at the boundaries.

The phenomenon of grain boundary segregation has been extensively studied in metals,⁽⁹⁻¹⁰⁾ such as lead, zinc and tin; and in some ceramics,⁽¹¹⁾ notably alumina and magnesium oxide. The studies have shown that only a very few impurity atoms are required to produce a significant increase in the microhardness of the grain boundary region. Very little work has yet been done on segregation of impurities at grain boundaries in ionic crystals.

The object of the work carried out by the author has firstly been to study the intrinsic and extrinsic conduction in pure and manganese doped single crystals of sodium chloride, so as to obtain reliable values of the enthalpies of formation and motion of point defects. The results from both a.c. and d.c. conductivity measurements have been compared and the discrepancy between them has been interpreted in terms of electrode blocking effects. These electrode blocking effects have been studied in some detail.

The second aim of the work has been to carry out parallel studies on hot-pressed and extruded polycrystals

so that the diffusion processes at high temperatures in grain boundary regions may be studied. The interfacial blocking characteristics of grain boundaries was also investigated.

The segregation of impurities at grain boundaries has been studied using a microhardness technique developed by Westbrook. The design and development of a high temperature microhardness tester will be described and a few preliminary tests will be discussed. It is hoped that the segregation processes can be studied by the microhardness and conductivity techniques.

The remainder of this chapter will discuss in some detail the transport of matter and charge in the bulk and interfacial regions.

1.2. STRUCTURE OF SODIUM CHLORIDE.

1.2.1. Perfect Crystal Lattice.

The sodium chloride type lattice consists of two interpenetrating face centred cubic lattices; on one are situated the sodium ions and on the other the chloride ions. The unit cell for the perfect lattice is shown in fig.1.1. The bonds between the ions are almost entirely ionic, thus resulting in a strong electrostatic attraction between anions and cations. There is a large band gap between the valence and conduction band which results in a very low contribution to the charge transport by the movement of electrons.

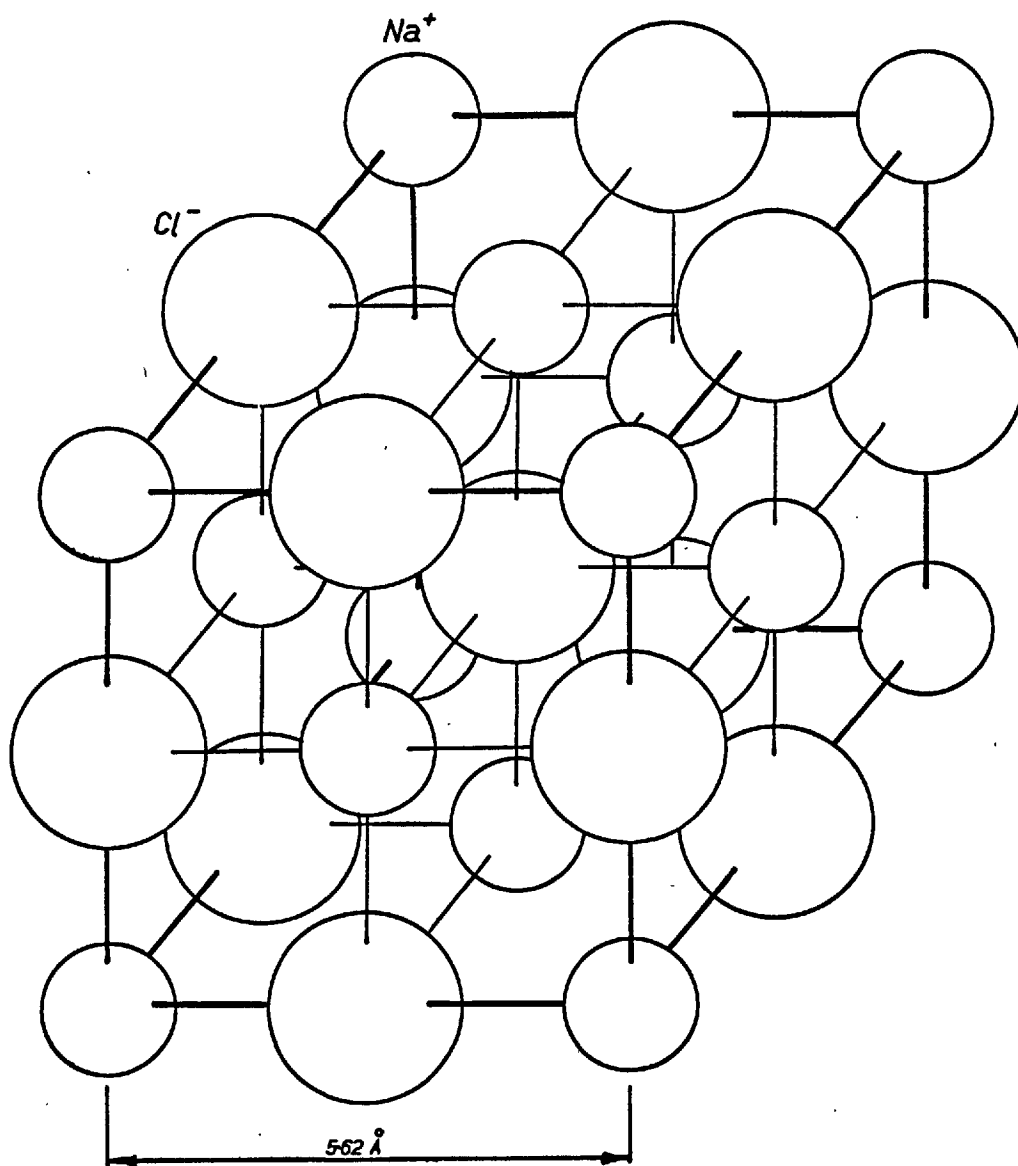


Fig.1.1. UNIT CELL OF NaCl

The transport of mass could occur if two adjacent ions exchange places but to do this would require a considerable dilation of the lattice, together with the moving ions having to pass through a position of very high electrostatic repulsion. The transport of ions can only really be explained in terms of ions moving in a defect structure, and the movements of defects themselves. The different types of defect present in the lattice will be briefly described in the remainder of this chapter.

1.2.2. Point Defects.

The subject of point defects in ionic crystals has been thoroughly dealt with by several authors; notably Van Bueren⁽¹²⁾ has presented a general introduction, Lidiard⁽¹⁵⁾, Supitz and Teltow⁽¹³⁾, and more recently Barr and Lidiard⁽¹⁴⁾ have given excellent reviews of experimental and theoretical work.

Point defects can be divided into two classes. Frenkel defects which consist of a vacancy on a lattice site associated with an interstitial ion, and Schottky defects consisting of a separated pair of anion and cation vacancies. In sodium chloride the Schottky defect predominates due to its lower formation energy.

The concentration of vacancies in an alkali halide crystal is given by the equation:

$$x_a x_c = \exp (-G_s/kT) \approx x_o^2 \quad 1.1.$$

where x_a and x_c are the molar fractions of anion and cation

vacancies and G_s is the free energy of formation of a Schottky pair. T is the absolute temperature and k the Boltzmann constant. The derivation of this equation can be found in a text by Lidiard⁽¹⁵⁾. The free energy of formation of a Schottky pair can be divided into an enthalpy, h_s , and an entropy, S_s , of the formation, thus:

$$G_s = h_s - TS_s \quad 1.2.$$

The product relationship of equation 1.1. is found always to hold in thermal equilibrium since it is derived from the need to maintain the crystal structure and charge neutrality. This product relation does not consider the interaction between defects which result from long range

Coulombic forces. The interaction between defects will result in anion and cation vacancies not being randomly distributed throughout the crystal and the effect of this is to lower the effective formation energy at high defect concentrations and temperatures. This can be taken into consideration using the Debye-Hückel theory of electrolytes as described by Lidiard⁽¹⁵⁾.

Anion and cation vacancies which are close to each other can be considered as distinct defects, known as vacancy pairs. The vacancy pair is strongly bound and behaves as a dipole. The molar concentration of such pairs is given by:

$$x_p = Z \exp (-G_p/kT) \quad 1.5$$

where Z is the number of orientations of the pair and G_p the free energy of formation of the pair. Two theoretical estimates of x_p ⁽⁸⁵⁾ as a function of temperature are shown in fig.1.2.

Much work has been done on crystals containing a molar fraction c of aliovalent ions; most work being on alkali halides doped with divalent cations. The divalent cations generally go into substitutional solid solution, the interstitial sites being too small to accomodate them. This will yield one impurity ion plus one cation vacancy to maintain charge neutrality, thus:

$$x_c = c + x_a \quad 1-3.$$

and the concentration of cation vacancies is given by

$$x_c = \frac{c}{2} \left[1 + \left(1 + \frac{4 x_o^2}{c^2} \right)^{\frac{1}{2}} \right] \quad 1-4.$$

when $x_o \gg c$ then $x_c = x_o$ as for Schottky disorder and when $x_o \ll c$ then the concentrations of defects are controlled by the amount of dopant added, that is $x_c = c$. The concentration of anion vacancies is similarly given by:

$$x_a = \frac{c}{2} \left[\left(1 + \frac{4 x_o^2}{c^2} \right)^{\frac{1}{2}} - 1 \right] \quad 1-6.$$

Fig.1.2. (14) shows the effect of divalent cation additions to the concentration of anion and cation vacancies. The cation vacancies are seen to change from the intrinsic thermal concentration to the concentration controlled by the impurity content. The concentration of anion vacancies is seen to be correspondingly depressed.

The preceding discussion has assumed that the concentration of vacancies introduced by the impurities was constant and equal to c . This is not necessarily so since

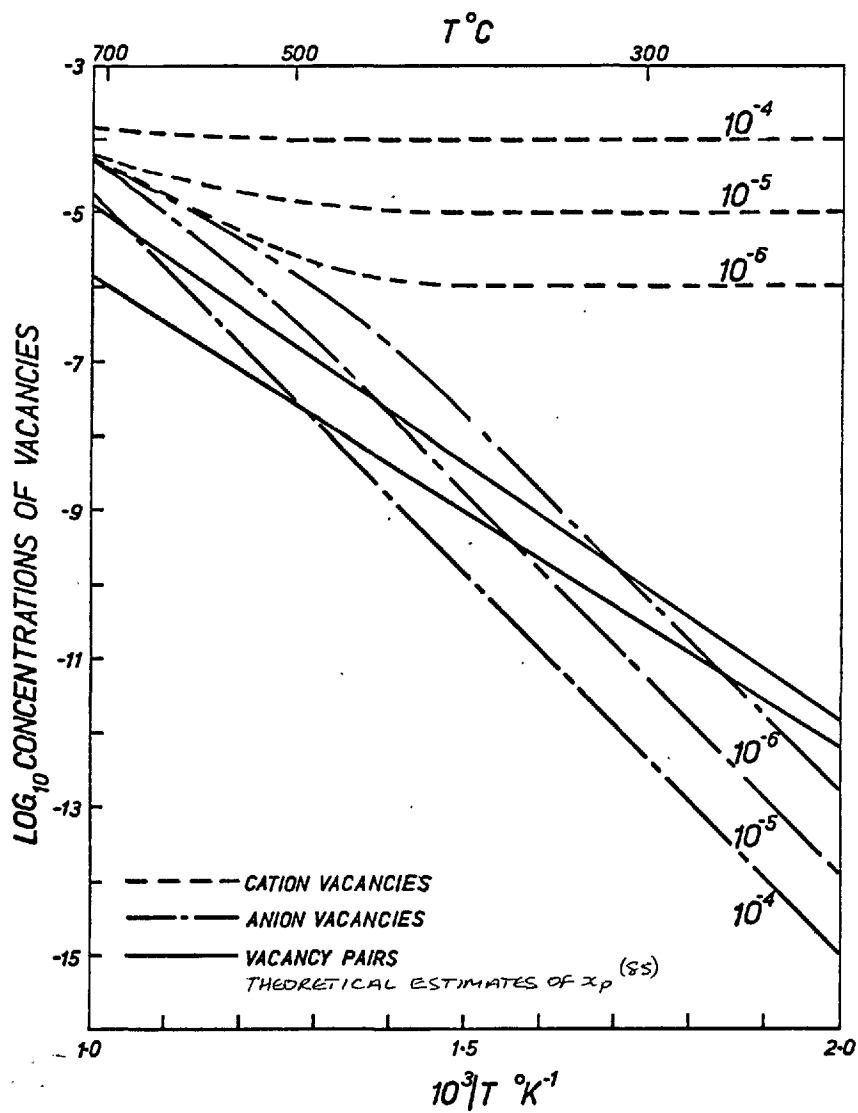


FIG1.2 (BARR AND LIDIARD)¹⁴
CONCENTRATION OF ANION AND CATION VACANCIES
AS A FUNCTION OF TEMPERATURE AND IMPURITY
CONCENTRATION

pairs of ^{impurity} cations and cation vacancies are stable just as vacancy pairs are stable. The impurity cation-vacancy pairs are electrically neutral but do act as dipoles. The equation for the concentration of associated pairs x_k , is

$$\frac{x_k}{x_c (c - x_k)} = Z \exp (G_k / kT) \quad 1.7.$$

where G_k is the free energy of association of the pair. This equation ignores the long-range interaction.

Higher impurity-vacancy complexes will form at lower temperatures and at high impurity concentrations. At low temperatures it is possible that the solubility limit of the impurity is exceeded and this will result in the precipitation of a second phase.

The impurity has been assumed to be evenly distributed throughout the crystal, and although this is the equilibrium situation it will not necessarily happen practically. Certain regions of the crystal such as crystal surfaces, dislocations and internal boundaries will act as sources and sinks for vacancies and require no charge neutrality. The distribution of impurities and vacancies will vary with position within these regions. Barr and Lidiard ⁽¹⁴⁾ state that the width of these regions will be about κ^{-1} , where κ is the Debye-Hückel screening constant given by

$$\kappa^2 = \frac{8\pi q^2 x_c}{V\epsilon kT} \quad 1.8.$$

where q is the charge on a vacancy, V is the volume per

molecule in the perfect crystal and ϵ is the dielectric constant.

1.2.3. Line Defects.

Dislocations are classed as line defects and in ionic crystals a dislocation will disturb the regular pattern of

positive and negative ions. The dislocation line can be charged, or, if the line is not charged, then equal numbers of half-jogs of opposite sign within it will carry a charge. The dislocation line may also be surrounded by an atmosphere of charged defects.

Motion of jogs with dislocations can lead to the transport of charge, but only in the direction of the Burgers vector. Vacancies can move in any direction within the slip plane. The

reader is referred to the work of Whitworth and co-workers⁽¹⁶⁻²⁰⁾ Caffyn and Goodfellow⁽²¹⁻²⁴⁾, Davidge⁽²⁵⁾ and Eshelby et al.⁽²⁶⁾ for detailed theory and experiments relating to the transport of charge and matter by dislocations.

The transport of charge by dislocations has been seen as an enhancement of the conductivity after deformation⁽⁴⁸⁾. In many materials ions have been shown to move more readily in the dislocation core, resulting in an apparent increase of the bulk diffusion.

1.2.4. Planar Defects.

Surfaces and grain boundaries can be considered as defects within the crystal lattice and they can either enhance or impede the transport of charge or matter. Grain boundaries can play two important roles in polycrystalline materials. Firstly, many properties are affected by the presence of separate crystals within the bulk, which are mutually misorientated, whilst other properties are affected by the structure of the boundary itself. The mechanical properties fall into the first category, whilst charge and mass transfer are affected by the structure of the boundary.

Similarly the surface of a crystal will affect the above mentioned properties. The surface condition will markedly affect the mechanical strength of the crystal.

Charge and mass transport in the bulk could also be affected by the nature of the surface.

1.3. GRAIN BOUNDARIES IN IONIC CRYSTALS.

1.3.1. Grain Boundary Models.

Grain boundaries in metals can be generally represented by a simple geometrical array of monosize spheres, such as a bubble raft model. This type of approximation is not applicable in ionic crystals since there are usually two

types of ion present in the lattice, and they are generally of differing sizes. The charge neutrality of the crystal as a whole must also be considered.

Many of the proposed models for grain boundaries, in general have been extensively reviewed by McGee⁽²⁷⁾. Low-angle boundaries have been generally described in terms of arrays of edge and screw dislocations, giving rise to tilt and twist boundaries respectively as shown in figs.1.3. and 1.4. Generally, low-angle boundaries will be a combination of tilt and twist components. A summary of these models has been given by Amelinckx and Dekeyser⁽²⁸⁾.

The limiting angle of mismatch between two grains resulting in a boundary which can be analysed in terms of a dislocation model will depend to a large extent on the crystalline structure and impurities present. Usually the angle will be of the order of 15 to 20 degrees.

Models for high-angle boundaries are also reviewed by McGee⁽²⁷⁾. Brandon⁽³⁰⁾ has recently proposed a model based on the coincident site model of Kronberg and Wilson⁽³¹⁾. The basis of this model is that for certain specific axes and angles of misorientation, two grains separated by a boundary will contain a number of lattice sites in common; a twin boundary is an example of this. Brandon⁽³⁰⁾ has modified this model, combining it with a dense dislocation array model⁽³²⁾, making it more compatible with observed results from field-ion microscope studies⁽³³⁾.

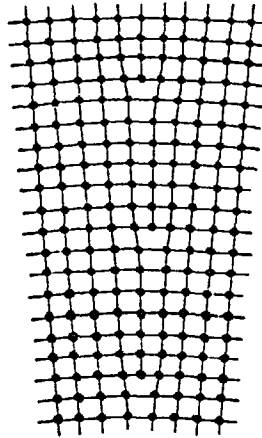


Fig.1.3. SIMPLE TILT BOUNDARY
(AMELINCKX AND DEKEYSER²⁸)

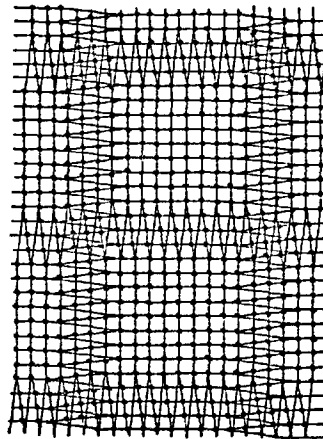


Fig.1.4. SIMPLE TWIST BOUNDARY
(READ²⁹)

1.3.2. Structure of Grain Boundaries in Sodium Chloride.

The structure of grain boundaries in ionic crystals has been studied by a number of workers, in particular work on the alkali halides has provided useful information about the structure in cubic ionic systems. Fuschillo, Gimpl and McMaster (34,35) have studied both tilt and twist grain boundaries by pulling apart the bicrystals at the grain boundaries and then examining the surface of the boundary. They found that twist boundaries were apparently only held together by small regions or spots of continuity, whereas they could detect no surface features for pure tilt boundaries. The lack of continuity in twist boundaries they attributed to lattice mismatch and to impurity segregation. They suggested that twist boundaries with such a structure would explain the lack of ductility of many polycrystalline materials.

Martin, Fehr and McGee (36) produced bicrystals and tricrystals using a hot-wire technique and they studied the interaction of dislocations with both tilt and twist boundaries. They found that propagation of slip was hindered by the presence of grain boundaries, and the degree of hindrance was higher for twist type boundaries and generally increased with ^{the} angle of mismatch. Tilt boundaries of angle less than 12° were shown to have a dislocation structure conforming to the low angle dislocation model.

Gimpl, McMaster and Fuschillo (37) have recently extended their earlier work by studying the effects of various impurities on the nature of the boundaries. They again found 'pips' on the grain boundary surfaces of twist

and double-tilt* boundaries in high-purity sodium chloride, but not in simple tilt boundaries. Separate additions of 100ppm of SiO_2 , CaCl_2 , FeCl_3 and KCl had no effect on the character of the grain boundary. However, 6000ppm of CaCl_2 nearly doubled the strength of a 30° twist boundary and considerably weakened a 45° tilt boundary. They believe the strengthening effect may be due to segregation, but they offer no explanation for the weakening effect in tilt boundaries. They also noted the presence of spots in the boundary plane in bicrystals with misorientation greater than 15° . These have been observed in magnesium oxide and it is thought they are due to impurities segregated at defects. This work does appear to suggest that Mott's islands of mismatch model ⁽³⁸⁾ has some validity although the areas of mismatch appear to be on a macro rather than atomic scale.

The study of diffusion processes in grain boundaries has yielded some information about the structure of grain boundaries in sodium chloride and other alkali halides. McGuhae ⁽⁶⁾ has measured the electrical conductivity of tilt boundaries using a probe technique developed by Moment and Gordon ⁽³⁹⁾, who did similar work on lithium fluoride. Their work, together with diffusion work by Cabané ⁽³⁾ and Laurent and Benard ^(1,2), suggests that grain boundaries are regions containing a high vacancy density and tend to confirm the work on grain boundary structure.

1.3.3. Segregation of Impurities in Grain Boundaries.

The fact that grain boundaries contain local variations in composition has long been established. These variations

*Double-tilt refers to boundaries tilted on two perpendicular axes.

arise from non-equilibrium conditions such as preferential transformations, freezing or diffusion. Other chemical variations arise from equilibrium or quasi-equilibrium conditions; this aspect has been extensively reviewed by westbrook ⁽⁴⁰⁾. Most of the work has been done on metal systems, only recently has some work been done on ceramic systems despite the importance of segregation in the sintering processes used in the manufacture of commercial ceramic materials.

Prior to the early work of westbrook and wood ^(41,42) the idea of equilibrium segregation at grain boundaries was a concept of long-standing, although unambiguous experimental verifications were few in number, this being largely due to the difficulty in measuring small local variations in compositions. westbrook and wood ^(41,42) found that microhardness measurements could detect the presence of local concentrations of solutes at grain boundaries in a wide variety of materials. They found that when positive segregation of some solute species has occurred at a grain boundary, the microhardness of the boundary region increased from 10 to 50 per cent above that of the interior of the grain. This hardened region extends for several microns either side of the boundary.

This work was extended by westbrook and Aust ⁽⁴³⁾ to detect segregation in various lead plus solute systems. They found that the type of the solute, concentration of solute, structure of the boundary and temperature affect the hardening of grain boundaries. The effects brought about by different solutes were found to be related to their relative solubility in the base metal. Very low-energy

boundaries such as coherent twin boundaries show no hardening effect, and low-energy boundaries such as incoherent twin boundaries and certain grain boundaries display less hardening effect than high energy boundaries. The disappearance of the boundary hardening effect at high temperatures was attributed to a decrease in impurity concentration at the boundary, but not due to an absence of impurity at the boundary. Their results suggest that the effect is not a simple solute concentration but more likely a complex mechanism involving other types of defect in the boundary regions.

The microhardness technique has been used by Aust, Peat and Westbrook⁽¹⁰⁾ for the study of the changes in defect concentration in quenched crystals of zone-refined lead. A marked softening of the boundary region was found over a distance of about 30 to 50 microns from the boundary. Aust and Westbrook⁽⁴⁴⁾ proposed that the boundary hardening is due to the presence of solute clusters resulting from the decomposition of vacancy-solute complexes near the boundary sink. Recent work by Aust et al.⁽¹⁰⁾ showed a linear relationship between the distribution coefficient of the solute and the presence or absence of grain boundary hardening as predicted by the solute-clustering model. The hardening was present when the distribution coefficient was greater than unity and grain boundary softening occurred when the distribution coefficient was less than unity.

Segregation of impurities at grain boundaries in ceramic systems has been reviewed by Westbrook^(40,11). The same problems of detection apply to ceramics that apply to metals. The segregation of Ni⁶³ in high purity alumina has been detected by Jorgensen and Westbrook⁽⁴⁵⁾

using an autoradiographic technique. Other techniques, such as the electron beam microprobe, have been used with some success. The microhardness technique has also been applied to ceramic systems by Westbrook and Jorgensen ⁽⁴⁶⁾, to study the segregation of magnesium oxide in alumina. A typical hardness profile is shown in fig.1.5. Many attempts by other workers to use the microhardness technique satisfactorily have failed, this has been largely due to incorrect use of the technique.

Evidence for the presence of grain boundary segregation in sodium chloride has been presented by Muller ⁽⁴⁷⁾ who concluded that the retarding of grain growth, as shown in fig.1.6, ⁱⁿ strontium doped crystals was the result of grain boundary segregation of the impurity. This phenomenon is widely used in the sintering of ceramics to obtain a greater density. Cabané ⁽³⁾ has shown that the grain boundary diffusivity of anion vacancies is markedly affected by the presence of water, which appears to be preferentially located at grain boundaries. The segregated solute may affect the effective width of the boundary itself and the diffusion coefficient of the species moving within this region. The mechanisms for the segregation process which are applicable to metals as far as it is known are present in ceramics, but it is possible that new mechanisms are also involved. These additional mechanisms may arise from the low solubility of many solutes and the variety of electrostatic anomalies possible at grain boundaries.

The early models of steady-state segregation envisaged a simple absorption of solute by the boundary, the extent of which can be estimated from thermodynamic or strain energy

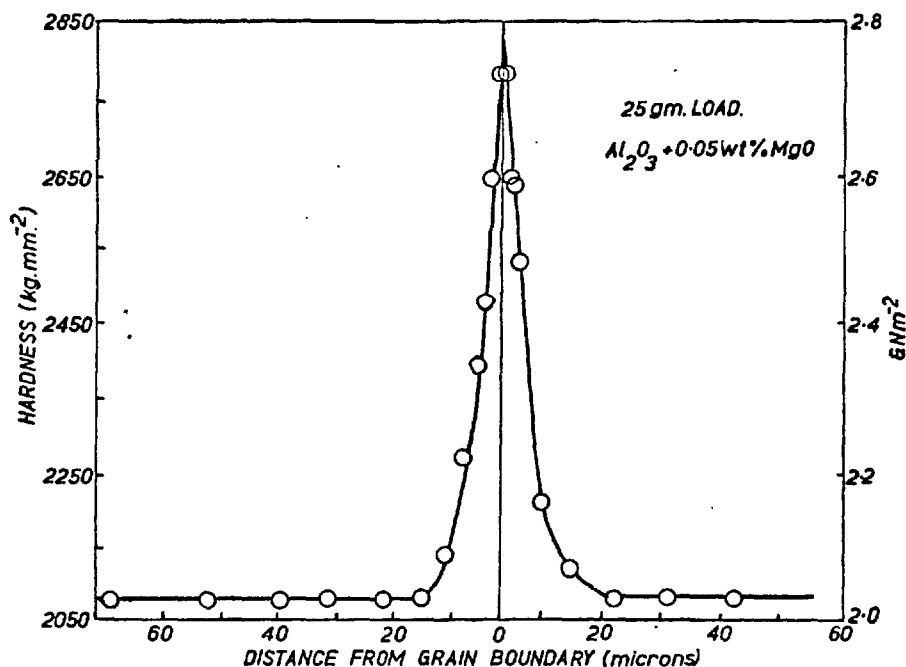


Fig.1.5. HARDNESS PROFILE ACROSS A GRAIN BOUNDARY
IN Al_2O_3 CONTAINING MgO . (JORGENSEN AND WESTBROOK)⁴⁵

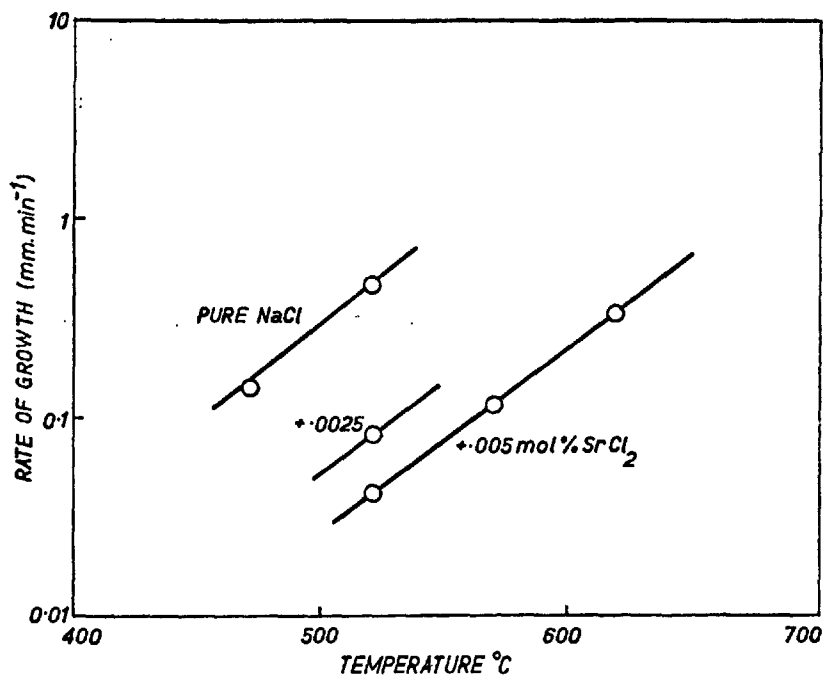


Fig.1.6. EFFECT OF SrCl_2 ADDITIONS ON RATE OF GRAIN
GROWTH IN NaCl . (MÜLLER)⁴⁷

considerations. These ideas result in the segregated solutes occupying sites very close to the boundary, only two or three atom spacings from the boundary, and this is not born out by experiment.

More recent models proposed by Westbrook⁽¹¹⁾ suggest that the concentration gradient arises from a gradient in the vacancy concentration near grain boundaries. Some of the vacancies present will be associated with impurity atoms or ions as impurity-vacancy complexes. The boundary acts as a sink for the vacancies and the impurity-vacancy complexes will tend to move towards the boundary. The vacancies will be annihilated at the boundary and the impurities will remain at the boundary or near to it.

These models do not account for the increased hardening effect at the boundary, as Westbrook⁽¹¹⁾ has pointed out that an asymmetric defect is required to explain the hardening. He has suggested that in metals the solute may go into interstitial sites near the boundary giving rise to an increased concentration of asymmetric defects in these regions.

An alternative model for the hardening suggests that the solute atoms are unable to redistribute themselves by diffusion and so cluster to form asymmetric defects. These two hardening mechanisms as yet cannot be distinguished between but experimental evidence cited by Westbrook⁽¹¹⁾

does suggest that solute segregation occurs by the action of the vacancy-sink on solute-vacancy complexes.

Recent work by Jorgensen (171) would suggest the assumption that segregation is an equilibrium effect is not valid, and that non-equilibrium effects are observed.

1.4. TRANSPORT PROPERTIES IN IONIC CRYSTALS.

1.4.1. Ionic Conduction in Single Crystals.

The measurement of ionic conductivity is relatively easy experimentally for the study of transport phenomena in sodium chloride. Energies of motion of sodium vacancies can be determined fairly easily as can the energy of formation of Schottky defects. The association and precipitation of divalent impurities can also be studied. It is, of course, only possible to determine the motion of charged defects; neutral defects, such as vacancy pairs, will not contribute to the conduction processes.

The features of the Arrhenius conductivity plot are shown in fig.1.7. The high temperature region is due to the conduction of intrinsic defects and is dependent only on the energy of formation of Schottky pairs and the energy of motion of the sodium ion. The motion of chlorine ion vacancies are generally considered insignificant in this region. The lower temperature region, region II, is strongly impurity dependent and is dependent on the motion of cation

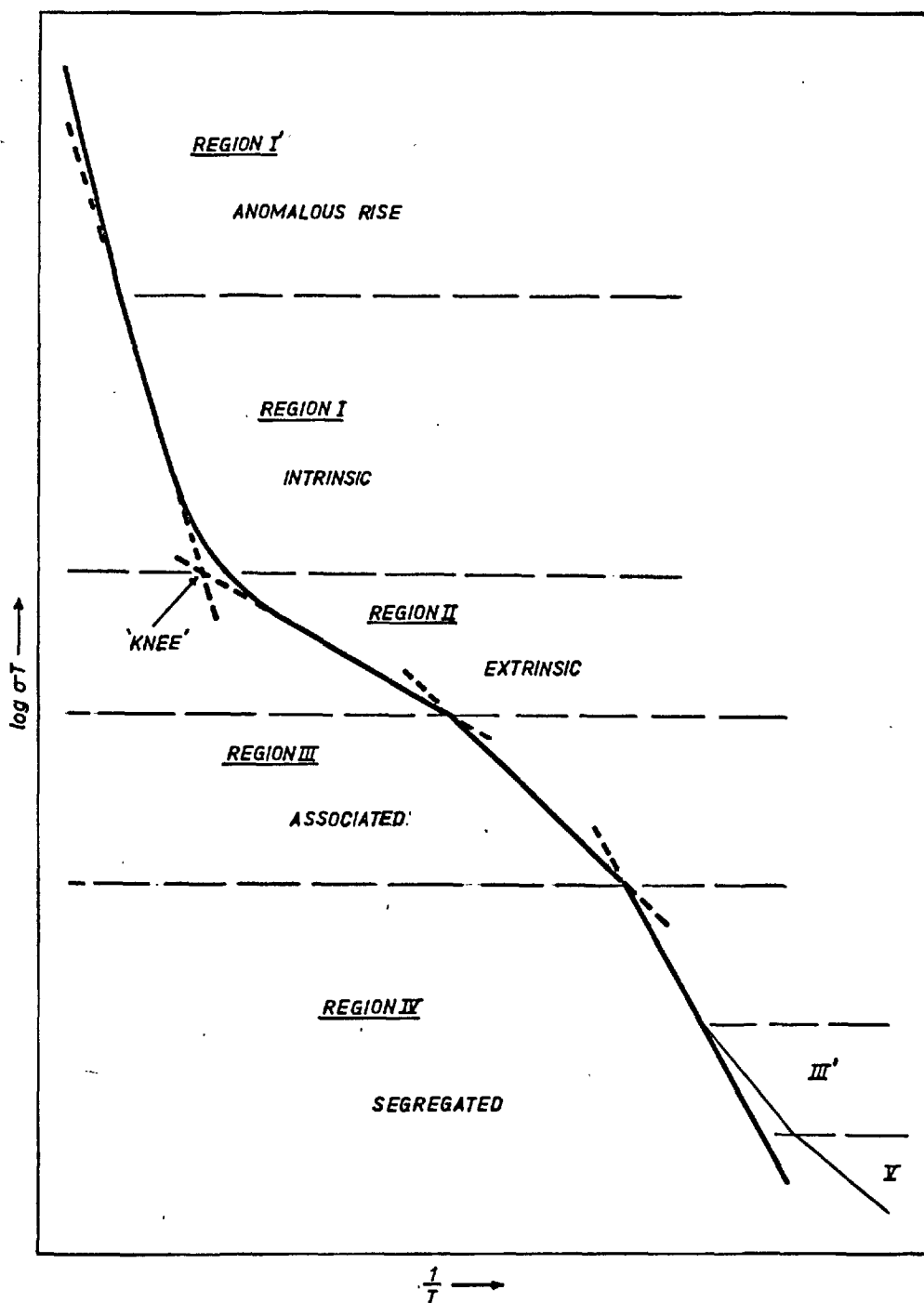


Fig.1.7. SCHEMATIC CONDUCTIVITY-TEMPERATURE PLOT
FOR NaCl.

vacancies present as a result of aliovalent impurity additions. The conduction in this region increases with addition of divalent cation impurities and is decreased by the addition of divalent anion impurities.

Stage III is the result of the association of impurity ions and vacancies into complexes. This association region leads into the precipitation region, region IV, which results from the precipitation of the divalent impurities. Region I is often modified at high temperatures by a region of increased gradient, known as region I'. It is thought that this is due to the motion of anion vacancies becoming significant at high temperatures near the melting point, although the values found for the transport number of the anion vacancies at high temperatures by previous workers have not been consistent.

The theory relating to ionic conduction in sodium chloride has been covered by many previous authors, notably : Lidiard ⁽¹⁵⁾ ^{who} gives an excellent account of the basic theory whilst many other authors have supplied modifications to the theory. No attempt will be made to derive the equations in the text and only those equations of relevance will be quoted. Likewise no attempt will be made to present a full account of previous experimental work since several previous reviews are available. ^(13,14,48)

The basic definitive equation concerning conduction in any material is given by:

$$\sigma = \sum_i N_i q_i \mu_i \quad 1.9.$$

where i refers to the different charge carriers, N, is the

density of carriers per unit volume and q , is the charge and, μ , the mobility of the carriers. In sodium chloride where Schottky disorder is predominant and the cation vacancy predominates over the anion vacancy in the charge transference, it is possible to calculate the temperature dependence of conductivity if the vacancy concentration and mobility as a function of temperature are known.

The mobility of the cation vacancy, μ_c , is dependent on the jump frequency of the sodium ion. The temperature dependence of the mobility is as follows:

$$\mu_c = \frac{4a^2 e \nu_c^0}{kT} \exp \frac{\Delta S_c}{k} \exp - \frac{\Delta h_c}{kT} \quad 1.10.$$

where a is the lattice spacing, ν_c^0 is the cation vacancy vibrational frequency, ΔS_c is the entropy of motion and Δh_c is the enthalpy of motion of cation vacancies.

When a cation vacancy is formed by the removal of a cation then there will be a change in the Gibbs, free energy of the system, described by the equation 1.2. To ensure charge neutrality when a cation vacancy is formed an anion vacancy must also be formed hence:

$$x_a = x_c = x_0 \quad 1.11.$$

Considering the intrinsic region and the general case when both anion^{and} cation vacancies contribute to the conduction then:

$$\sigma = \sigma_c + \sigma_a \quad 1.12.$$

and:

$$\sigma = (n_c e \mu_c) + (n_a e \mu_a) \quad 1.13.$$

Combining equations 1.1., 1.2., 1.10-13., then:

$$\sigma = \frac{4Na^2 e^2}{kT} \exp \frac{S_s}{2k} \exp - \frac{h_s}{2kT} \left[v_c^0 \exp \frac{\Delta S_c}{k} \exp - \frac{\Delta h_c}{kT} \right. \\ \left. + v_a^0 \exp \frac{\Delta S_a}{k} \exp - \frac{\Delta h_a}{kT} \right] \quad 1.14.$$

when cation mobility is alone significant then:

$$\sigma = \frac{4Na^2 e^2 v_c^0}{kT} \exp \left[\frac{S_s}{2} + \Delta S_c \right] \frac{1}{k} \exp - \\ \left[\frac{h_s}{2} + \Delta h_c \right] \frac{1}{kT} \quad 1.15$$

Thus in an Arrhenius plot of $\log \sigma T$ against $\frac{1}{T}$ cation motion is characterised by a straight line of slope

$$- \left[\frac{h_s}{2} + \Delta h_c \right] \frac{1}{k} \quad 1.16$$

The expression inside the bracket is the activation energy, Q_I . where both anion and cation vacancies contribute significantly the slope of region I will increase as it does in region I'. The gradient of this region will be dependent on the enthalpy of motion of both anion and cation vacancies as well as h_s .

At high temperatures, where the concentration of anion and cation vacancies becomes appreciable, attraction between the defects will produce vacancy pairs. These pairs will not contribute towards electrical conduction since they are electrically neutral. They will, however, contribute to the diffusion processes.

Fig.1.7. shows that the high temperature intrinsic region is transformed at lower temperatures to a straight

line region of reduced slope, region II. This region is controlled by the divalent impurity ion concentration, and the concentration of vacancies is determined by the need to maintain charge neutrality. The concentration of vacancies is given by equation 1.1. and the condition of charge neutrality in the following equations:

$$x_c = c + x_a \quad 1.3.$$

with excess divalent cations present and

$$x_c = x_a - c \quad 1.19.$$

with excess divalent anions present.

Thus from equations 1.1., 1.3. and 1.19.

$$x_c = \frac{c}{2} \left[1 + \sqrt{1 + \frac{4x_o^2}{c^2}} \right] \quad \text{for divalent cations. 1.20.}$$

and

$$x_c = \frac{c}{2} \left[1 - \sqrt{1 + \frac{4x_o^2}{c^2}} \right] \quad \text{for divalent anions. 1.21.}$$

thus it is seen that divalent cations will enhance conduction and divalent anions will suppress it. At these temperatures it can be assumed that the anion conduction is negligible and then:

$$\sigma = \frac{4 n_c a^2 e^2 \nu_c^0}{kT} \exp \frac{\Delta S_c}{k} \exp - \frac{\Delta h_c}{kT} \quad 1.22.$$

The slope of the Arrhenius plot will give a value of Δh_c and the intercept on the log. T axis will give ΔS_c .

The change from region I to region II occurs gradually. The temperature at which the straight lines of these two regions meet is called the 'knee temperature', T_k . At T_k it can be assumed that the equilibrium concentration of Schottky defects satisfies both intrinsic and extrinsic conduction. At the 'knee temperature':

$$c = \exp \frac{S_s}{2k} \exp - \frac{h_s}{2kT_k} \quad 1.23.$$

hence a plot of c against $\frac{1}{T_k}$ will give values of S_s and h_s .

The correlation of conductivity measurements with diffusion measurements is an important aspect of this subject since the transport of matter is studied by both methods. The two methods may be compared using the Nernst - Einstein equation:

$$\frac{\sigma_i}{D_i} = \frac{Ne^2}{KT} \quad 1.24$$

where σ_i and D_i are the conductivity and diffusion coefficient respectively of the moving species. For sodium chloride the equation can be written as:

$$\sigma = \frac{Ne^2}{kT} (D_a + D_c) \quad 1.25.$$

True diffusion coefficients are derived from completely

random motion. A vacancy can exchange places with any of its neighbours, an ion which has jumped into a vacancy has a finite probability of jumping back into the vacancy it leaves behind. Thus not all tracer ion jumps will necessarily contribute to the general diffusion flow. This effect is accounted for by using a correlation factor, f , where:

$$f = \frac{D_t}{D} \quad 1.26$$

where D_t is the tracer diffusion coefficient and D is the true diffusion coefficient. The correlation factor is dependent on the lattice structure and the diffusion mechanism. For the F.C.C. lattice of sodium chloride where diffusion proceeds via jumps into vacant lattice sites, $f = 0.7815$. The Nernst - Einstein equation now becomes:

$$\sigma = \frac{Ne^2}{kT} (D_a + D_c) \frac{1}{0.7815} \quad 1.27.$$

The present discussion relating to the intrinsic and extrinsic conduction has assumed that no association occurs

between impurities and vacancies. At lower temperatures association does occur and gives rise to region III, the slope of this region is given by

$$\left(h_c + \frac{h_k}{2} \right) \frac{1}{k} \quad 1.28$$

where h_k is the enthalpy of association of the impurity vacancy pairs.

An important consideration, particularly when fitting conductivity plots to empirical equations, is the Debye - Hückel interaction between vacancies. Vacancies in the lattice are surrounded by a symmetric atmosphere of oppositely charged vacancies. When a field is applied the vacancies are set in motion and the surrounding atmosphere changes, this results in a reduction of the speed of the vacancies.

The net effect of Debye-Hückel interactions is to lower the effective formation energy at high defect concentrations and temperatures, that is to increase the defect concentration to a value greater than would be expected by extrapolation from the behaviour at lower temperatures; equation 1.1. is modified to:

$$x_c x_a = x_o^2 \exp \left[\frac{q^2 \kappa}{\epsilon kT (1 + \kappa R)} \right] \quad 1.29.$$

where κ is the Debye-Hückel screening constant given in equation 1.8.

1.4.2. Mass transport in single crystals. Previous Work.

Ionic conduction and diffusion studies have been reviewed extensively in the past (13,15,48), in addition these authors have reviewed work concerned with N.M.R., thermoelectric power, dielectric loss and ionic thermocurrent (I.T.C.) measurements. In this chapter it is intended only to discuss briefly the work already reviewed and to introduce more recent work which is of importance. The various parameters used to describe cation and anion motion have been listed in tables 1 to 4.

The values of the parameters of motion and formation of defects show a considerable divergence, the reasons for this can generally be summarised as being due to differences in experimental technique and ^{the} analysis of the results. The values obtained for cation enthalpies of motion and Schottky formation enthalpies are reasonably consistent in most a.c. conductivity measurements, whilst there values differ considerably from values obtained by d.c. conductivity, diffusion and N.M.R. techniques. The low values of Schottky formation energy obtained by d.c. conductivity techniques can be attributed to the presence of interfacial polarisation effects at high temperatures resulting in a decreased slope of region I (57). The interfacial polarisation effects will be dealt with at length later. Other errors in the determination of the slope of region I can arise from the curvature of this region at high temperatures. Differences in the material itself may also affect the results. High dislocation densities can result in a considerable increase in the curvature of region I (48,81) and the type and concentration of impurity could alter the slope of region II.

TABLE 1:

PARAMETERS OF CATION MOTION IN NaCl. A.

SOURCE	SYSTEM	TECHNIQUE	h_s (eV)	S_s (eV°K ⁻¹)
Mott and Littleton (49)	NaCl	Theory	1.96-2.12	5.34x10 ⁻⁴
Mapother et al. (50)	NaCl	Diffusion D.C. cond	2.06 2.12	
Etzel and Maurer (51)	NaCl	D.C. cond.	2.02	
Fumi and Tosi (52)	NaCl	Theory	1.96-2.12	
Taylor (53)	NaCl	D.C.	2.04	
Biernan (54)	-	D.C.	2.19	
Dreyfus and Nowick (55)	-	D.C.	2.12 [±] .07	
Jain and Dahake (56)	NaCl+Ni ²⁺	D.C.	2.34 [±] .01	
Kirk and Pratt (57)	NaCl+Mn ²⁺	A.C.	2.30 [±] .02	
Brown and Hoodless (58)	NaCl+Sr ²⁺ +Ba ²⁺	A.C. A.C.	2.28 2.26	
Graham et al. (5)	NaCl	A.C.	2.26	

TABLE 1 CONT'D:

SOURCE	SYSTEM	TECHNIQUE	h_s (eV)	S_s (eV ⁰ K ⁻¹)
Kirk (48)	NaCl	A.C.	$2.30 \pm .02$	5.2×10^{-4}
Allnatt and Pantalis (59)	NaCl	Diffusion	2.17	2.1×10^{-4}
Beniere et al. (60)	NaCl+Sr ²⁺	A.C.	2.50	9.6×10^{-4}
Laredo and Dartyge (61)	NaCl+Sr ²⁺	A.C.	2.30	6.78×10^{-4}

TABLE.2.

PARAMETERS OF CATION MOTION IN NaCl. B.

SOURCE	SYSTEM	TECHNIQUE	Δh_c (eV)	ΔS_c (eV ^o K ⁻¹)
(50)	NaCl	Diffusion	0.77	2.84×10^{-4}
		D.C.	0.83	
(51)	NaCl	D.C.	0.85	
(62)	NaCl	A.C.	$0.78 \pm .02$	
(63)	NaCl	Diffusion	0.86	
(64)	NaCl	N.M.R.	0.66	
(2)	NaCl	Diffusion	0.60	
(53)	NaCl	D.C.	0.69	
(65)	NaCl	Theory	0.87	
(54)	NaCl	D.C.	0.74	
(66)	NaCl	A.C.	0.74	
(55)	NaCl	D.C.	0.79	
(67)	NaCl	Diffusion	0.71	
(56)	NaCl+Ni ²⁺	D.C.	$0.75 \pm .01$	
(68)	NaCl	D.C.	$0.69 \pm .03$	
	+Na ₂ SO ₄	D.C.	$0.72 \pm .03$	
	+Na ₂ O ₂	D.C.	$0.69 \pm .03$	
(57)	NaCl+Mn ²⁺	A.C.	0.67-0.73	
	NaCl	A.C.	$0.69 \pm .01$	
(58)	NaCl+Sr ²⁺	A.C.	$0.72 \pm .04$	
	+Ba ²⁺	A.C.	$0.74 \pm .04$	

TABLE 2.

PARAMETERS OF CATION MOTION IN NaCl. B. (CONT'D.)

SOURCE	SYSTEM	TECHNIQUE	Δh_c (eV)	ΔS_c (eV ^o K ⁻¹)	$\frac{h_c + \Delta h_c}{2}$ (eV)	$\frac{S_c + \Delta S_c}{2}$ (eV ^o K ⁻¹)
(5)	NaCl	A.C.	0.74			
(48)	NaCl	A.C.	0.67 [±] .01	1.8x10 ⁻⁴		
	+Mn ²⁺	A.C.	0.69 [±] .03			
(69)	NaCl	D.C.	0.720 [±] .010			
	Mg ²⁺		0.734 [±] .015			
	Ca ²⁺		0.743 [±] .025			
	Sr ²⁺		0.740 [±] .020			
	Ba ²⁺		0.780 [±] .010			
(70)	NaCl	Diffusion			1.78 [±] .03	
(59)	NaCl	Diffusion	0.66	2.75x10 ⁻⁴		
(71)	NaCl	A.C.			2.06	7.44x10 ⁻⁴
		Diffusion			2.10	
(60)	NaCl+Sr ²⁺	A.C.	0.72	1.78x10 ⁻⁴		
	NaCl	A.C.	0.70			
(61)	NaCl+Sr ²⁺	A.C.	0.75	2.61x10 ⁻⁴		

TABLE 3.

PARAMETERS OF ANION MOTION IN NaCl. A.

SOURCE	SYSTEM	TECHNIQUE	Δh_a (eV)	ΔS_a (eV $^{\circ}$ K $^{-1}$)	$\frac{h_a + \Delta h_a}{2}$ (eV)	$\frac{S_a + \Delta S_a}{2}$ (eV $^{\circ}$ K $^{-1}$)
(72)	NaCl	Diffusion			2.70 free	
(2)	NaCl	Diffusion			2.23	
(73)		Isotope exchange	1.67			
(74)	NaCl	Diffusion			2.29	
(75)	K Cl	D.C.	1.86			
(76)	NaCl	Diffusion	1.10		2.12	6.46×10^{-4}
	NaCl+Ca $^{2+}$	Diffusion			2.49	
(77)	NaCl	Diffusion	0.90		1.92(free)	3.86×10^{-4}
					2.37(pair)*	
(78)	NaCl				2.30-2.60	
(79)	NaCl				2.37	
(48)	NaCl	A.C.	1.60	1.57×10^{-3}		
			2.00			
(59)	NaCl	Diffusion	1.15	8.15×10^{-4}		
(71)	NaCl	Diffusion			2.08	7.11×10^{-4}
(60)	NaCl	Diffusion	0.86	1.96×10^{-4}	2.14	

*Activation enthalpy for motion of vacancy pairs.

TABLE.4.ENTHALPY OF MOTION OF VACANCY PAIRS.

SOURCE	SYSTEM	TECHNIQUE	h_p eV
(76)	NaCl	Diffusion	1.07
(80)	NaCl	Dielectric Loss	1.25
(77)	NaCl	Diffusion	1.30

Kao et al.⁽⁶⁹⁾ have shown that the enthalpy of motion of the cation vacancy is dependent on the cation impurity present and Redfern and Pratt⁽⁶⁸⁾ have seen a similar effect as a result of anion impurity additions.

The choice and the method of application of electrode material is particularly important and care must be taken to ensure that the electrode material or the testing environment does not accidentally add impurities to the crystal. Recent work by Laredo and Dartyge⁽⁶¹⁾ showed that anomalous effects were observed using graphite 'dag' electrodes when testing strontium doped sodium chloride.

Recent measurements of h_s and Δh_c show reasonable consistency. Values of about 0.70 eV for Δh_c and 2.30 eV for h_s in sodium chloride are acceptable to most of the data. A notable exception to this is the value of 2.50 eV for h_s obtained by Beniere et al.⁽⁶⁰⁾. The values of the entropy of motion of the cation vacancy, ΔS_c , obtained by Beniere et al.⁽⁶⁰⁾ are in close agreement with Kirk⁽⁴⁸⁾ and Allnatt and Pantalis⁽⁵⁹⁾. The entropies of formation of the Schottky pair are not so consistent and vary from $9.6 \times 10^{-4} \text{ eV } ^\circ\text{K}^{-1}$ to $2.10 \times 10^{-4} \text{ eV } ^\circ\text{K}^{-1}$. The values obtained by Nelson and Friauf⁽⁷¹⁾ for the slope of the intrinsic region (2.06 and 2.10 eV) appear to be rather high compared to other work, if a value of 0.70 eV for Δh_c is assumed there values would give values of h_s of 2.72 eV and 2.80 eV. Their experimental curves show a considerable curvature in the region where measurements have been taken, 823°K to 973°K and it seems that these values of activation energy are more appropriate to region I' than region I.

The study of the diffusion of chlorine ions in sodium chloride received little attention until Chemla⁽⁷²⁾ developed a technique for studying Cl^{36} diffusion. This technique was later used by Laurent and Benard^(1,2), and Schamp and Katz⁽⁶³⁾. Ewles and Jain⁽⁷⁵⁾ measured the decay of conductivity with time in quenched potassium chloride. They deduced that the enthalpy of motion of the chlorine vacancy was 1.86eV, a value too high compared with recent measurements.

A technique involving a radioactive gas exchange developed by Harrison et al.⁽⁷⁴⁾ greatly improved the study of anion diffusion. Their results showed a 'knee' at 670°K and they suggested that the anion vacancy concentration became fixed at this temperature. Lidiard⁽⁸²⁾ later suggested that diffusion might be due to vacancy-pairs at temperatures above the 'knee'.

Further evidence for the presence of vacancy pairs is provided by the high temperature dielectric loss measurements of Sastry and Srinivasan⁽⁸³⁾, Sack and Smith⁽⁸⁴⁾, and Economu and Sastry⁽⁸⁰⁾. The absorption peak is found in the temperature range 873°K to the melting point. They found a rotational energy of 1.26eV compared with Lidiard and Tharmalingham's⁽⁸⁵⁾ theoretical values of 1.16eV; and a formation energy of 1.32eV against a theoretical value of 1.28eV. The binding energy was found to be 0.78eV. The data did suggest an unreasonably large number of pairs and the explanation of this is not clear. It has been suggested by Barr and Lidiard⁽¹⁴⁾ that these peaks can be better accounted for in terms of interfacial polarisation at the electrodes.

Recently obtained values (see Table.3) of the enthalpy of motion of anion vacancies are of the order of 0.9 to 1.1eV. These values compare well with values obtained by Rolfe (86), Chandra and Rolfe (87) and Fuller and Reilly (88) for anion diffusion in potassium chloride, that is 0.87eV, 0.99eV and 0.92eV respectively. The values of ΔH_a obtained by Kirk (48) were calculated from the enhanced conduction in region I' of plastically deformed crystals, and it was assumed that these values correspond to anion diffusion in sub-grain boundaries, not in the bulk.

The presence of divalent impurity ions in sodium chloride, as it has already been stated, markedly affects the level of conduction in region II of the conductivity plot. Studies of aliovalent impurity ions in sodium chloride has led to an understanding of impurity-vacancy interactions. Workers in this field are numerous and readers are again referred to the reviews for details. The work of Rao et al. (69) and Beniere et al. (60) has recently provided values of enthalpies of motion of cation vacancies in the presence of divalent cations, in particular Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . Their results indicate that the binding energy of the complex and the solubility of the impurity in the crystal lattice are dependent on the divalent ion radius but the enthalpy of motion of the cation vacancy is not. These results are in contrast to previous work by Dreyfus and Nowick (55) who found a systematic dependence of the enthalpy of motion of cation vacancies on impurity ion radius.

The association of manganese impurity has been studied by Kirk and Pratt (57), and Kirk (48) using conductivity, dielectric absorption and I.T.C. techniques. The different

forms of the associated states of the impurity ion, that is the free ion, impurity-vacancy complexes and aggregated phase were investigated. They found values of 0.30-0.40eV for the enthalpy of association of the manganese ion and the cation vacancy, which are in good agreement with values obtained by Lure et al. (67) and Brown and Hoodless (58), an average value of 0.68eV for the enthalpy of reorientation of the manganese ion-vacancy complex and 0.88eV for the enthalpy of solution of the manganese ion into the sodium chloride lattice.

The effects of aliovalent and monovalent anion impurities have also been studied by several workers. Divalent anions will depress the conduction since the number of cation vacancies is effectively reduced to maintain charge neutrality. Monovalent anion impurities will also suppress the extrinsic conduction since they will tend to form divalent cation-anion complexes and tie up a cation vacancy in the complex.

Redfern and Pratt (68) introduced sulphate and oxygen ions into the lattice with the effect of reducing the level of conduction but not significantly altering the slope of region II, thus cation motion appears to remain predominant. Auger, Fritz and Luty (89), after doping crystals of KCl with hydroxyl ions, found that complexes with the divalent cation impurities were formed. Stoebe and Pratt (90) attributed the reduction in conductivity of hydroxyl ion doped lithium fluoride to the formation of magnesium-hydroxyl ion complexes. These results are in contrast to those of Pashkovskii, Tsal' and Tkachuk (91) who found an enhancement of conduction in hydroxyl-ion doped KBr which they attributed to the formation of nonsymmetrical ionic configurations (Cl - K - OH for example) which makes the formation of cation vacancies

more probable.

Kirk ⁽⁴⁸⁾ found (in manganese ion doped sodium chloride) that extrinsic isotherms did not

extrapolate to the origin but to a point on the concentration axis. It was assumed that this was due to the presence of anion impurity forming complexes with the manganese impurity. This would effectively reduce the manganese concentration within the crystal. The absence of hydroxyl or carbonate peaks in the infra-red suggested that the impurity was oxygen, the crystals being air grown.

1.4.3. Diffusion in Dislocations.

During the prior discussions of grain boundary models and structures it became evident that dislocations can be arranged to form low angle grain boundaries. Thus it is interesting to investigate ion transport in dislocations with the hope that the information obtained will be relevant to the study of transport in grain boundary regions.

Dislocations can affect the conductivity in two ways, by altering the distribution of vacancies and by providing paths of enhanced conduction. Lehovec ⁽⁹²⁾ pointed out that the surface of an ionic crystal will be positively charged whilst the bulk of the crystal will be electrically neutral. The surface contains excess anion vacancies and the bulk of the crystal contains equal numbers of anion and cation vacancies. The positive charge on the surface is compensated by a space charge of opposite sign extending into the crystal.

The presence of charge on dislocations was first proposed by Pratt ⁽⁹³⁾ who suggested that excess jogs of one sign lying on the dislocation core surrounded by a charge cloud of opposite sign could exist. Eshelby et al. ⁽²⁶⁾ attempted to determine the potential associated with space-charge and argued for the existence of an "isoelectric temperature" ^{which} is impurity dependent and occurs when cation and anion vacancy concentrations at the boundaries are equal. Below the isoelectric temperature the dislocation core has an excess of negative jogs (Na^+ vacancies) and above this temperature an excess of positive jogs (Cl^- vacancies).

Kochler, Lengeth and Von Turkovich ⁽⁹⁴⁾ obtained an energy of formation of the cation vacancy of 0.53eV and Brown ⁽⁹⁵⁾ has given a complete analysis of the space charge potential about a dislocation core.

The diffusion of ions down dislocation cores was first studied by Tucker, Leskar and Thomson ⁽⁹⁶⁾ who measured the transport of sodium ions in dislocations in lithium fluoride by conductivity techniques. Large scale diffusion with sodium dendrite formation was observed, and the diffusion was measured by radioactive tracer methods and measurement of charge transport. Transient conductivity experiments yielded an activation energy of diffusion of 0.30eV for edge and screw dislocations and a frequency factor, D_0 of $0.01 \text{ cm}^2 \text{ sec}^{-1}$. Analysis of charge effects in the core of the dislocation lead to a proposition of a high vacancy density in the core. Geguzin and Dobrovinskaya ⁽⁹⁷⁾ studied sodium ion diffusion in dislocations in sodium chloride by standard tracer techniques. Their results agreed well with Hart's ⁽⁹⁸⁾ model of overlapping diffusion channels and Smoluchowski's ⁽⁹⁹⁾ model of diffusion

"tubes". The results showed:

$$D_d S_{\text{edge}} = 7 \times 10^{-12} \exp \left[\frac{-0.61}{kT} \right]$$

and: $D_d S_{\text{screw}} = 8 \times 10^{-10} \exp \left[\frac{-1.10}{kT} \right]$

where S is the 'tube' area, and D_d is the coefficient of diffusion along dislocations. These results show that edge dislocations allow a higher diffusion of cations than the bulk but they are difficult to analyse without further information on the diffusion "permeability" of dislocations to the motion of chlorine ions and values of the "tube" area, S .

Prior to the work of Tucker et al.⁽⁹⁶⁾, Barr et al.⁽⁷⁸⁾, using an isotope exchange technique, found that a decrease in dislocation density reduced the anion diffusion coefficient and increased the apparent activation energy, they also found that Hart's ⁽⁹⁸⁾ model was applicable. Kanzaki, Kido and Ohzura ⁽¹⁰⁰⁾, also found an increase in conductivity with increase in dislocation density in zone refined potassium chloride. They noticed an anisotropy of conductivity in bent and annealed single crystals with electric fields applied parallel and perpendicular to oriented edge dislocations. The temperature dependence of the anisotropy^{ratio} gave a formation energy of positive ion vacancies of 0.5 to 0.7 eV. The results from the purest crystals showed agreement with charged dislocation theory, but the understanding of the less pure crystals was not complete.

More recent work by Kirk (48) on deformed sodium chloride showed that deformation results in a definite enhancement of conduction in the temperature range 870°K to 920°K . It was found that the enhancement decreased after prolonged annealing at 873°K . These results were interpreted as the enhanced conduction ^{of the} anion vacancies down the sub-grain boundaries formed by the annealing of the deformed dislocation structure. Prolonged annealing resulted in an increase in the sub-grain size, and a decrease in the total volume of grain boundaries and hence a decrease in the enhanced conduction.

1.4.4. Diffusion in Grain Boundaries.

Many researchers have been interested in the diffusion of matter down grain boundaries although most of the early work was concerned with metals. Laurent and Benard (1,2) studied the self-diffusion of sodium and chlorine ions in polycrystalline sodium chloride. Their work indicated that no increase of the diffusion coefficient of sodium ions was apparent, but they did notice an increase in the diffusion coefficient of the chlorine ion. The diffusion coefficient increased with decreasing grain size, but the activation energy remained constant. Their results are shown in fig.1.8. Later results by the same workers (2) showed a similar behavior for other alkali chlorides and potassium halogens. They also concluded that the self-diffusion coefficients showed a linear dependence on the polarizability of the diffusing species.

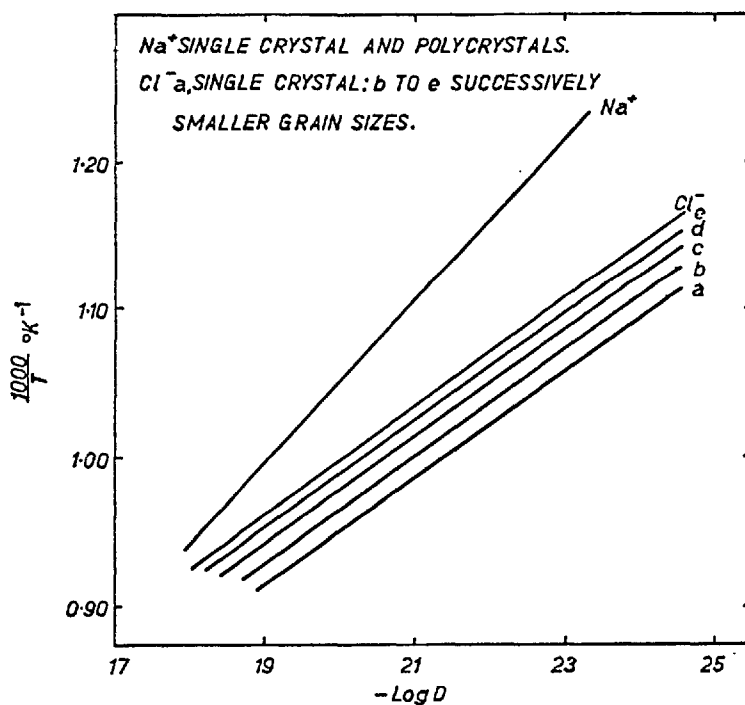


Fig.1.8. DIFFUSION IN POLYCRYSTALLINE NaCl.¹²

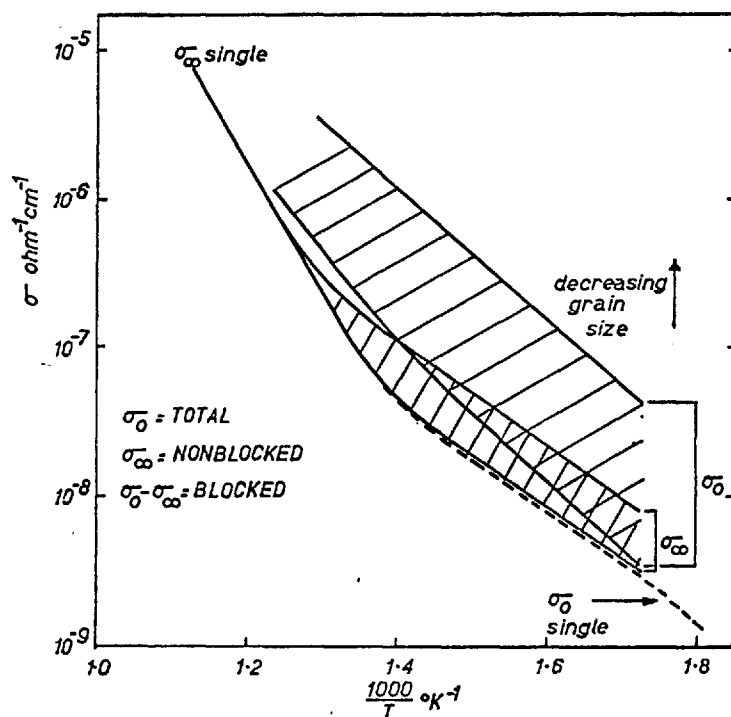


Fig.1.9. CONDUCTIVITY OF POLYCRYSTALLINE NaCl.⁵

Cabané (3) later pointed out that the analysis of Laurent and Benard was incorrect and that the analysis of Whipple (101) was more correct. Laurent and Benard used Fisher's (102) analysis which is only applicable under certain conditions.

Fisher's mathematical analysis of diffusion down a grain boundary applied the condition that the boundary is perpendicular to the diffusing surface and parallel to the diffusing direction. This is only useful when ratios of $D_{\text{BOUNDARY}} \delta$ to D_{BULK} are large (δ is the effective width of the boundary). The Fisher analysis also leads to anomalously high activation energies for grain boundary diffusion, especially in low angle boundaries. Whipple's analysis is more precise and takes into account diffusion direct from the surface and sideways diffusion from the grain boundary. The different analyses of grain boundary diffusion have been discussed by Le Claire (103).

Cabané (3) studied the effect of different methods of preparation of polycrystals on the diffusion of ions. He found that polycrystals produced from carefully dried powder were completely transparent and were completely dense. Polycrystals from undried powder were opaque and the grain boundaries were easily etched in comparison with the dried polycrystals. He found that none of the specimens exhibited enhanced cation diffusion, but the undried opaque specimen did show an enhanced anion diffusion. These results are in agreement with Wuensch and Vasilos (104) who concluded that enhanced diffusion in polycrystalline magnesium oxide was due to segregation of impurities. Geschwind and Machlin (105) have also noticed an enhancement of grain boundary conduction

which they attributed to the presence of water. This evidence would suggest that the enhanced conduction of chlorine ions in grain boundaries is the result of the association of hydroxyl ions with impurities or defects in the boundary region.

Cabane (3) found that although the value of $D_{\text{BOUNDARY}}^{\delta}$ increased with decreasing grain size in the opaque specimens the activation energy remained constant. He also noticed a second diffusion mechanism, which was apparent only in his transparent specimens, that had an activation energy of about one half of that found in single crystals. The parameter $D_{\text{BOUNDARY}}^{\delta}$ was therefore less temperature dependent than D_{BULK} and hence only noticeable at low temperatures. This leads to the conclusion that the boundary width δ is small, which is in agreement with models of grain boundary structure.

Tilt boundaries in lithium fluoride have been studied by Moment and Gordon (4) using a conductivity probe technique; this method was later used by McQuhae (6) to study diffusion in tilt boundaries in sodium chloride. Moment and Gordon doped boundaries with sodium ions and found that the enhanced conduction had an activation energy of 0.32eV which was independent of grain misorientation. This activation energy is the same^{as} found by Tucker et al. (96) in sodium doped edge dislocations in lithium fluoride. Moment and Gordon interpreted their results in terms of a disordered boundary structure containing a high vacancy concentration.

McQuhae (6) "injected" sodium, potassium, and cesium ions into tilt boundaries in pure sodium chloride and found the energies of motion to be 0.32, 0.55 and 0.65eV respectively

in the boundary. The enhanced conduction indicates a high vacancy density and the dependence of activation energy on ion radius was suggested to indicate a structure with discrete sites rather than the disordered structure suggested by Mott and Gordon. The lack of dependence on tilt angle was interpreted as arising from a common vacancy mechanism of motion. McQuhae also noticed an anisotropic behaviour of the conductance for low-angle boundaries, indicating that a **columnar** dislocation structure is applicable. The 'island' model is more in line with results for high angle boundaries.

Graham, Tallan and Russell⁽⁵⁾ investigated the particle size dependence of the conductivity of polycrystalline sodium chloride. They postulated that the interfacial blocking found at high temperatures is due to the blocking of anions only, at the electrodes. The difference between the steady-state d.c. conductivity, σ_{ss} , and the short time d.c. or a.c. conductivity, σ_0 , is the contribution of the anions to the conduction. Their data for polycrystals showed that the a.c. conductivity increased inversely with particle size and the d.c. steady-state conductivity increased only slightly. The increase in a.c. conductivity was associated with the increase in the motion of the chlorine ion in the boundary regions. Their results have been summarised in fig.1.9. and table 5 gives their values of Δh_a for different particle sizes. The results indicate that the bulk diffusion is important until the grain size is reduced to below about 74-44 microns, that is when the grain boundary volume becomes appreciable compared to the bulk volume. The value of about 1.0eV for Δh_a is in good agreement with bulk diffusion measurements. Graham et al. found the thickness of the enhanced boundary layer to be

about 0.1 microns at 623°K , this is in good agreement with the thickness of space-charge layers calculated by Lehov~~ec~~ (92)

TABLE 5.

GRAIN - SIZE (microns)	Δh_a (eV)
147	1.27
147 - 74	1.14
74 - 44	1.18
44 - 38	0.97
38	0.98
1 - 2	0.99

Results of Graham, Tallan, and Russell ⁽⁵⁾ for Δh_a in polycrystalline sodium chloride.

1.5. POLARISATION PHENOMENA IN IONIC CRYSTALS.

1.5.1. Introduction.

It is well known that frequency dependent **resistance** and capacitance effects are observed in ionic crystals when an a.c. electric field is applied to the crystal via metallic or graphite electrodes. These effects are observed at most temperatures from the melting point down to room temperature.

At very high temperatures near the melting point a high frequency dispersion, between 1 and 10 MHz, of the capacitance and conductance has been observed (80,83,84) and is attributed to the reorientation of vacancy pairs. Interfacial polarisation phenomena, and electrode blocking effects, are present over a wide range of temperatures. The effects are manifested as a decay of current after the application of a d.c. field and as a frequency dispersion of conductance and capacitance if an a.c. field is applied.

Dielectric relaxation of impurity-vacancy complexes below 420°K gives rise to a further polarisation, phenomenon occurring in sodium chloride doped with divalent cations. This again can be observed as a transient decrease in current in a d.c. field or as an a.c. field relaxation in the 100-10. kHz range.

1.5.2. Space Charge.

Frenkel (106) was first to suggest that the concentration of vacancies may be different in surface regions than in the bulk. Later Lehovec (92) analysed this space-charge layer and the distribution of lattice defects at the surface of ionic crystals. The space-charge in the surface region causes an electrostatic potential between the bulk and the surface of the crystal. Lehovec suggested that there would be an excess of positive ion vacancies, giving rise to a negative space-charge. He deduced that the width of the space-charge layer at 600°K is 2.2×10^{-5} cm and at 900°K is 1.3×10^{-6} cm. The width of a layer of bulk material, with a conductivity equal to the extra conduction introduced by a space-charge layer being 4.7×10^{-4} cm at 600°K and 1.10×10^{-5} cm at 900°K. Lehovec suggested that there should be some effect of the space-charge conduction on the conduction of microcrystalline samples of grain sizes $\leq 10^{-4}$ cm. He also suggested that only about 0.01% of the negative ions on the surface need be missing to give rise to the charge.

Eshelby et al. (26) predicted that the presence of divalent cations would give rise to a negative surface charge at lower temperatures. An increase in temperature would see this change to a positive charge. The temperature at which no charge existed being the "isoelectric temperature". Eshelby et al. confined their studies to dislocations but Schwensfeier and Elbaum (107) have observed a similar effect in grain boundaries.

Lifshits and Geguzin⁽¹⁰⁸⁾, and Lifshits, Kosevich and Geguzin⁽¹⁰⁹⁾ proposed that the distribution of vacancies shown in fig.1.10. should exist at the surface. This

distribution is dependent on the state of the surface, temperature and impurity content. Kliever⁽¹¹⁰⁾ has extended the theory concerning the distribution of defects in ionic crystals containing divalent cations. For crystals in the temperature range where defect concentrations are governed by the impurity content, the impurities tend to concentrate in the vicinity of the surface. Nadgorni and Stepanov⁽¹¹¹⁾ found evidence of impurity accumulation in calcium doped sodium chloride. Kliever suggests that the excess of divalent cations is compensated by the negative surface charge, the result of excess anions in the surface. This fact being corroborated by the ease with which isotopic exchange occurs between sodium chloride and a gaseous halogen.

1.5.3. Interfacial polarisation.

Interfacial polarisation arises from

the presence of surface layers and is manifest in a frequency dependence of capacitance and conductance in a.c. measurements and a transient decay of current in d.c. measurements.

The frequency and temperature dependence of capacitance and conductance in a.c. measurements is often best depicted in curves of the dissipation factor, or loss tangent, $\tan \delta$, against temperature and frequency. The dissipation factor

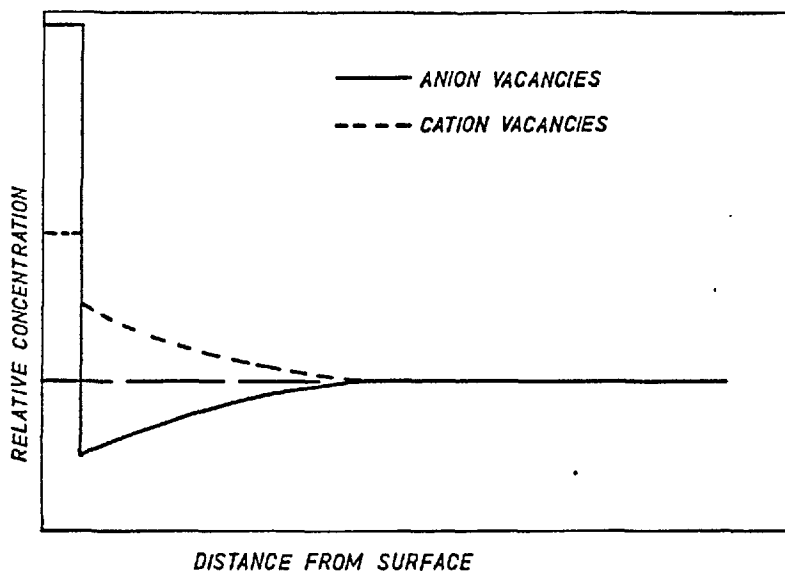


Fig.1.10. DISTRIBUTION OF VACANCIES IN THE SURFACE AND NEAR SURFACE REGION¹⁰⁷

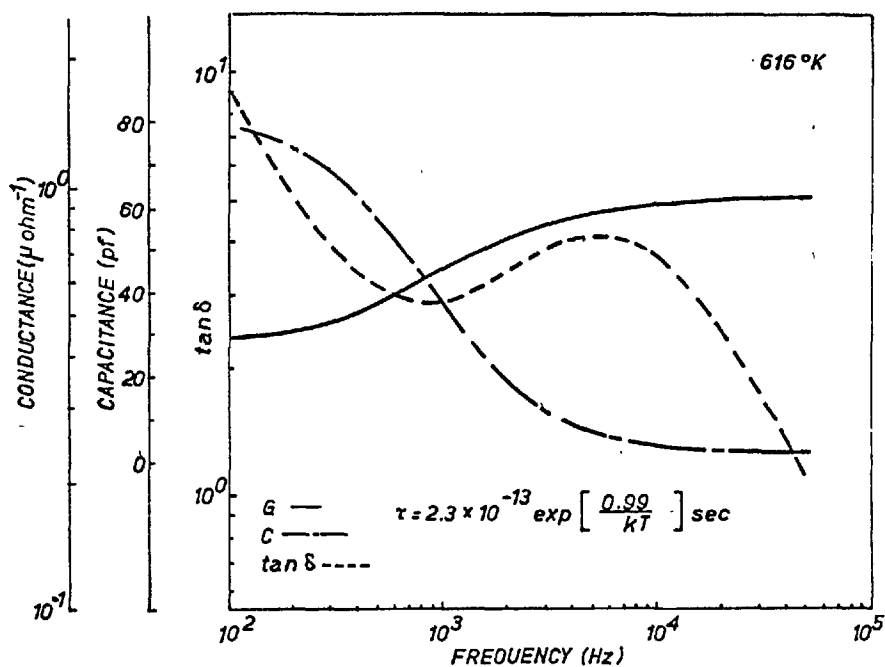


Fig.1.11. DISSIPATION FACTOR MAXIMUM AND CONDUCTANCE AND CAPACITANCE DISPERSIONS IN NaCl RESULTING FROM INTERFACIAL POLARIZATION¹¹³

is a function of both capacitance and conductance. A dielectric behaviour of the crystal will result in a peak in $\tan \delta$ versus frequency plots. The loss tangent is given by the equation:

$$\tan \delta = \frac{G}{2\pi fC} \quad 1.30.$$

where C is the capacitance, G is the conductance and f is the frequency of the applied a.c. field.

Volger (112) has presented a review of dielectric behaviour in materials containing thin surface layers whose electrical properties differ from those of the bulk, and some of the experimental observations of these interfacial polarisation effects in polycrystalline materials. In the case of surface layer polarisation,

$$\epsilon = \epsilon_b + \frac{\epsilon_a - \epsilon_b}{1 + \omega^2 \tau_\epsilon^2} \quad 1.31.$$

$$\sigma = \sigma_b - \frac{\sigma_b - \sigma_a}{1 + \omega^2 \tau_\sigma^2} \quad 1.32$$

$$\text{and } \tan \delta = \frac{\sigma_a}{\epsilon_a \omega} \frac{1}{1 + \omega^2 \tau_\delta^2} + \frac{\sigma_b \tau_\delta}{\epsilon_b} \frac{\omega \tau_\delta}{1 + \omega^2 \tau_\delta^2} \quad 1.33.$$

where ϵ and σ are the permittivity and conductivity respectively at any angular frequency ω , the subscripts a and b refer to low frequency and high frequency limiting values and represents effective relaxation time. Also

$$\left(\frac{\epsilon_a}{\epsilon_b}\right)^{\frac{1}{2}} \tau_\delta = \tau_\epsilon = \tau_\sigma = \frac{\epsilon_1 d_2 + \epsilon_2 d_1}{\sigma_1 d_2 + \sigma_2 d_1} \quad 1.34$$

the subscripts 1 and 2 refer to properties of the thin layer and the bulk respectively and d is the thickness of these regions. From equations 1.31 - 34 it is apparent that for given values of ϵ , σ and d for each region, the permittivity and, hence the capacitance of the specimen will fall from its low frequency value to its high frequency value in a range of frequency centred about $\omega = \tau_{\epsilon}^{-1}$; the conductivity will increase from its static to high frequency value in the same frequency range; and the dissipation factor $\tan \delta$, which varies as ω^{-1} at low frequencies, will pass through a maxima at $\omega = \tau_{\sigma}^{-1}$. Approximate expressions for various quantities in the two layer model have been listed by Volger⁽¹¹²⁾ and by Tollen, Graham and Wimmer⁽¹¹³⁾. Typical results of Tollen et al. for interfacial polarisation in sodium chloride are shown in fig.1.11. Their results were discussed and analysed in terms of Volger's two layer model.

Releigh⁽¹¹⁴⁾ has recently reviewed the theoretical and experimental data available in the study of a.c. polarisation effects arising from carrier blocking at the electrodes. The basic situation consists of an a.c. potential applied to a crystalline ionic solid by means of a set of identical metallic electrodes which are chemically inert with respect to the crystal. The theory generally involves complex mathematical expressions, even if simple and idealised boundary conditions are involved. Exact solutions of the differential field and flux equations are not possible but Chang and Jaffe⁽¹¹⁵⁾, MacDonald⁽¹¹⁶⁾ and Friauf⁽¹¹⁷⁾ have all made approximations. Their solutions were derived assuming the crystal to be a complex circuit containing parallel capacitance and resistance networks. The individual solutions differ due to different assumptions and boundary conditions. The most interesting boundary condition is the complete blocking of

carriers at the electrodes, as one would expect with sodium chloride or potassium chloride with platinum or graphite, that is inert electrodes.

Jacobs and Maycock (118) simplified MacDonald's expressions for the case of positive carriers fixed, negative carriers mobile and small carrier concentrations to,

$$C_p = \left(\frac{2 \pi k T}{C_p} \right)^{\frac{1}{2}} \frac{2 \sigma^2}{\omega^2 (2L)^2} \quad 1.35$$

for potassium chloride between 873°K and 973°K where σ is the specific conductance, $2L$ the crystal thickness, C_0 is the low frequency limiting capacitance and C_p is the capacitance of

the parallel network. They found that this modified expression appeared to be more general than was assumed by MacDonald and applies when there are equal mobilities, and unequal mobilities of the different carriers, and where one carrier is immobile.

Agreement of experiments with equation 1.35. is erratic, Jacobs and Maycock (118) reported good agreement for pure crystals of potassium chloride but doped crystals did not agree so well. Earlier work by Allnatt and Jacobs (119) gave values of C_p which were too small and were not in good agreement with the predicted ω^{-2} dependence. More recently Beaumont and Jacobs (120) have developed a theory based on the partial blocking of carriers at the electrodes to explain the doped potassium chloride results. Although better agreement was found Raleigh (114) has pointed out that there is no thermodynamic justification for assuming partial blocking for doped crystals and complete blocking for pure crystals. Wintle and Rolfe (121) also noted approximate

agreement with Jacobs and Haycock's simple theory in studies on doped KBr, but serious other discrepancies arise, namely a capacitance variation by a factor of twenty between gold and graphite electrodes, also in other work a dependence on thermal history was noted, this being not dealt with by existing theories.

Raleigh has pointed out that a clearer picture is obtained if the a.c. polarisation effects are considered in terms of a series representation of resistance and capacitance as opposed to the previously adopted parallel representation. The equation of Jacobs and Haycock ⁽¹¹⁸⁾ is identical with the following expression of Friauf ⁽¹¹⁷⁾,

$$C_p = \frac{C_o}{1 + (\omega R_o C_o)^2} \quad 1.36.$$

where R_o is the intrinsic ionic resistance. For the case of complete blocking the change in conductance of the crystal due to polarisation effects is given by,

$$-\Delta \frac{1}{R} = \frac{1}{R_o} - \frac{1}{R_p} \quad 1.37.$$

The net parallel resistance in the circuit is,

$$R_p = R_o \left[1 + \frac{1}{(\omega R_o C_o)^2} \right] \quad 1.38.$$

If the expressions of C_p and R_p are converted to equivalent series parameters where,

$$C_s = C_p + \frac{1}{\omega^2 C_p R_p^2} \quad 1.39$$

$$\text{and} \quad R_s = \frac{R_p}{1 + (\omega C_p R_p)^2} \quad 1.40$$

then substituting 1.36. and 1.37. in 1.39. and 1.40

$$C_s = C_o$$

$$\text{and} \quad R_s = R_o$$

Thus the previous parallel relationships are the parallel capacitance and resistance of a frequency-independent capacitor and resistance in series.

The model of an ionic solid between blocking electrodes now becomes a resistor between two capacitors. Intrinsic resistive and capacitive effects are now separated and a number of parameters previously thought to be significant are effects of the parallel representation. The dispersions of series capacitance and series resistance will occur if the frequency of the charging process at the electrode is comparable with the frequency of the a.c. test.

Rayleigh also pointed out that the physical state of the electrodes and the state of the contact between the electrodes and the crystal are also very important and that experiments with carefully controlled electrode surfaces and contact would be of considerable value.

Work by Kessler and Moriani (122-125) has shown the presence of ^arelaxation maximum in pure and calcium doped sodium chloride, and these peaks were observed apart from

the relaxation maxima of the calcium-vacancy complexes. The temperature of the maxima shifts to lower temperatures with increasing calcium content (from 632°K to 415°K in sodium chloride containing 0.0001% to 1.0% calcium). Their early work ⁽¹²²⁾ attributed these peaks to the relaxation loss of the crystal lattice itself. Later work ⁽¹²³⁻¹²⁴⁾ suggested that the maxima may be due to interfacial polarisation and the recent work ⁽¹²⁵⁾ noted a considerable dependence of the loss peaks on the state of the electrodes and they concluded that the maximum was due to interfacial polarisation.

Tallan et al. ⁽¹¹³⁾ have also observed a loss maximum in the same temperature range which they interpreted as interfacial polarisation. They found that the relaxation time obeyed the following relationship:-

$$\tau = 2.3 \times 10^{-13} \exp \left[\frac{0.99}{kT} \right] \text{ sec.}$$

They also suggested that their work agreed with the two-layer model of Volger ⁽¹¹²⁾. The insulating surface layer having a thickness of 10 - 20 microns. Wimmer and Tallan ⁽¹²⁶⁾ have found a large potential drop in a thin region adjacent to the electrodes using a probe technique. This they interpreted as being due to interfacial polarisation arising from the presence of a surface layer having a higher resistivity than the bulk and is in agreement with the results of Tallan et al. ⁽¹¹³⁾ Recent work by McQuhae ⁽⁶⁾ using a similar probe technique did not detect any such potential drop at the electrodes. He concluded that the effects seen by Wimmer and Tallan ⁽¹²⁶⁾ were the result of the external circuitry of the apparatus.

The relaxation maxima were found by Kaderka (127) to be affected by the addition of OH^- and CO_3^{--} ions. MacFarlane and Weaver (128) have investigated the low frequency dielectric losses in thin films of sodium chloride. They found two regions of dielectric dispersion, having loss maxima typically near 1Hz and 0.003 Hz at room temperature. They found activation energies associated with these peaks of $0.9 \pm 0.2\text{eV}$ and $0.95 \pm 0.1\text{eV}$ respectively. MacFarlane and Weaver suggested that these results may be interpreted in terms of two interfacial polarisation mechanisms, which involve blocking of cation vacancies, firstly at the intercrystalline boundaries and secondly at the electrodes, the latter predominating at sufficiently low frequencies.

It has been previously mentioned that information concerning interfacial polarisation can be studied by measuring the current decay after the application of a d.c. field. The observation of a time dependence in the polarisation of dielectrics followed by a "dielectric aftereffect" has been observed for many years. These phenomena are shown diagrammatically in fig.1.12. This shows that under an applied field, E , the current falls from an initial value i_0 to a finite constant value, i_∞ . When the field is removed a negative current flows, as shown. This "aftereffect" is due to the discharge of the dielectric layers. The area under the two curves is the same.

Parker (129) and Sutter and Nowick (130) have studied the time-dependent polarisation in pure and doped crystals of sodium chloride at fairly low temperatures (220°K to 470°K). The latter authors also studied the effects of air gaps at the electrodes, deformation, irradiation and annealing.

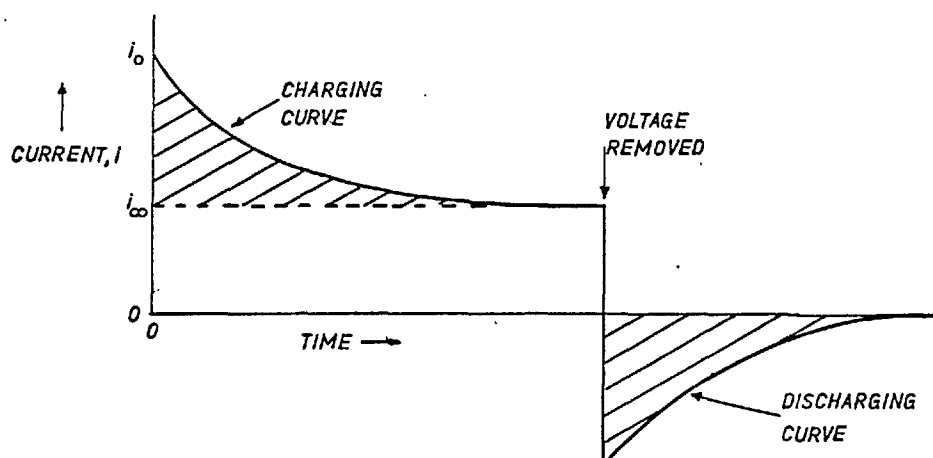


Fig.1.12. SCHEMATIC DIAGRAM SHOWING THE VARIATION OF CURRENT WITH TIME UNDER AN APPLIED D.C. FIELD AND THE AFTEREFFECT WHEN THE FIELD IS REMOVED

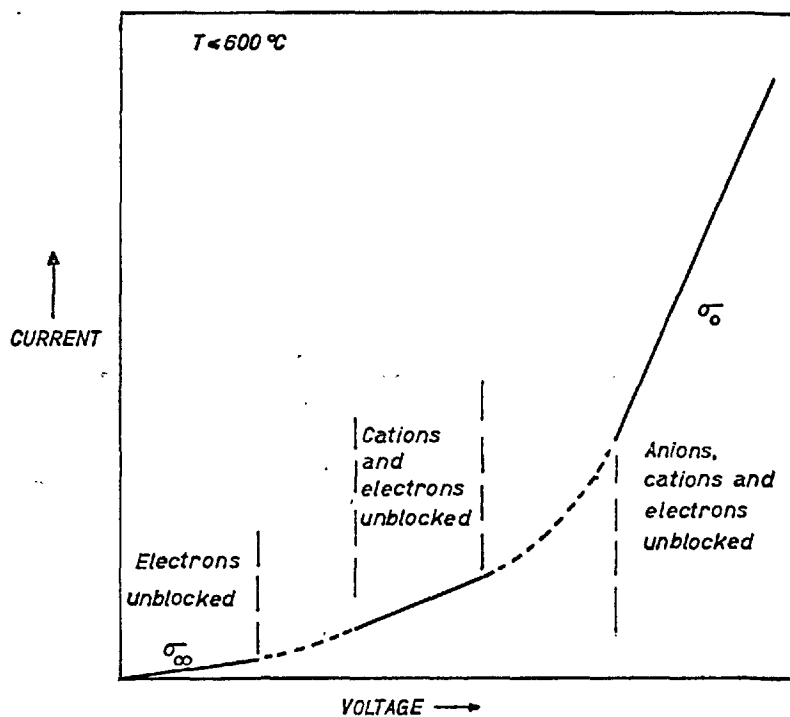


Fig.1.13. DIAGRAMATIC OHM'S LAW PLOT FOR KCl¹³⁵

They concluded that the results were not consistent with space-charge polarisation theory, but were consistent with a dielectric relaxation phenomenon. Several possible mechanisms were discussed including defect clusters and charged-jogs on dislocations. The presence of a dielectric absorption maximum in a.c. measurements has been detected by Dryden (131) and other workers (132) in this temperature range. It has been attributed to the reorientation of impurity-vacancy dipoles.

Later work by Bucci and Riva (133) on pure and doped potassium chloride in the same temperature range has shown similar effects. However, a careful study of Ohm's law and of ionic thermoconductivity revealed the presence of a polarisation phenomenon which could not be explained as a dielectric relaxation alone and the results did show that an interpretation in terms of ionic space charge formation was realistic.

Parker (129) concluded that the polarisation effects were due to the blocking of vacancies at mosaic boundaries about 20 microns apart. Recent work by Kao, Whitham and Calderwood (134) measuring the polarisation in the temperature range 370°K to 620°K in pure and doped sodium chloride has again suggested that the polarisation is due to the presence of dislocations and internal surfaces. Their observations did not support an interpretation based on space charges at blocking electrodes or the reorientation of divalent cation-vacancy complexes.

Maycock (135) has reported a polarisation phenomenon at high temperatures (670°K to 930°K) in zone-refined potassium chloride. He found that the current decay curves can be

plotted in the form $\log i_p$ against t , where $i_p = i_t - i_\infty$, i_t is ^{the} current after time t . The theory of Jaffe (136-139) considered the movement of charged species under an applied field, and the idea that at the boundaries of the medium certain ions can discharge whereas others cannot, thereby producing a space charge. The theory suggests that i_p can be represented by a sum of exponential terms,

$$i_p = Ae^{-\alpha t} + Be^{-\beta t} \quad 1.4 \text{ l.}$$

Maycock found that the charging curves did obey such a relation and thus concluded that the polarisation was due to electrode blocking effects. He also proposed that the steady-state conduction was due to the electrons produced at the electrodes by the discharge of the potassium ions at the cathode, which produces an F-centre which is thermally ionized to form an electron and an anion vacancy. He also found that Ohm's Law was not obeyed with applied fields greater than 100mV and that the current-voltage curve is complex, as shown in fig.1.13. He relates this curve to the unblocking of the electrode as the applied field is increased. Kirk and Pratt and Graham et al.⁽⁵⁾ have also reported a polarisation phenomenon in region I of the conductivity curve. Both works have attributed this to be the result of electrode blocking, but neither have confirmed that σ_∞ is the conduction due to electrons. Graham et al.⁽⁵⁾ suggested that the blocked conductivity ($\sigma_0 - \sigma_\infty$) was due to anions only, that is only the anions are blocked at the electrodes.

1.5.4. Other polarisation phenomena.

It has already been mentioned that at low temperatures, below about 400°K, a dielectric absorption is obtained, which has been attributed to the reorientation of vacancy-impurity dipoles. The resonant absorption can be obtained by a suitable choice of temperature and applied a.c. field (≈ 1 kHz at 303°K) as a peak in the plot of $\tan \delta$ against $\log f$. This absorption can be described in terms of the classical Debye equation. Dryden⁽¹³¹⁾, Cook and Dryden^(139,141), Haven⁽¹⁴⁰⁾, and Quin⁽¹³²⁾ have studied several systems. The ageing of the Debye peak was found to give important information concerning the kinetics of association of the dipoles into higher complexes.

The presence of a further dielectric relaxation^(80,83,84) at temperatures near the melting point has already been discussed and is attributed to the reorientation of vacancy pairs.

CHAPTER 2.

EXPERIMENTAL METHODS.

2.1. CRYSTAL GROWTH AND PURIFICATION.

2.1.1. Purification of Sodium Chloride.

For an effective study of grain boundary segregation it is desirable that only one solute species should be present in the crystal, since different impurities may modify the grain boundary hardness differently.

As a first step sodium chloride was produced which contained as little divalent cation impurity as possible. From this ^{material} crystals could be grown with a single species of impurity ion added during the growing process. Very pure single and polycrystals for conductivity measurement were also produced.

Divalent cation impurities were removed from Analaar grade sodium chloride using a solvent extraction and ion exchange technique previously described by McQuhae (6). This method is more effective than zone-refining which cannot be used to remove calcium ions, as the partition coefficient is approximately unity. McQuhae has shown that the ion exchange technique will effectively reduce the concentration of each divalent cation to less than 5ppm.

The presence of anion impurities is known to affect the bulk conductivity of ionic crystals, but their effect on grain boundary segregation is not known. Considerable enhancement of grain boundary diffusion in polycrystals has been observed, due to the presence of hydroxyl ions (3).

The removal of hydroxyl ions from polycrystalline sodium chloride will be discussed later.

Various methods have been described for the removal of hydroxyl ions from the melt. To reverse the hydrolisation process chlorine, hydrogen chloride or phosgene gas have been bubbled through the melt. However, the presence of one of these very corrosive gases combined with molten salt requires the use of elaborate safety precautions and complex apparatus. A description of the use of chlorine and hydrogen chloride in the purification of sodium chloride has been given by Butler et al.⁽¹⁴²⁾, Otterson⁽¹⁴³⁾, Barr et al.⁽¹⁴⁴⁾ and Agarwal et al.⁽¹⁴⁵⁾ have found that the hydroxyl ion concentration can be effectively reduced by treatment of the melt with dry nitrogen gas. Further, Etzel and Patterson⁽¹⁴⁶⁾ have found that crystals grown from the melt contained in silica or quartz beakers contained less hydroxyl ions than those grown in platinum containers. The crystals used in this work were grown from silica beakers in an inert atmosphere or in air. No further attempts were made to remove hydroxyl ions.

3.1.2. Growth of Crystals.

The crystals were grown using the Kyropoulos method. This method has been described by many previous authors⁽⁶⁾, and so no further details will be given.

Two different growing rigs were used. The first was a simple rig which consisted of a motor driven seed withdrawal mechanism placed above a resistance furnace. The silica

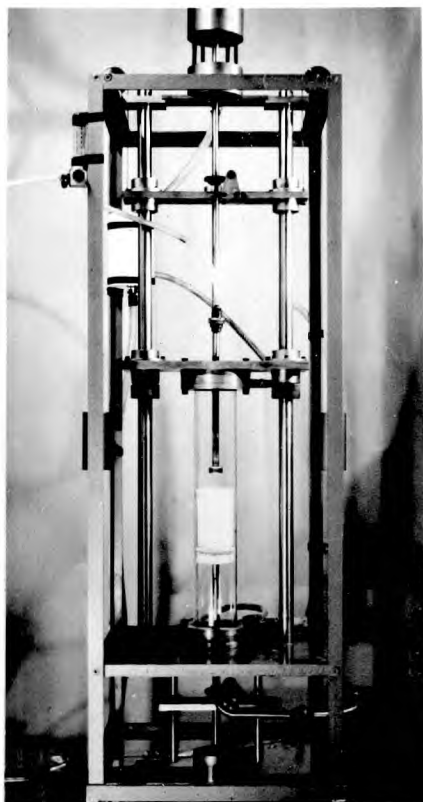


Fig.2.1.

GENERAL VIEW OF
THE CRYSTAL GROWER
WITH FURNACE REMOVED.

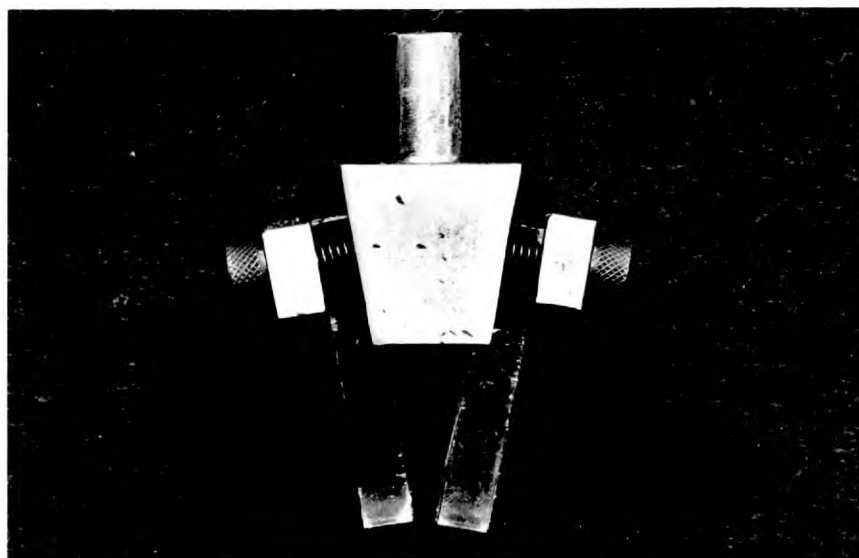


Fig.2.2. SEED CHUCK AND SEEDS.

beaker which contained the sodium chloride was placed in the centre of the furnace. The crystal was drawn from the melt in air, no attempt being made to provide an inert growing atmosphere. The crystals grown in the rig were about 2.5cm in diameter and up to 10cm. long. The grown crystals were annealed in a separate furnace for 24 hours at about 970°K and then slowly cooled to room temperature over a period of 48 hours.

This growing rig was used for growing crystals from Analar grade sodium chloride, and for growing the manganese doped crystals. The manganese ion was added to the melt in the form of manganese chloride, which was of Analar grade and was carefully predried at 600°K .

The second growing rig, shown in fig.2.1., has been previously described by McQuhrie (6). The silica growing beaker was enclosed with the seed and chuck in a transparent quartz tube. The beaker support shaft and seed-chuck drive shaft pass through the water-cooled end-caps of the quartz tube. Vacuum tight seals were provided using 'O'-rings and Wilson-type seals. The growing enclosure was attached to a vacuum system. Inert gas could also be fed into the enclosure; high purity argon was used. The resistance furnace, not shown in fig.2.1., was situated outside the quartz tube. The seed rotation, withdrawal and beaker rotation were all independently driven by small synchronous electric motors, and the speed of each could be varied independently.

The growing chamber was evacuated and the sodium chloride was then heated to about 900°K and left overnight. The chamber was filled with argon which was allowed to flow

through the chamber at a steady rate. The salt was then melted and the crystal was grown. After the growing was completed the beaker was lowered to let the remaining salt solidify whilst the crystal was kept at 970°K for

24 hours and then slowly cooled for 48 hours to room temperature, the inert atmosphere being maintained during the annealing procedure. The crystals measured about 2.0cm diameter by about 6 to 8cm long.

Crystals grown in the inert atmosphere were generally from purified sodium chloride. Bicrystals were also grown in this rig. They were grown using specially made seed chucks, fig.2.2., which could hold two single crystal seeds held at an angle to each other. By carefully controlling the growing condition it was found that bi-crystals could be produced with perfectly planar boundaries. Using seed chucks of different angles symmetrical tilt boundaries of 10° to 80° could be grown.

2.1.3. Analysis of Single Crystals.

Three methods of analysis of impurities were employed. The general level of cation impurities was obtained using an emission spectrographic technique. (Emission spectroscopy by American Spectrographic Labs. 557 Minna Street, San Francisco, California. U.S.A.) The exact concentrations of manganese and calcium were found using atomic absorption, and anion impurities were detected using infra-red spectroscopy. The results of the analysis are summarised in table 6.

TABLE 6:ANALYSIS OF CATION IMPURITIES

MATERIAL	TREATMENT	IMPURITY					
		Mn	Ca	Cu	Fe	Mg	Al
PURE A (Analar)	Air grown single crystal	2 ^b	10 ^a 2 ^b	5 ^a -			
PURE B (Purified)	Single crystal grown in argon	2 ^b	10 ^a 2 ^b	15 ^a -			
ANALAR (Specification)	As received powder	-	30	0.5	5	10	2

Concentrations are shown in mppm (molar parts per million)

a Analysed by emission spectroscopy.

b Analysed by atomic absorption.

Concentration of elements not stated was below the detection limit of emission spectroscopy.

Manganese ion doped crystals same as PURE A + stated manganese concentration determined by atomic absorption.

For the analysis of manganese and calcium a Perkin-Elmer Model 290 atomic absorption spectrometer was used. The analysis of manganese was straightforward, the minimum detection limit was found to be about 0.1ppm of manganese ion in solution. The only problem arose if the concentration of sodium chloride in solution exceeded 100gm./litre when the peak height was considerably reduced presumably due to interference from sodium ions. However, the low detection limit enabled solutions of much less than 100gm./litre to be used.

The interference caused by sodium to the calcium spectra was reduced by the addition of lanthanum oxide to the solution. The minimum detection limit was about 0.2ppm of calcium ion in solution. For both elements the reproducibility of the analyses was better than $\pm 5\%$. It was concluded that atomic absorption was particularly effective for analysing metal radicals in sodium chloride.

The anion impurities were detected using a Perkin-Elmer Model 237 infra-red spectrometer. The pure and low manganese doped crystals did not show any absorption peak for hydroxyl ions at 3600cm^{-1} even for crystals up to 5cm thick. The crystal containing 300ppm of manganese did show a peak at 3650cm^{-1} indicating that a considerable number of hydroxyl ions were present in the crystal. The absence of a peak in the remaining crystals does not mean that hydroxyl ions are not present, but rather the concentration is below the detection limit of the spectrometer.

The purified crystals also have a pair of peaks at 1997cm^{-1} and 2067cm^{-1} , which it would appear correspond to the absorption peaks of metaborate ions. It is thought that

the borate ions are introduced into the salt during the purification procedure, probably from the glassware, which is all of borosilicate glass. The emission spectroscopy also indicates that the purified crystal contains a considerable amount of copper, it is not clearly understood where this has come from, but it is possible that it is introduced into the melt during the growing procedure, since it is only found in those crystals grown in the inert atmosphere growing rig.

The analyses also clearly indicate that the crystal grown from Analar grade material was as pure as the crystal grown from purified material. Indeed the purity of the pure A crystal is very much greater than previously quoted for crystals grown from Analar material ⁽⁴⁸⁾. Although the zone-refining effect of the growing procedure would reduce the impurity content, it is thought that the Analar material used for growing these crystals was of particularly good quality.

2.2. PREPARATION OF POLYCRYSTALLINE SODIUM CHLORIDE.

2.2.1. Introduction.

Several methods have been previously used to produce polycrystalline sodium chloride from single crystals or from powder. Stokes and Li⁽¹⁴⁷⁾ produced polycrystals of sodium chloride by extrusion of a single crystal. Although sodium chloride is brittle it will extrude very easily at 570°K or above. The advantage of this method is that it can produce very "clean" grain boundaries, containing none of the impurities that are likely to arise from sintering. It is, however, difficult to control the grain size, and the grain size varies across the cross-section of the extruded rod, and it is also difficult to obtain small grain sizes. This method has been used in this work and found successful for pure crystals.

Alternative methods of producing polycrystals involve the sintering of a powder compact. There are two basic techniques that can be used, sintering and hot-pressing. Sintering has been used widely for the production of polycrystalline ceramics and ionic crystals. The method involves the pressing of powdered material at room temperature in air, a vacuum or inert atmosphere. The compact is then annealed at a suitable temperature to obtain a dense solid. Several models exist to explain the densification process during the annealing. The reader is referred to a review by White⁽¹⁴⁸⁾ for further details.

The sintering of sodium chloride has been described by Ammer and Budworth (149), who investigated the effects of temperature, time, atmosphere, particle size and green density on the sintering process. They found an increase in density of up to 20% in certain conditions. Kingery and Berg (150) had previously reported that the evaporation-condensation mechanism is predominant, and hence it is not expected that densification would result from sintering. Ammer and Budworth's results appear to suggest that evaporation-condensation is not so important and other processes must be at work to explain the densification.

The second pressing technique is known as hot pressing or pressure sintering. This technique differs from the previous one in that the pressing is done at elevated temperatures, generally in vacuum to exclude air from between the particles. The advantage of this method is that generally maximum theoretical density can be achieved by choosing the correct pressing conditions. Ammer and Budworth (151) found that the major contribution to densification of sodium chloride by cold and hot pressing is from plastic flow, although it is not suggested that diffusion processes are unimportant in other materials of different structure. Vasilos and Spriggs (152) have reviewed hot-pressing in ceramics in general and McClelland and Zehms (153) have discussed alumina in particular. McClelland and Zehms found that an end-point density, that is a density less than the maximum theoretical density, was always reached and hence plastic-flow could explain the results. However, work of Coble and Ellis (154) suggests that diffusion may be an important process.

2.2.2. Preparation of Powdered Sodium Chloride.

The powder used to produce polycrystals was obtained by crushing single crystals, in this way single crystal specimens could be obtained from the ~~same~~ material. The single crystals were first cleaved into small cubes about 0.5cm x 0.5cm x 0.5cm. These were then crushed and ground in an agate mortar. The powder was sieved in screens of 100, 200, 325 and 400 mesh size. The corresponding particle size of the five powder fractions obtained is shown in table.7. The sieves were shaken by a vibratory shaker for at least one hour, to ensure complete partitioning of the powder. The powder was then stored in pyrex tubes which were kept free from moisture in a dessicator. Throughout the powdering procedure great care was taken to ensure that the powder did not become contaminated with any foreign particles.

2.2.3. Vacuum Hot Pressing of Sodium Chloride.

The previous discussion of the relative merits of the different methods of production of polycrystalline sodium chloride showed ^{that} the hot pressing or pressure sintering produced theoretically dense polycrystals, and this method was chosen for the production of most of the polycrystals used in this work.

A vacuum hot-press has been designed to be operated simply, with easy removal of the pressed pellet. This factor being particularly important since any difficulty

TABLE.7:PARTICLE SIZES OF POWDER FRACTIONS.

MESH SIZE	MIN.PARTICLE SIZE (μm)	MAX.PARTICLE SIZE (μm)	MEAN.PARTICLE SIZE (μm)
> 100	150	-	150
100-200	75	150	113
200-325	44	75	60
325-400	37	44	41
< 400	-	37	37

in removing the pellet could result in damage to it. The press is shown in detail in fig.2.3. and photographs of the component parts in figs.2.4. and 2.5.

The press consists of a stainless steel body mounted on a ceramic support, the bore of the press is 1cm in diameter and is highly polished. The rams were made from a high tensile steel, E.N.24. The graphite spacers shown in fig.2.3. and 2.4. prevented the "chilling" of the pellet by the rams and also helped to lubricate the bore of the press to facilitate removal of the pellet. The operating temperature of the press was designed to be less than 700°K and so it was felt that the corrosion of the steel press would not be a serious problem. In fact it was found that pressing could not be done above 600°K since at 650°K the compact flowed freely under load and could force its way past the rams.

The press was heated by a nichrome resistance furnace which was vertically wound on an alumina tube. Electrical connections were made via a ceramic lead-through in the base of the press enclosure. The chromel-alumel thermocouple was also connected to the furnace temperature controller via a similar lead-through. The press and furnace were enclosed in a water-cooled vacuum tight cylinder. The press was attached to the vacuum pumping system by a 5cm diameter stainless steel flexible tube. A pressure of less than 10^{-2} N/m^2 ($10^{-4} \text{ mm. of Hg}$) could be attained using an oil diffusion pump and a rotary backing pump.

The load was applied to the press by a standard 10,000kg Instron testing machine. The press was mounted on the cross-head whilst the ram was pushed using a

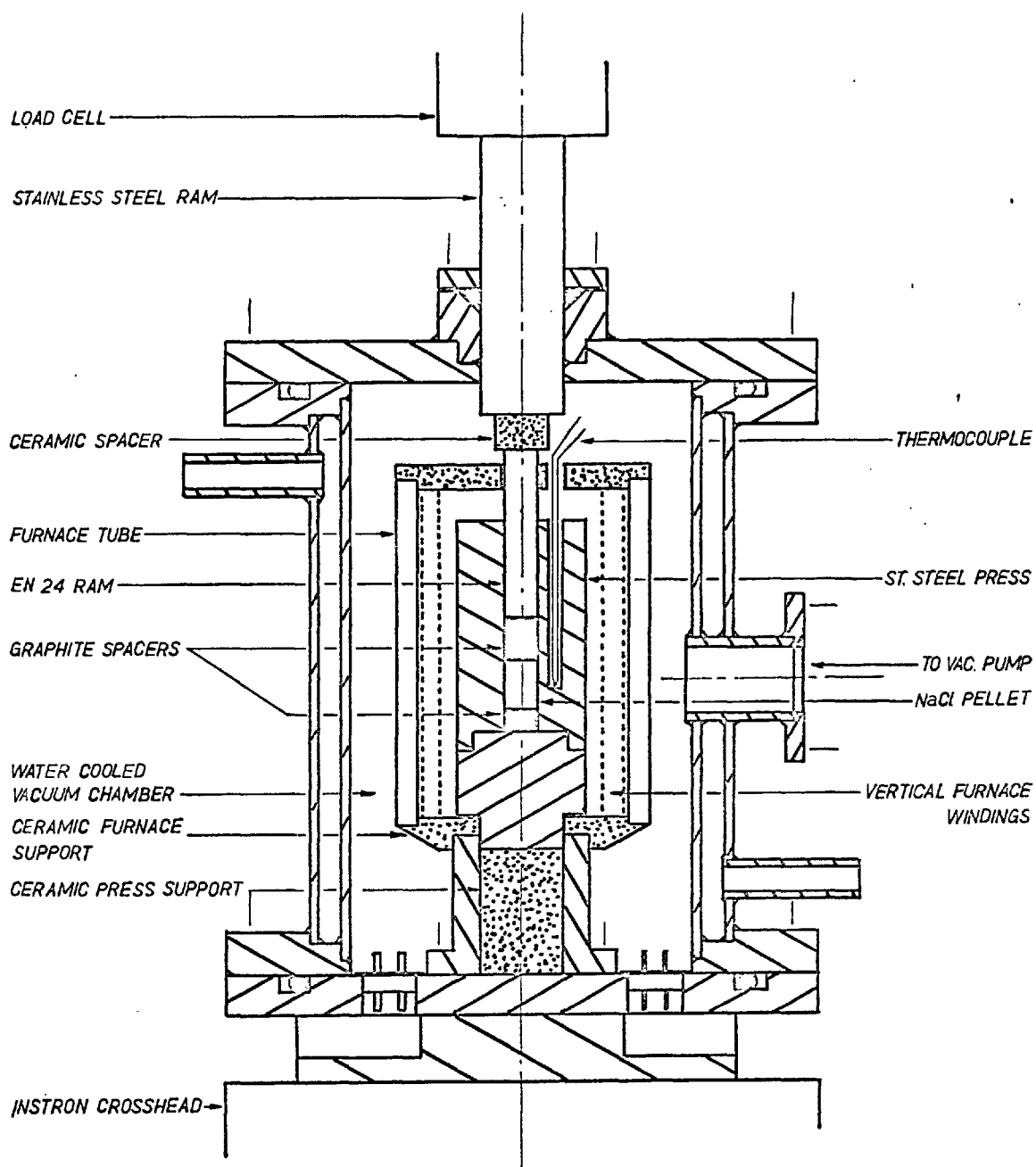


Fig.2.3. VACUUM HOT PRESS

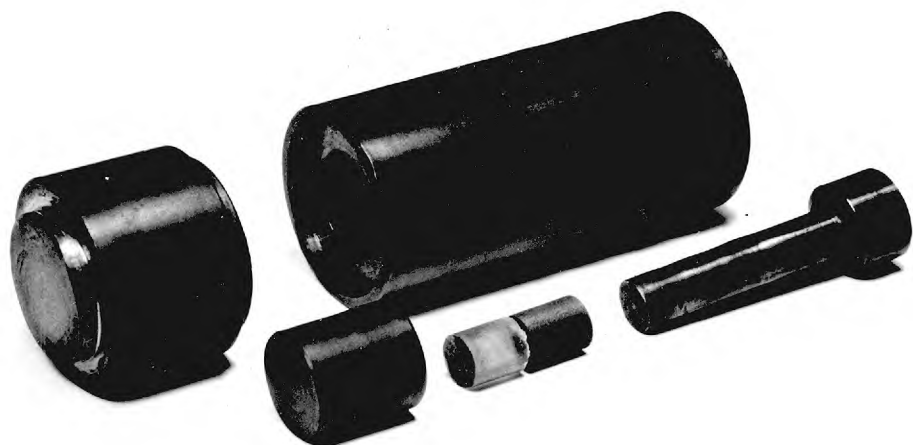
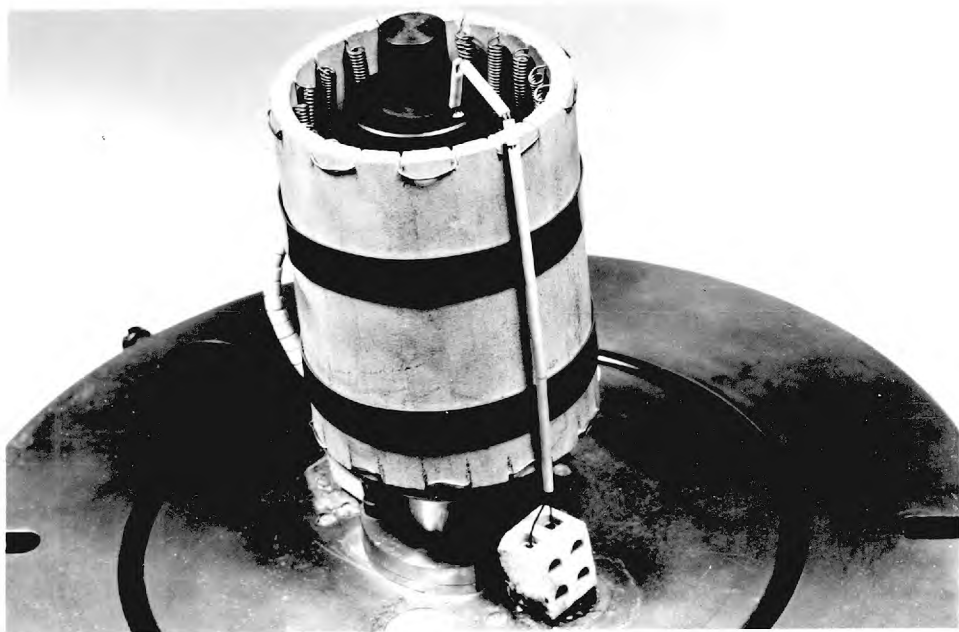


Fig.2.4. COMPONENTS OF PRESS



*Fig.2.5. PRESS AND FURNACE ASSEMBLED
ON BASE PLATE OF VACUUM CHAMBER.*

compression load cell mounted in the top frame. The maximum load that could be used was about 4,000kg, above this the ceramic support of the press body fractured. The maximum pressure that could be applied to the pellet was of the order of 500 MN m^{-2} ($5,000 \text{ kg cm}^{-2}$).

Cabané (3) has shown that the moisture content of the powder before pressing markedly affects the grain boundary diffusion coefficients of anions. Powder which had not been dried prior to hot-pressing produced opaque specimens, whilst dried powder produced completely transparent specimens. For this work the powder was dried in a vacuum at 770°K for 18 hours. The powder was then cooled to room temperature and put into the press, which was then evacuated immediately. It was hoped that this procedure would remove most of the absorbed water in the powder. The powder was pressed at 520°K .

Preliminary tests showed that a pressure of 350 MN m^{-2} was sufficient to obtain a compact of almost theoretical density. Fig.2.6. shows the increase in density with applied pressure. The density is expressed as a percentage of the density of a similar single crystal. The pressure was generally applied for one hour to ensure that maximum densification was achieved. The pellet was removed from the press after it had cooled to room temperature. The specimens obtained in this way were usually completely transparent. Opaque or slightly cloudy pellets were discarded. The pellet produced measured 1cm in diameter and about 1 to 2cm long.

The density was measured by using the method of hydrostatic

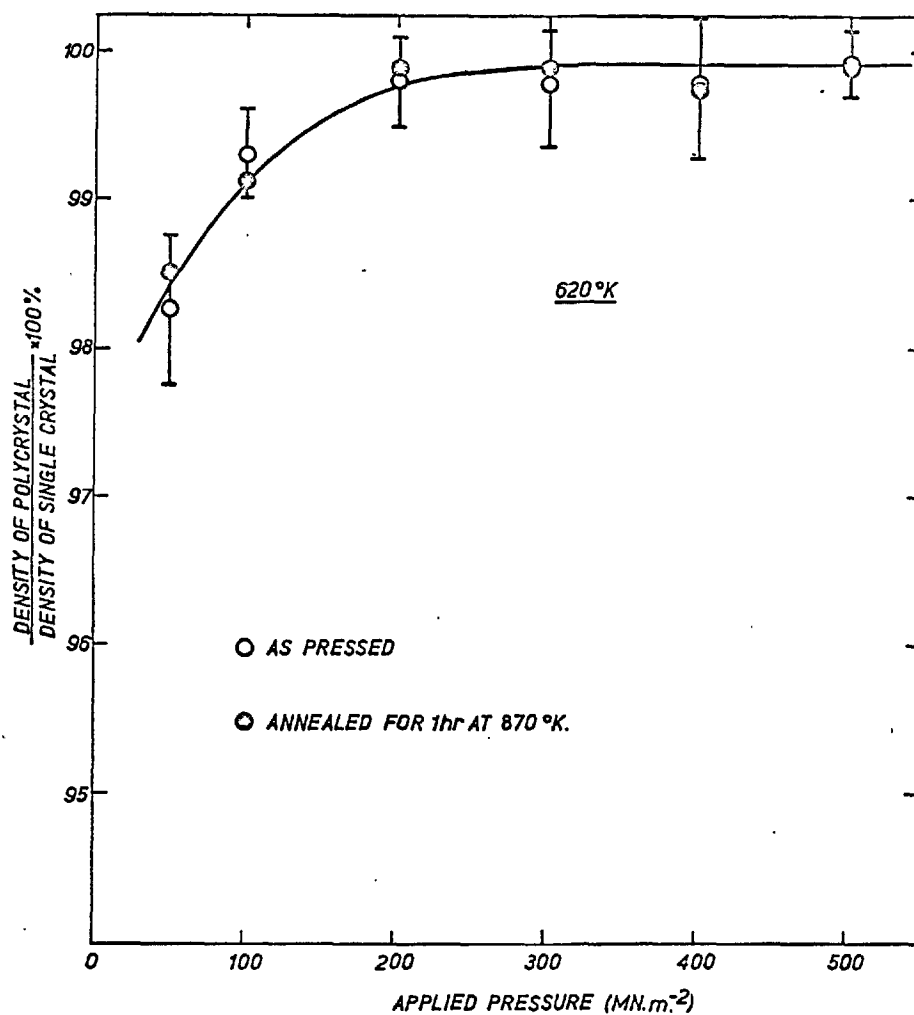


Fig.2.6. VARIATION OF DENSITY OF COMPACTS AS A FUNCTION OF PRESSING PRESSURE.

buoyancy in a high density liquid, 1-2 dibromomethane, this liquid being used since it wets the surface of ionic crystals very well. Errors due to the wetting of surface pores was not considered to be very large due to the high density of the compacts.

The absolute density of the compacts was not measured, the densities being expressed as a fraction or percentage of the density of a similar single crystal. Consecutive weighings, in air and liquid, of both a polycrystal sample and a single crystal sample enabled the ratio of the densities to be measured without a knowledge of the density of the liquid. Both single and polycrystalline specimens were prepared in the same way and were of similar dimensions. The specimens were cut using a Capco diamond slitting saw and then polished in a 5% ammonia solution in distilled water.

During the weighings the temperature of the liquid was found to alter by less than 0.1°K . The weighings were made to an accuracy of $\pm 0.1\text{mg}$. A series of density measurements on one specimen indicated a standard deviation of $\pm 0.5\%$.

2.2.4. Extrusion of Sodium Chloride.

The extrusion technique used was similar to that used by Stokes and Li ⁽¹⁴⁷⁾. The extrusion press is shown in fig.2.7. The press body was made of stainless steel and was bored to take a 2cm diameter single crystal of sodium chloride. The die was machined from a ninonic alloy, the bore of the die was highly polished. The rams were also made from ninonic.

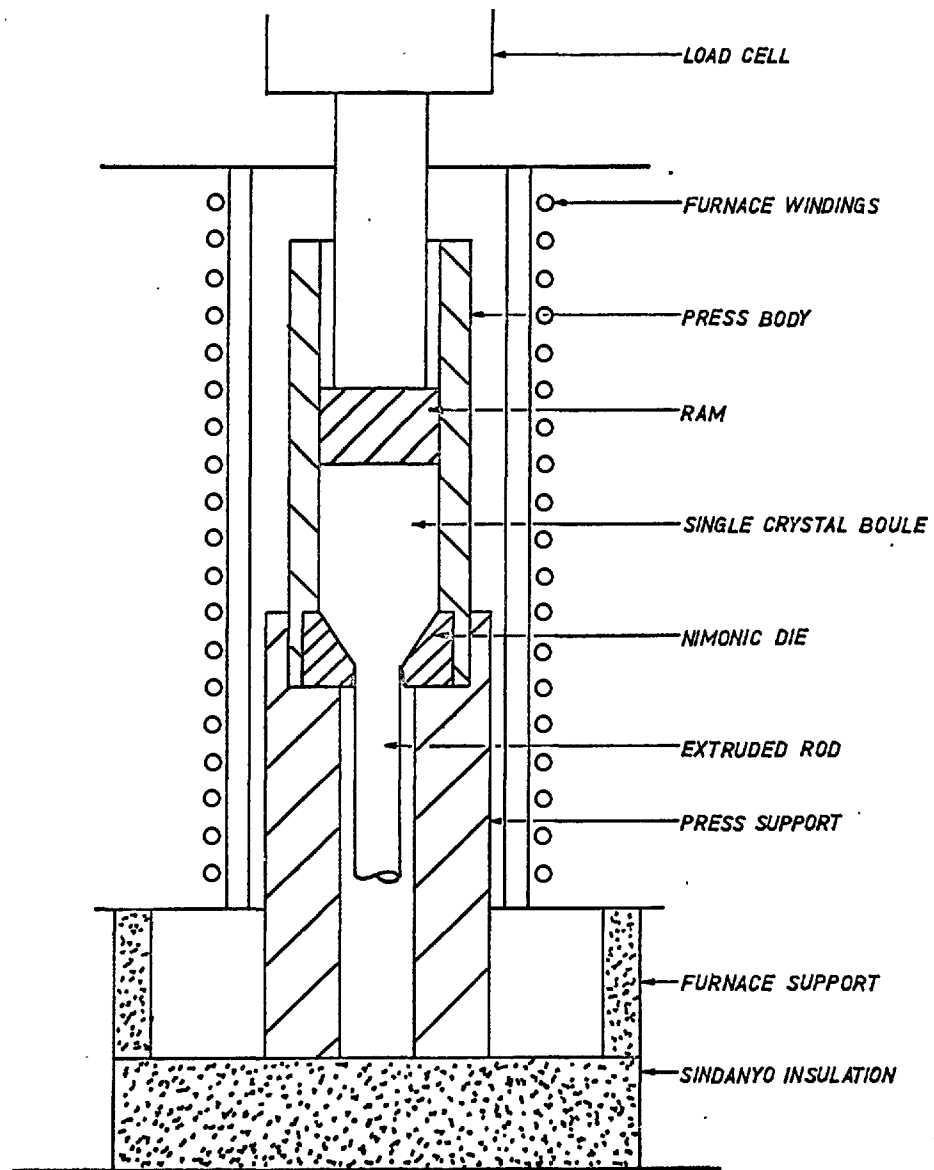


Fig.2.7. EXTRUSION PRESS.

The extrusion press was supported on a stainless steel block which was bored to take the extruded rod. The entire press was mounted on a sindanyo block and then attached to the crosshead of an Instron testing machine. The load was applied to the press using a 10,000kg compression load cell. The press was heated with a resistance furnace which was placed around the press as shown in fig.2.7. The extrusion rate could be varied from 0.005 to 5 cm min⁻¹ using the variable crosshead speeds of the Instron machine.

The single crystals used for the extrusion were prepared by water machining a single crystal boule to a 2cm diameter cylinder about 4cms long. The single crystal was cleaved at both ends and two brass discs 2cm in diameter were glued to each end. The boule could then be put in a lathe and machined to a cylinder using a felt pad soaked in water, by rubbing it against the crystal. The brass discs were removed and the crystal was then extruded. The extrusion temperature used was usually 520°K or above. The extruded rod was 0.8cm diameter and about 10cm long.

2.3. CONDUCTIVITY AND POLARISATION MEASUREMENTS.

2.3.1. Specimen Preparation.

Single crystal conductivity specimens were cleaved from the boule using single edged razor blades. Careful cleaving produced no visible damage to the crystal. The specimens measured about 0.5cm x 0.5cm x 0.2cm . The polycrystalline

specimens were cut from the hot-pressed pellet or extruded rod using a Capco diamond slitting wheel. This saw could be set to cut very slowly with minimum damage to the crystals. Conductivity measurements on both cleaved and sawn single crystals were identical and so it was thought not to be necessary to polish the surface of sawn specimens before testing. The damage on the sawn surface being no greater than the cleaved specimens.

Several electrode coating materials were used. A graphite dispersion in alcohol, supplied by Acheson Products Ltd., proved to be the easiest to apply and to give the most reliable results. Vapour deposited carbon was also just as reliable but more difficult to apply to the surface. Other electrode materials such as silver dispersion, and vapour deposited silver and several platinum compounds were tried but for one or other reason proved to be unsatisfactory. The effects of these electrode materials will be described in Chapter 3.

2.3.2. Conductivity apparatus.

The conductivity rig used for high temperature measurements is shown in fig.2.8. The two stainless steel electrodes were covered with platinum foil which were brazed in place. The electrodes were supported on two stainless steel rods, these rods being held in place by a P.T.F.E. insulator at the top of the furnace. The electrodes were shielded from the furnace windings by a stainless steel tube, which also formed part of the vacuum tight envelope in which the electrode assembly was

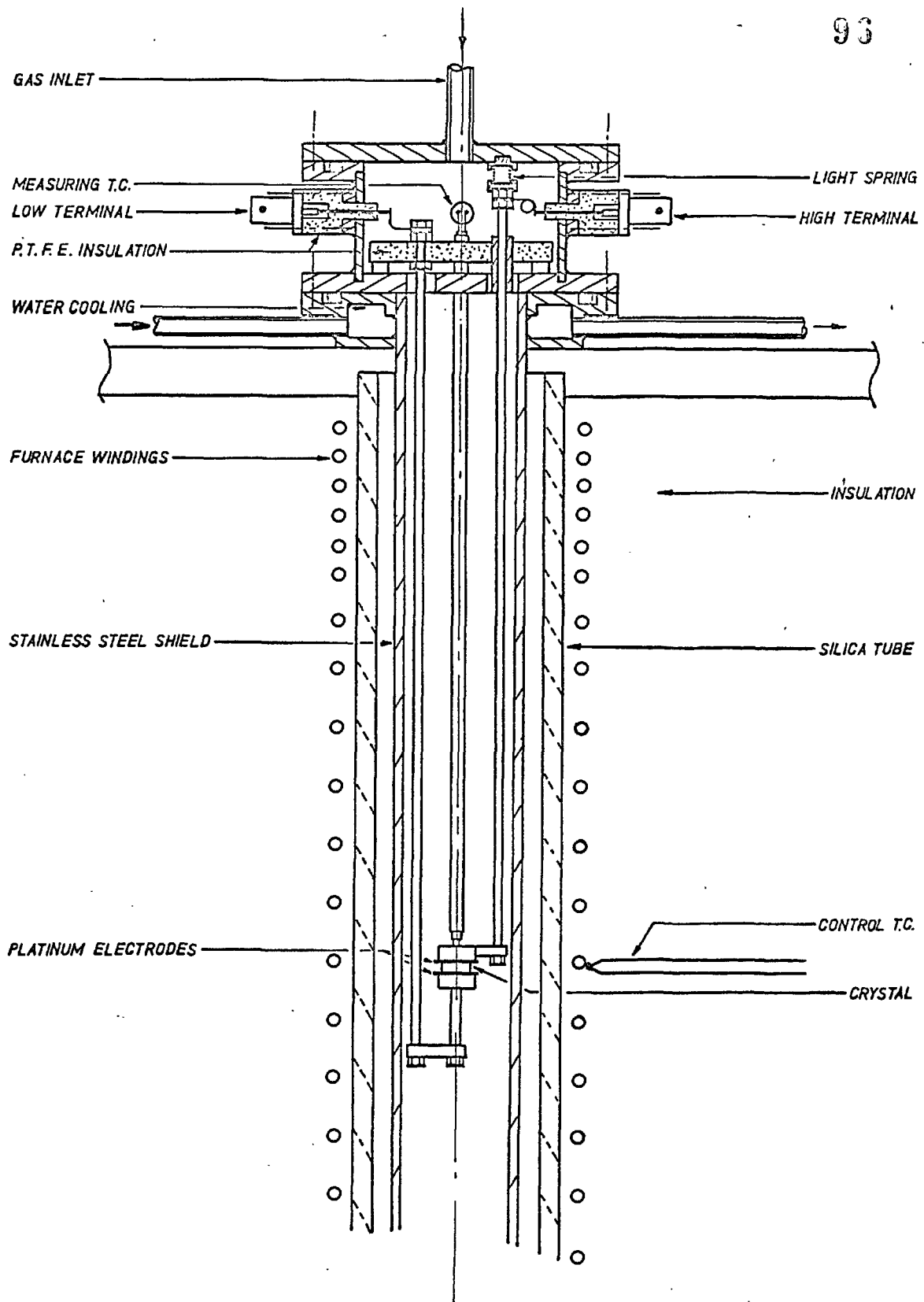


Fig.2.8. CONDUCTIVITY RIG

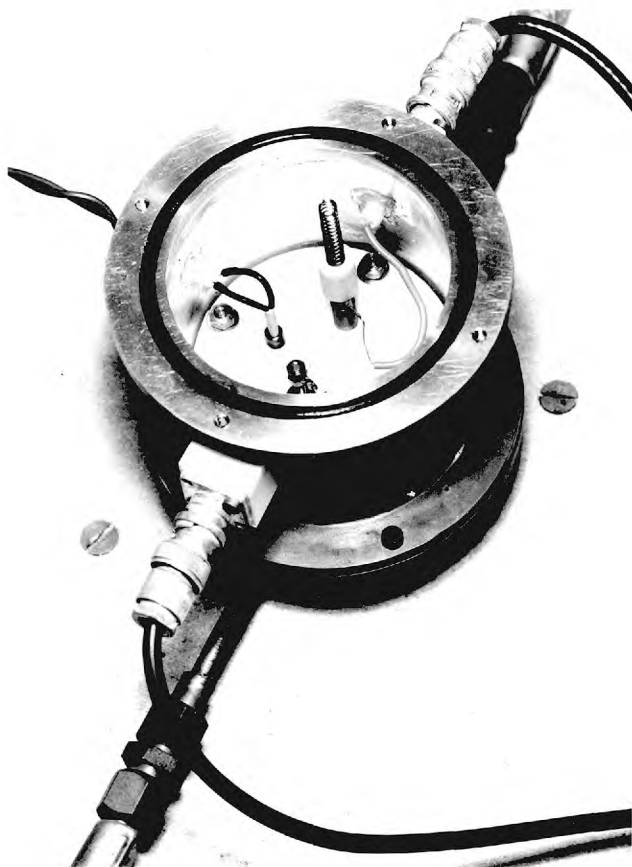


Fig. 2.9.

VIEW OF CONDUCTIVITY
RIG WITH TOP PLATE
REMOVED.

Fig. 2.10.

ELECTRODE ASSEMBLY.



enclosed. High purity argon was passed through the chamber to prevent oxidation of the graphite electrodes and contamination of the specimen. The temperature of the specimen was measured using a chromel-alumel thermocouple placed adjacent to the specimen. Electrical connections to the electrodes were made via screened connectors attached to the rig by P.T.F.E. insulators. Connections to the thermocouple were also made through P.T.F.E. insulators. The use of P.T.F.E. insulation ensured an insulation resistance of 10^{16} ohms or greater. A light spring applied a very small load to the high electrode, which was able to slide up and down, to keep it in intimate contact with the specimen.

The rig was heated by a nichrome wound resistance furnace. The temperature was controlled by an Ether Transistorol controller to about $\pm 2^\circ\text{K}$ over a long period. The power to the furnace was supplied by a smoothed d.c. 220 volt power supply. D.C. was used to minimize a.c. pick up in the conductivity circuit. The furnace windings were insulated by 25cm. of alumina brick and the furnace was 50cm. long. The furnace was wound on a silica tube in three sections, the outer ones being closer spaced than the centre.

The temperature of this furnace was found to rapidly come to equilibrium, which is important so that fairly rapid tests can be made, especially at high temperatures where the crystal could become contaminated by its environment. The stability after reaching equilibrium was better than $\pm 2^\circ\text{K}$ per hour. The temperature gradient across the diameter of the furnace tube was less than 1°K at 870°K and the vertical temperature gradient was less than 1°K at 870°K over a distance of 4cm. above and below the specimen position. The measuring

thermocouple was calibrated using a platinum, platinum-rhodium thermocouple calibrated by Johnson and Matthey Ltd. The calibration of the measuring thermocouple was checked at regular intervals.

The measuring apparatus is shown in figs.2.11-13. A.C. conductivity measurements were made using a Wayne-Kerr Bridge Type 221 using an external source and null-meter, a Wayne-Kerr Waveform Analyser Type A231. Frequencies between 70 Hz and 20 k Hz could be used.

D.C. conductivity measurements were made by applying a known potential, supplied by a bank of Mellory cells, across the crystals in series with a grid resistor of suitable value. The potential drop across the resistor was measured with a Vibron Electrometer type 33C. The electrometer output was fed into the Y-axis of a Bryans X-Y plotter, The X-axis being connected to the internal time-base of the plotter. The d.c. current could also be monitored using an oscilloscope. The voltage applied across the crystal was measured on a Solartron Digital Voltmeter. This voltmeter was also used to give a continuous display of the thermocouple output.

The grid resistor ranged from $1k\Omega$ to $100M\Omega$. The low value resistors were Welwyn 1% tolerance resistors whilst the high values, $1M\Omega$ to $100M\Omega$, were glass encapsulated resistors. The grid resistor selector switch was of very high quality, having a leakage resistance to earth of better than 10^{16} ohms and a negligible contact resistance. The resistors and selector switches were placed inside a metal box which acted as a screen. All leads were made from non-microphonic screened cable. All the screens were maintained

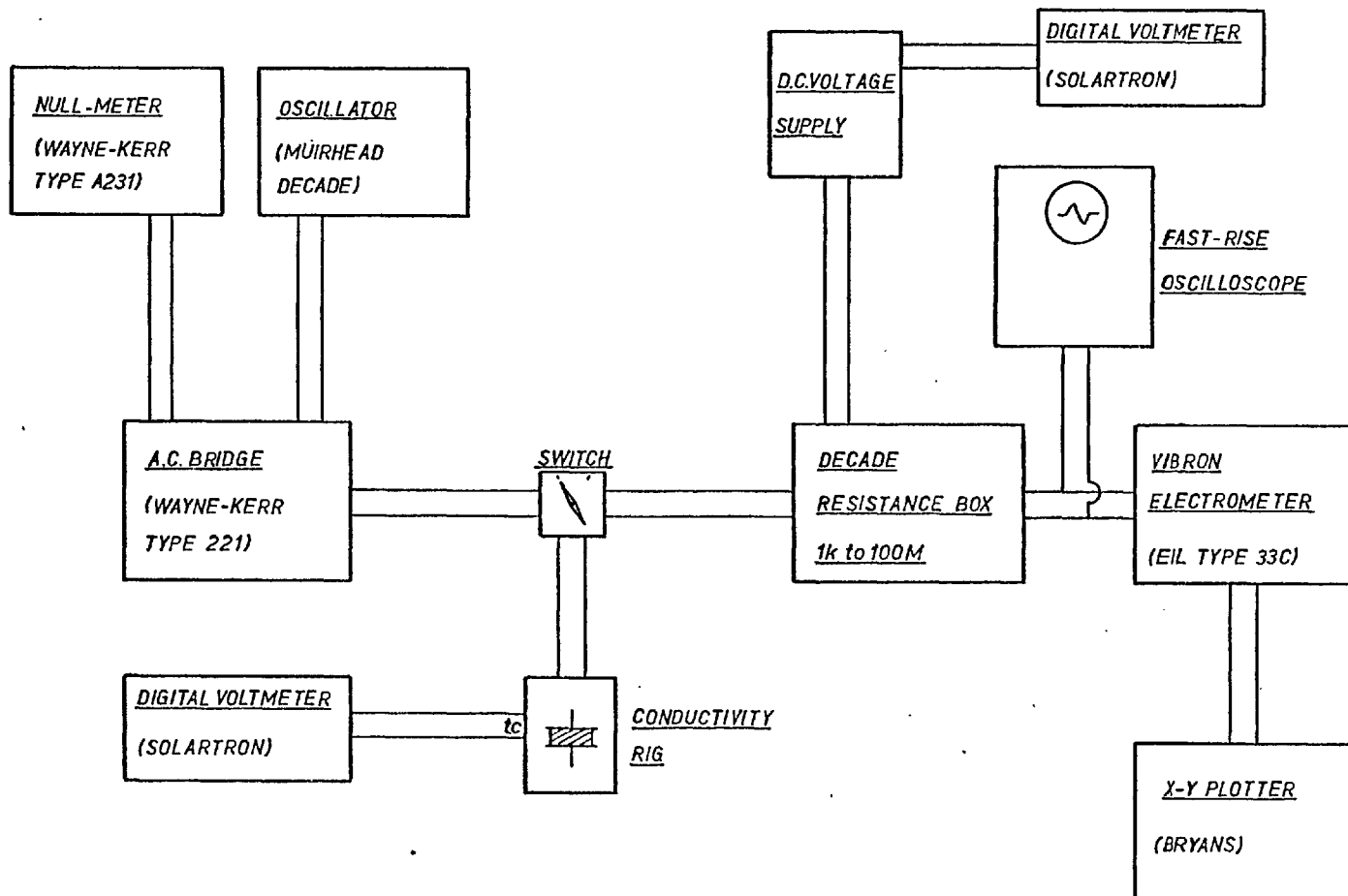


Fig.2.11. BLOCK DIAGRAM OF APPARATUS FOR A.C. AND D.C. CONDUCTIVITY MEASUREMENTS

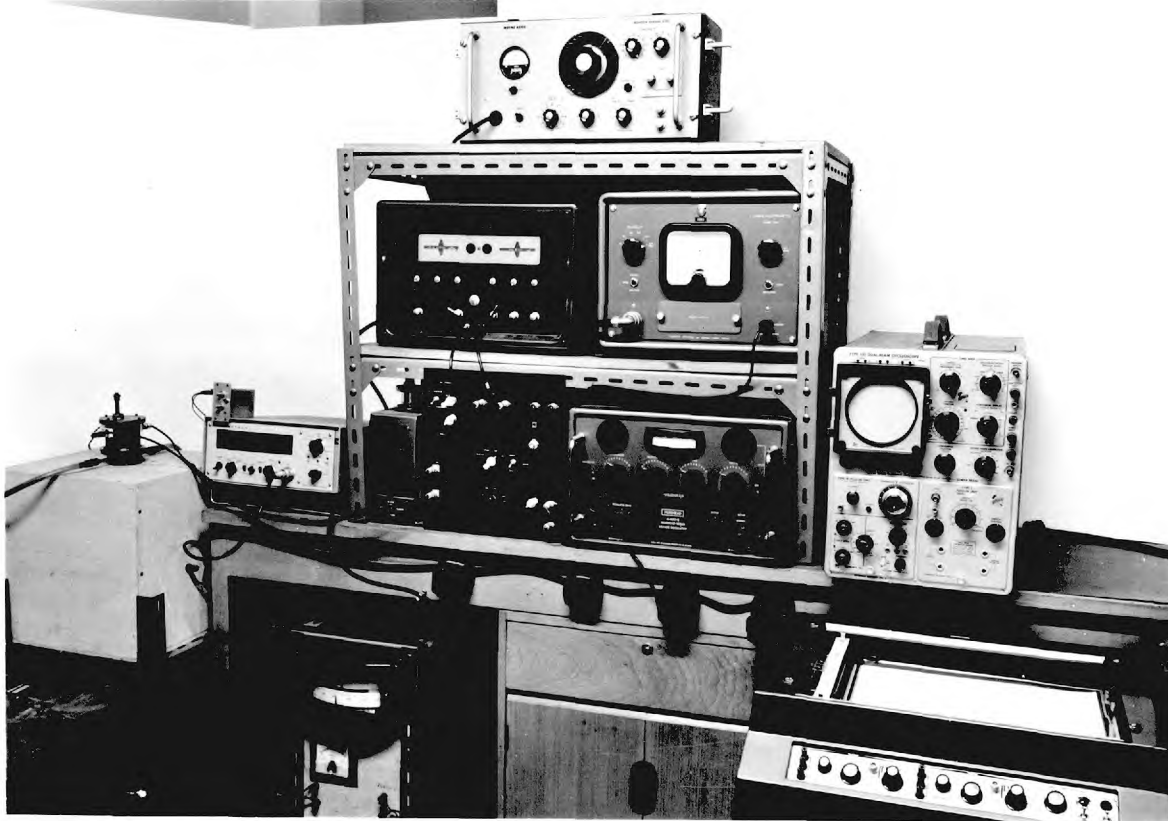


Fig.212. GENERAL VIEW OF CONDUCTIVITY APPARATUS.

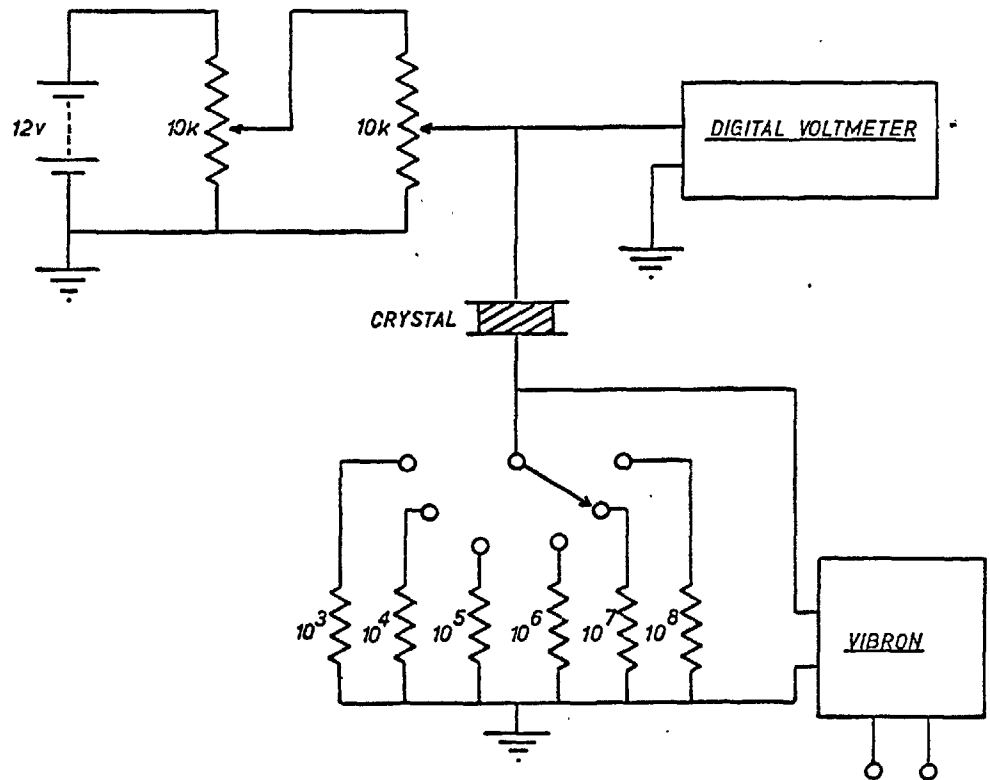


Fig.2.13. CIRCUIT DIAGRAM FOR D.C. CONDUCTIVITY MEASUREMENTS

at the same potential as the screen on the Vibron electrometer head. This effectively prevented any stray pick-up by the electrometer and very steady readings of very small potentials, less than 10mV could easily be obtained.

The entire apparatus had an insulation resistance of greater than 10^{14} ohms, and background noise was negligible. The a.c. conductivity could be measured to $\pm 0.5\%$ using the bridge with external source and detector. D.C. measurements were considered accurate to within $\pm 1-2\%$. Greater accuracy could not be attained due to the small variation in resistance of the grid resistors with changes in ambient temperatures, although the resistors were calibrated before each run using the a.c. bridge.

2.3.3. Experimental Procedure.

The specimen was coated with the graphite dispersion using a small camel hair brush. Care was taken not to let any graphite get onto the sides of the specimen. When a sufficiently thick ~~coat~~ of graphite had been applied the specimen was heated at about 370°K for several hours to dry out the electrodes. The specimen was then placed in the rig and a steady flow of argon ~~passed through it.~~

Conductivity measurements were made when the temperature of the specimen was constant. This was best done by observing the a.c. conductivity, readings being taken when this was observed to be constant over a period of at least 10 minutes.

layer

was passed through the rig.

A.c.measurements were made by selecting the required frequency on the oscillator and balancing the bridge using the waveform analyser as a null-meter. Measurements were made over a range of frequencies between 70Hz and 20kHz.

D.c.measurements were made by applying small potentials across the crystal, generally a potential of 5 volts was used. A grid resistor was selected to give a measurable potential drop across it. Potentials most conveniently measured were between 100mV and 500mV. The transient response of the crystal current was recorded on the X-Y plotter. The speed of the response of the electrometer and the plotter meant that only times of 2 secs and longer could be recorded with any reliability on the recorder.

The apparatus could be used to measure short-time transients (0 - 2 sec.) by applying the potential to the crystal using a low-frequency square-wave generator with a fast-rise time and recording the crystal current on a fast-rise oscilloscope, fitted with a camera attachment. For this work such an arrangement was not used.

2.4. A HIGH TEMPERATURE MICROHARDNESS TESTER.

2.4.1. Introduction.

The conductivity of polycrystalline sodium chloride, as it will be shown later, appeared to be influenced by the segregation of impurities at grain boundaries. It was

considered necessary to develop a further technique to study the effects of grain boundary segregation.

The most common, and well documented, technique to measure microhardness, which has been developed by Westbrook (11,40) and co-workers (9,10,41-46). This technique could provide useful information of a quantitative nature, particularly if the value of microhardness could be related to a more fundamental mechanical property of the crystal. Johnson and Nadeau (155) have tentatively suggested that microhardness on a $\{100\}$ face could be related to the yield stress, or proof stress of crystals when the secondary slip system was operative.

Alternative techniques have been developed for studying segregation, in particular autoradiography and electron probe microanalysis have been used. The recent advent of high voltage electron microscopy as a powerful tool for studying ceramic materials may prove useful for investigating precipitation in ionic crystals and could give information about segregation processes.

The use of the microhardness technique has many problems associated with it and Westbrook has summarised these problems and suggested methods by which the best results can be obtained. The indenting load is particularly critical, if too large the indent will be large compared with the width of the segregated region and so swamp the effect, and if too small instrumental errors, particularly vibration, will also mask the effect. The surface must be carefully prepared either by electro- or chemical polishing, any cold work in the surface will raise the bulk hardness. Ionic crystals are subject to

further modifications of bulk hardness due to the absorption of water from the atmosphere, this effect being known as the Rebinder Effect. Westwood (156,158) and other workers (157,159) have studied these effects.

The specimens should contain only one significant solute species, since there appears to be a marked interaction between coexisting solute species. The effects of grain boundary structure on the hardness of the boundary was also of interest and thus the preliminary work was carried out on bicrystals with grain boundaries of low and high tilt angles. It was also considered desirable to study the segregation at high temperatures, up to 900°K .

2.4.2. Design of Microhardness Tester.

The basic design of the microhardness tester is shown in fig.2.14. The indenter was designed to be capable of operating at loads of 5gm or less and preferably down to 1gm. The microhardness of pure sodium chloride at room temperature being in the region of 20 to 30gm mm^{-2} , a load of 1gm still produces an indent about 5 to 10 μm across. To operate at these very small loads a dead loading system employed in most commercially built testers was not suitable, a counterbalanced indenter assembly was, therefore, designed. The indenter was mounted on a stainless steel arm which was supported on two point pivots. The centre of gravity of the indenter assembly could be adjusted in both the vertical and horizontal planes, so that the centre of gravity could be adjusted to coincide with the line joining the two pivots. The indenter was then perfectly balanced and very sensitive to the application of small weights to the indenter arm. The indenter was a 136° pyramidal diamond set in a nimonic holder and was supplied by Nikon Ltd. The diamond holder was held firmly in the indenter arm by the use of a tapered split collet, which also enabled the diamond to be rotated to any desired orientation with respect to the specimen. The load was applied to the indenter by means of brass chemical balance weights placed on a small pan on the indenter arm.

The reduction of vibration to an absolute minimum was of utmost importance. The operation of the indenter was therefore made completely automatic. The indenter was lowered onto the specimen by means of a cam which was

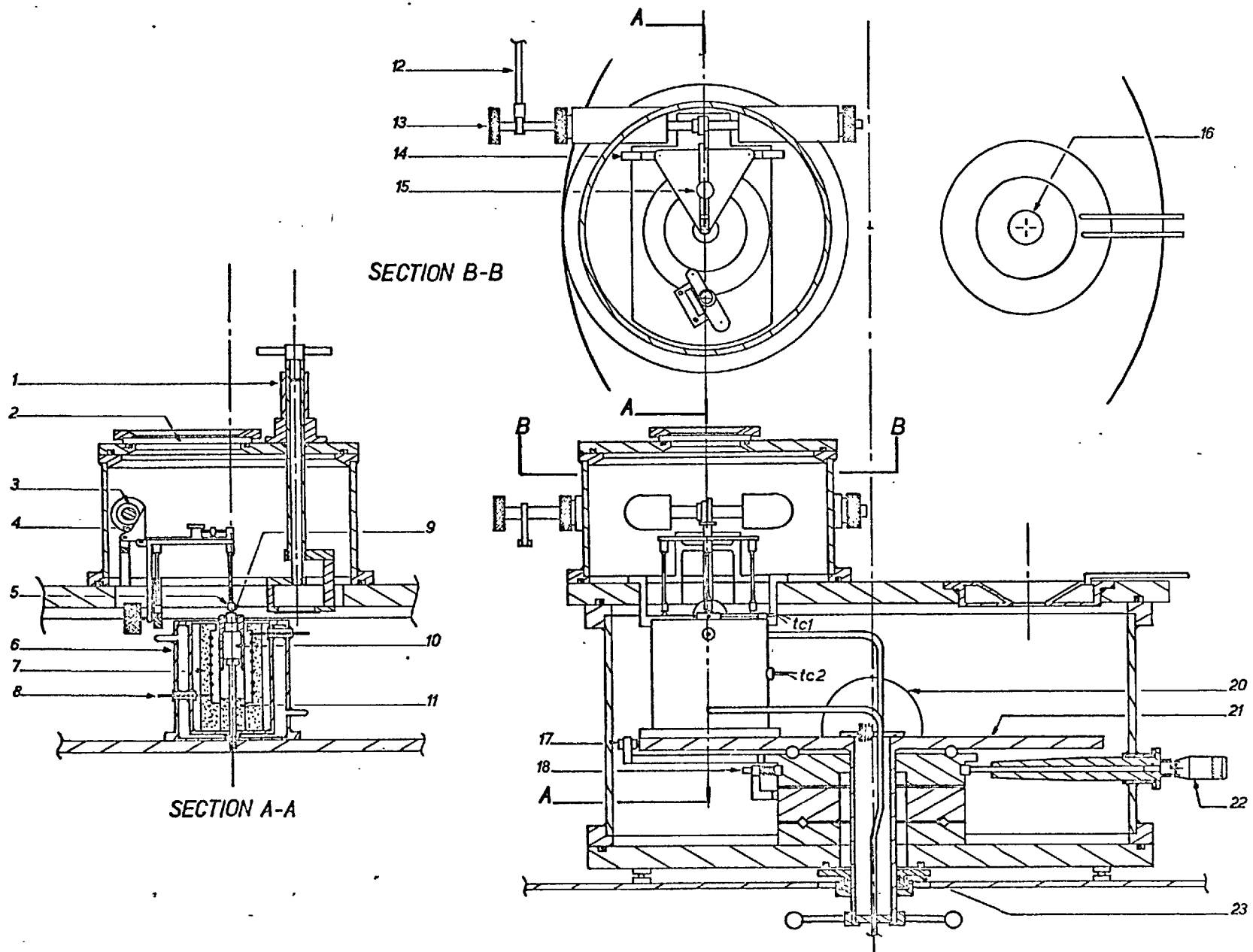


Fig.2.14. GENERAL ASSEMBLY OF HIGH TEMPERATURE MICROHARDNESS TESTER

KEY TO FIG.2.14.

- | | |
|----------------------------|---------------------------------|
| 1. Cleaver | 13. Camshaft |
| 2. Window-glass | 14. Indenter support |
| 3. Cam, brass. | 15. Weight pan. |
| 4. Cam Follower, P.T.F.E. | 16. Viewing port-quartz. |
| 5. Indenter | 17. Table location. |
| 6. Water-cooled jacket | 18. Traverse tensioning spring. |
| 7. Alumina insulation | |
| 8. Furnace windings | 20. Vacuum connecting port. |
| 9. Specimen stage | 21. Rotating table. |
| 10. Specimen stage support | 22. Micrometer Screw. |
| 11. Ceramic insulation | 23. Table top. |
| 12. Camshaft drive. | |

tc1 - Temperature measuring thermocouple

tc2 - Furnace control thermocouple

rotated by a small electric motor situated outside the indenter chamber. The indenter mechanism is shown in fig.2.15. The cam operated a P.T.F.E. follower which raised and lowered the indenter by rocking it on its pivots. The cam and follower were both highly polished to reduce friction and vibration. The driving motor was situated well away from the tester and operated the camshaft via a long rod and two cranks, the purpose of this was to reduce the vibration from the motor.

The specimen was mounted on a nimonic support which also formed a heat sink. The nimonic support was heated by a resistance, wire-wound furnace. The furnace was insulated by a cast alumina form which also acted as a spacer and support for the furnace windings. The furnace was enclosed in a water cooled jacket.

The furnace and specimen holder assembly were mounted on a table which could be rotated from outside the chamber. This enabled the specimen to be located under the indenter or the water cooled viewing window. The specimen could be observed through the quartz window (see fig.2.16) with a standard binocular reflected-light microscope; a maximum magnification of x 200 was possible using standard objectives. This magnification was not sufficient for accurate measurement of the indents but it did enable the operator to locate and position the indents with considerable accuracy. The rotating table was located in position by a spring loaded ball which was located in a recess on the edge of the table. The table was mounted on a stage which could be moved in two horizontal perpendicular directions by the use of micrometer screws mounted outside the chamber.

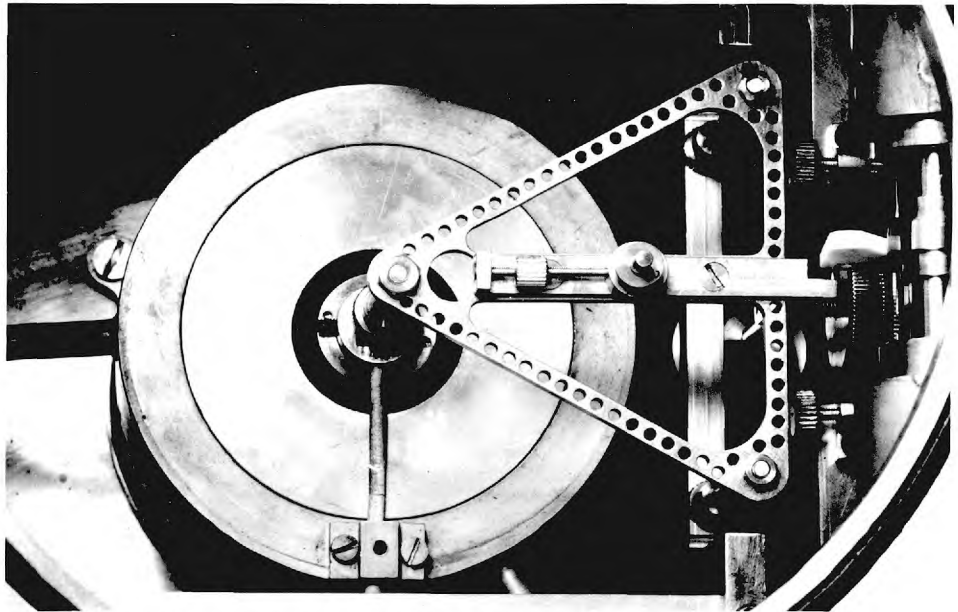


Fig. 2.15. VIEW OF INDENTER ASSEMBLY.

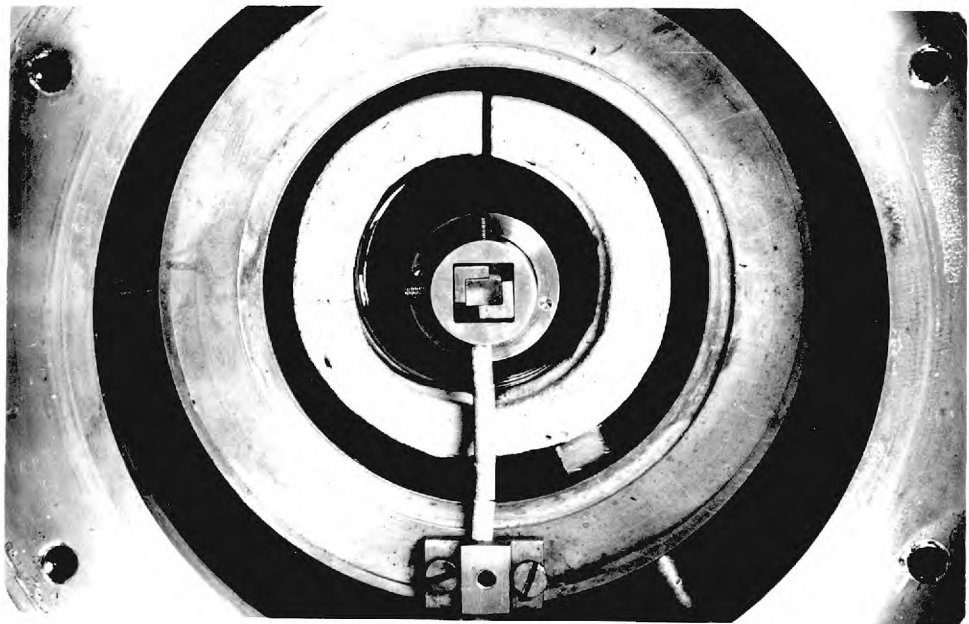


Fig. 2.16. SPECIMEN HOLDER AND FURNACE ASSEMBLY.

The tester also incorporated a cleaving device which could cleave off the top of the crystal whilst in the indenter and so reveal a clean, uncontaminated surface. The cleaver is shown in fig.2.17.

The indenter assembly, furnace and rotating table was contained within a vacuum chamber, shown in fig.2.18. The chamber can be evacuated by means of an oil diffusion pump and a rotary backing pump or filled with high purity argon. The argon was carefully purified before being passed through the chamber. The purification system consisted of two drying towers containing silica gel and calcium carbonate. One further tower containing sodiolite removed carbon dioxide. The gas then passed through a furnace containing titanium chips at 970°K which removed oxygen.

The motor was controlled by a series of relays, micro-switches and a timer, which operated the indenting cycle completely automatically after the sequence had been initiated. The automatic operation of the indenter ensured that each indent was made under identical conditions. Important factors, such as vibration, speed of the indenter as it touched the specimen surface, and time that the indenter was in contact with the surface, were all kept constant throughout the indentation sequences.

The furnace was controlled by an Ether Transistrol controller and the power supplied by a 20 ampere variac. The temperature was measured by a fine thermocouple placed against the side of the crystal in the specimen holder. The temperature gradient across the surface of the specimen was measured by placing a very fine thermocouple in small holes

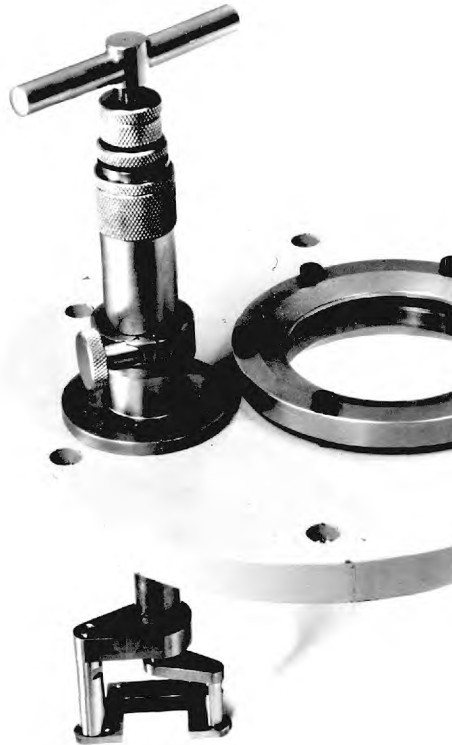


Fig.2.17.

CLEAVING DEVICE SHOWN
ATTACHED TO THE TOP
PLATE OF INDENTER
CHAMBER.

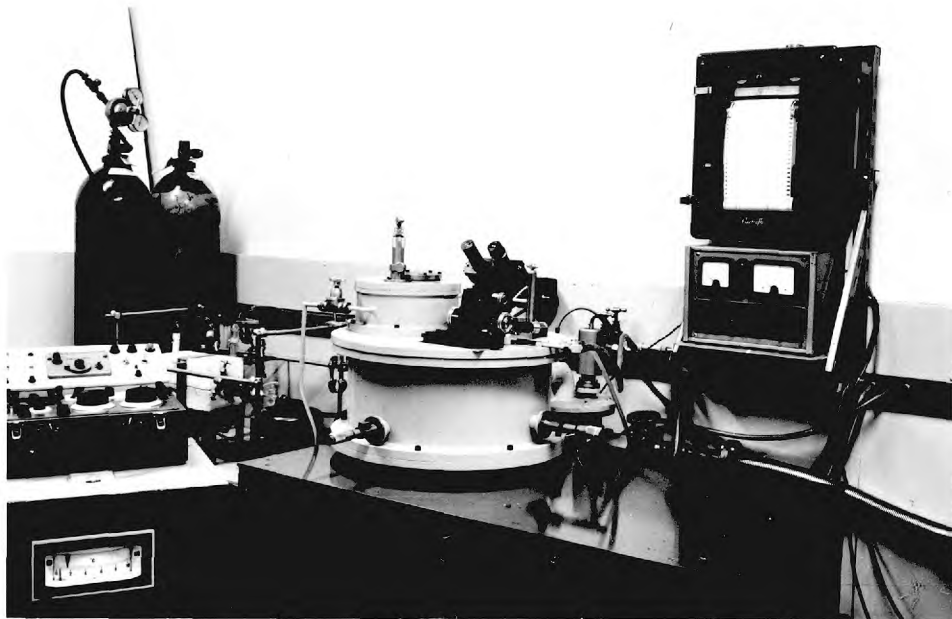


Fig.2.18. GENERAL VIEW OF MICROHARDNESS TESTER.

bored into the top of the specimen. The temperature difference was found to be less than 5°K at 670°K across a crystal, 0.7cm wide. The vertical temperatures difference in the specimen was found by a similar method and was about 10°K at 670°K from top to bottom of the specimen. The furnace control thermocouple was situated near the furnace windings.

Further modifications are being considered, in particular the crash-stop is to be rotated by a hydraulically operated piston, this will reduce the vibration from the electric motor. The indentation operation will be controlled by a thyristor controlled circuit, the removal of relays will again reduce vibration. Automation of the table feed could enable the indenter to be used in complete isolation from the operator.

2.4.3. Calibration and Microhardness Traverse Technique.

The indenter was calibrated by comparing the microhardness at different loads with similar measurements made at the same loads on the same specimen using a Reichert microhardness tester. The values of hardness found on both instruments were in agreement, within the limits of the error determined as the standard deviation. The microhardness was determined from the mean value of 30 to 50 indents. The standard deviation of the microhardness was found to be less than 3% with loads from 10gm to 2.5gm, and about 5% to 6% from 2.5gm to 0.5gm. These errors would appear to be very reasonable and the tester should be capable of detecting hardening at a grain boundary. The increase in the standard

deviation could be due to vibration effects and errors in the measurement of the indents. Fig.2.19. shows that the microhardness decreases as the load decreases. The effect of vibration will be more significant at low loads and so increase the size of the indent relatively more than the larger indents.

The specimens used were cut from bicrystals grown from the melt. The specimens were cut from the crystal using a Capco diamond slitting wheel. The orientation of the specimen with respect to the grain boundary is shown in fig.2.20. Specimens cut in this way were cleaved in the indenter, in vacuum or inert ^{an} atmosphere. Traverses were made at an angle of about 15° to the boundary so that a large number of indents on any one traverse were close to the boundary.

The specimen was placed in the holder after removing the viewing window for easy access. The specimen was held firmly in place by two screws which clamped two L-shaped pads against the specimen. The top of the crystal was cleaved off, after evacuating the chamber and filling it with argon, by applying a slight pressure to one corner of the crystal with the razor-blade. The specimen was cleaved off about 1mm from the top of the specimen holder, this left the indenter diamond about 0.5mm above the surface of the specimen.

The indents were measured after the specimen had been removed from the indenter. A standard bench microscope with a calibrated measuring eyepiece was used.

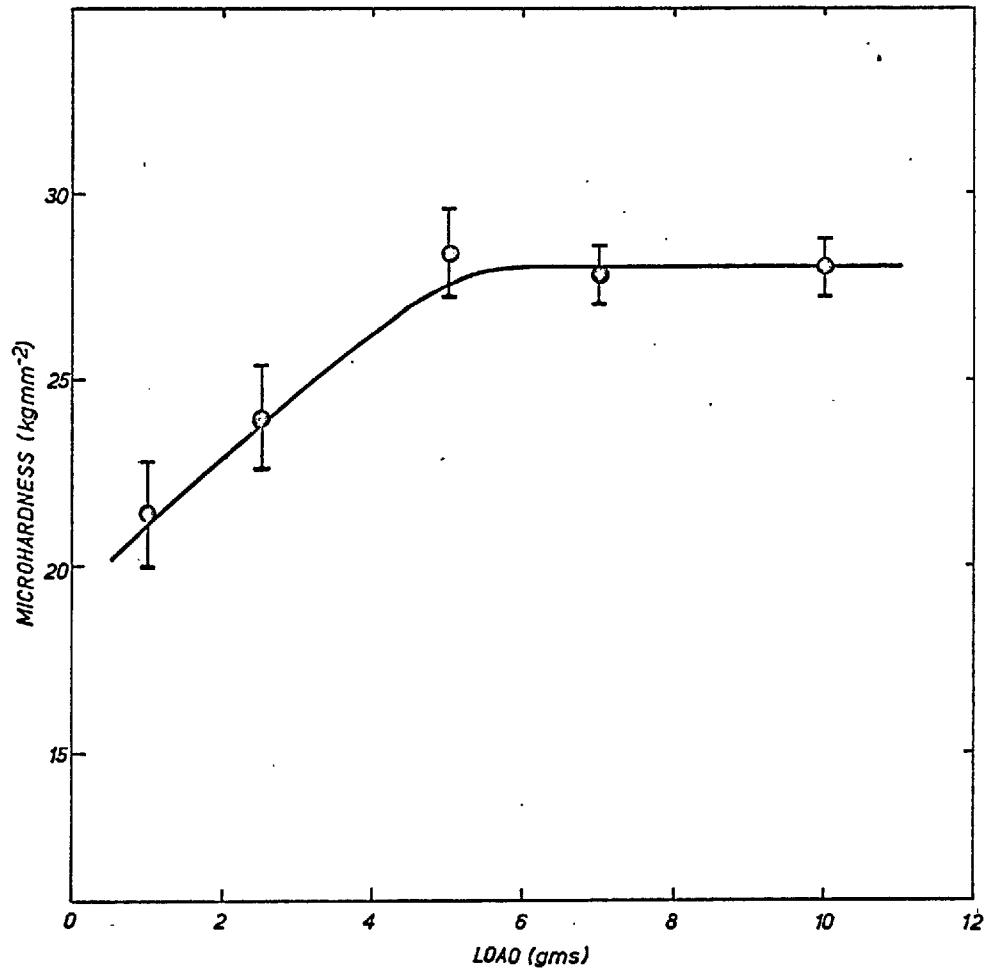
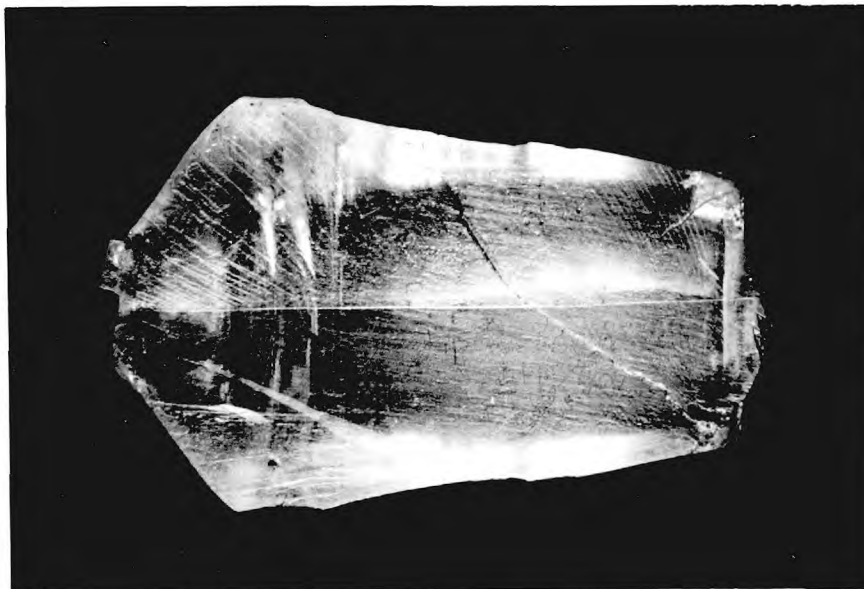


Fig.2.19. VARIATION OF MICROHARDNESS AS A FUNCTION OF INDENTING LOAD.



20°
CLEAVED
BICRYSTAL

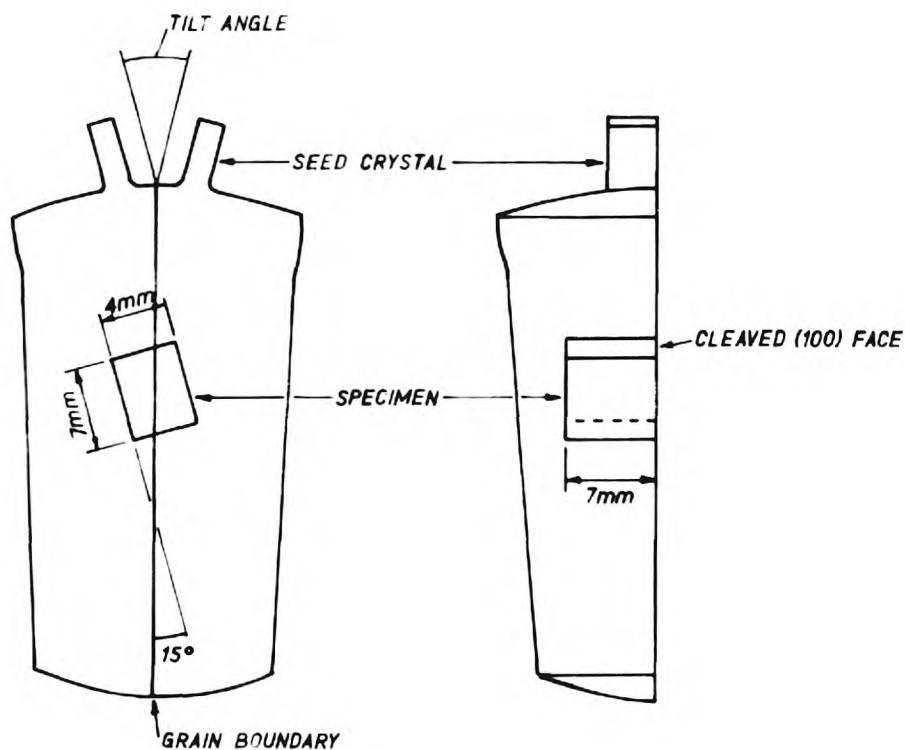


Fig.220 METHOD OF CUTTING SPECIMENS FROM BICRYSTALS

CHAPTER 3.

PRESENTATION AND DISCUSSION OF RESULTS I:

SINGLE CRYSTALS

3.1. INTRODUCTION

The results from conductivity measurements on pure and manganese doped sodium chloride will be discussed in this section. The parameters relating to the formation and motion of defects will be derived and compared with previous work.

The a.c. and d.c. conductivity have been measured, of both pure and doped crystals, in the temperature range 570°K to 920°K . The differences between the a.c. and d.c. conduction has been discussed in terms of interfacial polarisation at the electrode-crystal interfaces. The polarisation phenomenon was studied in greater detail from the deviations from Ohm's Law and the frequency dispersion of capacitance and resistance. The object of this work was to test the validity of assumptions made by previous workers, and to establish the nature of blocking in single crystals so that blocking effects of grain boundaries in polycrystals could be detected using similar a.c. and d.c. conductivity techniques.

3.2. A.C.CONDUCTIVITY MEASUREMENTS.

3.2.1. Behaviour of Electrode Material.

It was found that the choice of electrode coating materials was of very great importance. Fig.3.1. shows that different electrode materials can affect both the

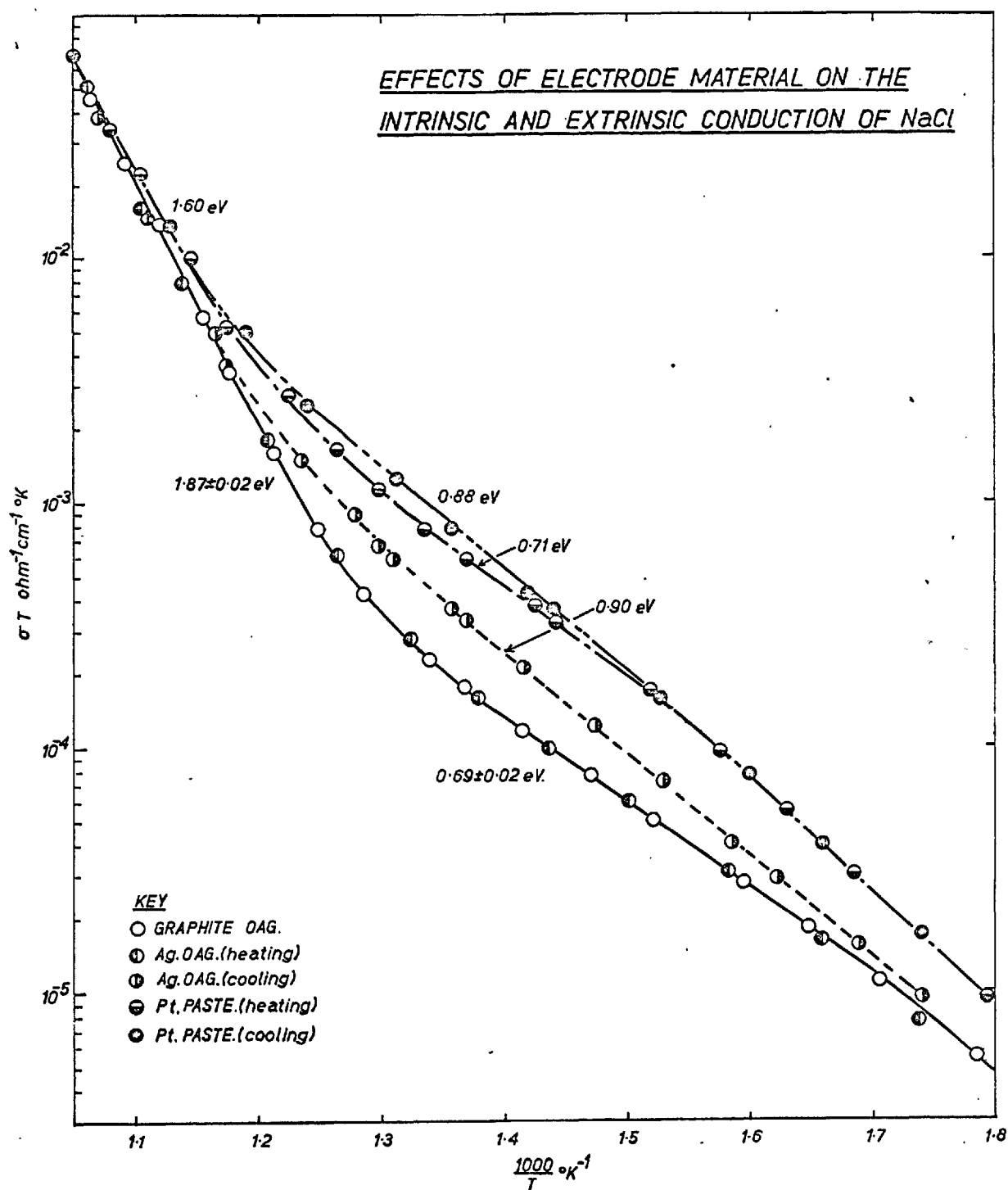


FIG. 3.1.

intrinsic and extrinsic conduction. Coatings which contain resins and ceramic bases, the silver dispersion (Acheson Dispersion No.962) and the platinum paste (Johnson Matthey Tl77), appear to dope the crystal and give completely erroneous values of the slope of the extrinsic and intrinsic regions. This 'doping' effect is clearly seen from the results when the silver dispersion electrodes have been used. The heating curve is coincident with the results from graphite coated crystals, whilst the cooling curve is completely different. The activation energy of the extrinsic region increases from 0.69eV to 0.90eV, indicating that a different diffusion mechanism is operative. Similar effects are noticed with platinum paste electrodes. The effect is possibly the result of the diffusion of impurities into the crystal at elevated temperatures, the impurities probably originating from the resins or base materials used in these preparations.

Similar effects were also observed when using Johnson Matthey Liquid Matt Platinum 121235G and Hanovia Platinum Paste 8972, the latter containing resins only, apart from platinum..

Graphite electrodes prepared by painting on an alcohol dispersion were found to be very satisfactory. The crystals could be thermally cycled without any deleterious effects to the conductivity plot; these electrodes were also found to adhere to the crystal very well. Graphite electrodes produced by vacuum deposition were found to be as good as the graphite dispersion electrodes but the results obtained were not found to be any more consistent.

Vacuum deposited silver, gold and platinum electrodes were also tried. Silver and gold electrodes tended to flake off above 720°K . Vapour deposited platinum electrodes were as reliable as the graphite electrodes but were extremely difficult to produce. All the following results were made using graphite dispersion electrodes, these providing both reliable and consistent results, and being very easy to apply to the crystal.

3.2.2. A.C. Conductivity of Pure Sodium Chloride.

The a.c. conductivity plot for a pure, single crystal of sodium chloride, hereafter known as pure 'A', is depicted in fig.3.2. These measurements were made at a frequency of 1592Hz, all subsequent measurements were made at this

frequency unless otherwise stated. The plot is drawn from an average of points obtained from several determinations using different specimens cleaved from the same platelet. The results from different specimens were reproducible (without the use of heat treatments described by Beaumont and Jacobs⁽⁸¹⁾ which resulted in a 10% compression of the crystal). The straight lines corresponding to regions I, I' and II were separately determined by the method of least squares. The limits of the straight lines are shown by the dashed lines in fig.3.2. The gradients and their errors were also found by the least squares fit.

The intrinsic region shows a definite curvature at temperatures above about $T^{-1} = 1.2 \times 10^{-3} \text{ }^{\circ}\text{K}^{-1}$. Below this temperature the slope of region I was found to be $1.87 \pm 0.02\text{eV}$, which is in good agreement with other a.c.

measurements of intrinsic conduction, in particular Kirk and Pratt ⁽⁵⁷⁾ and Laredo and Dartyge ⁽⁶¹⁾. The values obtained by Beniere et al. ⁽⁶⁰⁾ and Nelson and Friauf ⁽⁷¹⁾ appear to be somewhat larger, this would suggest that they were measuring the slope of region I' and not region I. Fig.3.2. shows that region I' has a slope of $2.02 \pm 0.02\text{eV}$ which is in good agreement with the activation energies obtained by Beniere et al. and Nelson and Friauf for region I.

The magnitude of the intrinsic conduction should in principle be identical for all determinations on all crystals. Fig.3.3. shows that this is not necessarily true. The present work is in good agreement with the majority of previous determinations, particularly that of Jain and Dahake ⁽⁵⁶⁾, Beniere et al. ⁽⁶⁰⁾ and Laredo and Dartyge ⁽⁶¹⁾

(not shown in fig.3.3.) The magnitude of the conduction found by Kirk ⁽⁴⁸⁾ and Bean ⁽⁶²⁾ appears to be larger than the bulk of the work.

this is not easily explained. The good agreement with this work and that of Kirk, with respect to activation energies, would indicate that the discrepancy is not very serious and may be due to experimental inaccuracies. The anomalously low conduction obtained by Rothman et al. ⁽¹⁶⁰⁾ is also not readily explained.

The method of determining the slope of region II, has been described previously. Care was taken when making a least squares fit that the points at either end of the straight line, that is the points where the slope was increasing into region I or region III, were not used to define the slope of region II. The activation energy was found to be $0.69 \pm 0.02\text{eV}$. This activation energy is the enthalpy of motion of the cation vacancy. This value is in good agreement with the work of Kirk ⁽⁴⁸⁾, Redfern and Pratt ⁽⁶⁸⁾ and Beniere et al. ⁽⁶⁰⁾

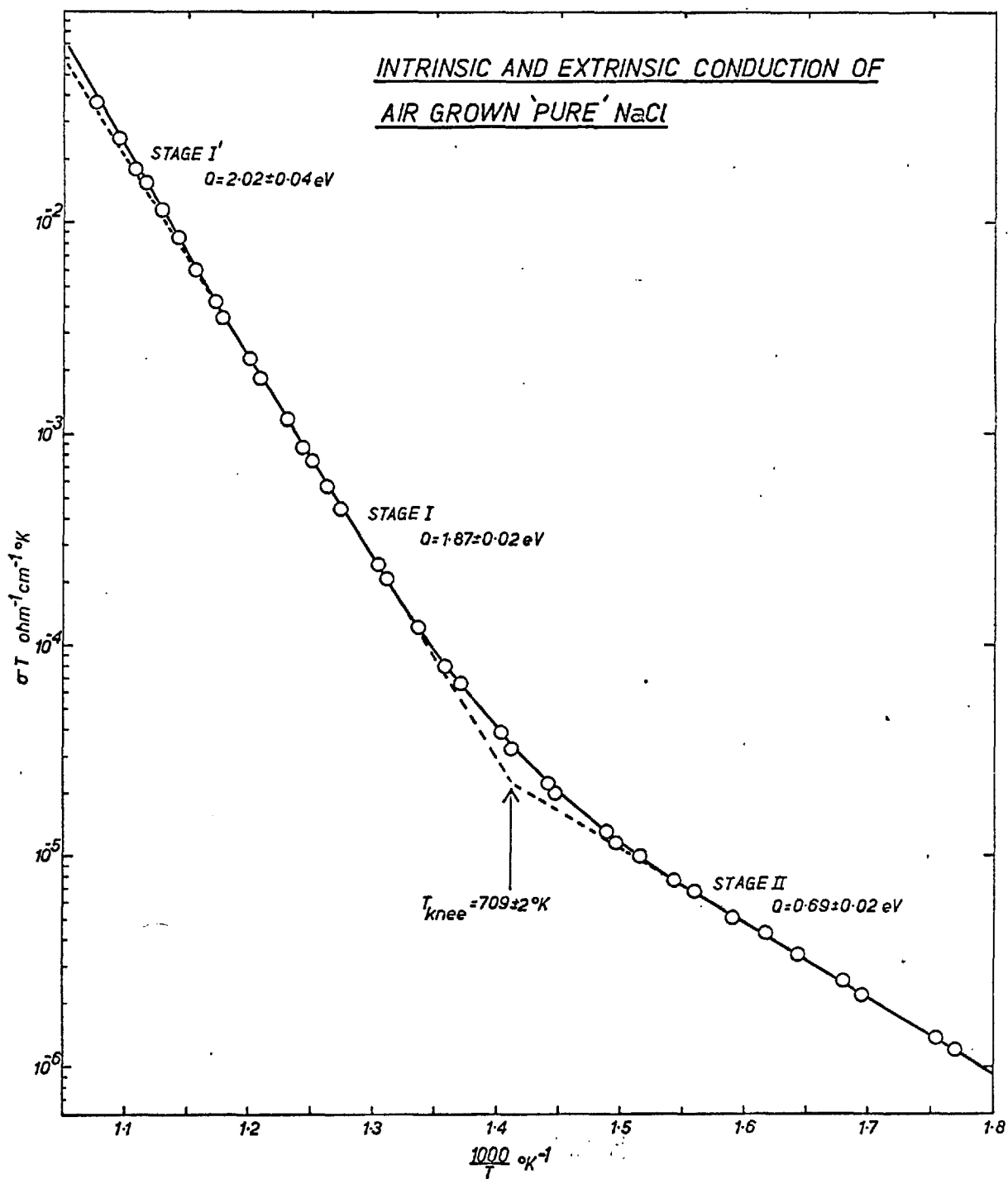


FIG. 3.2.

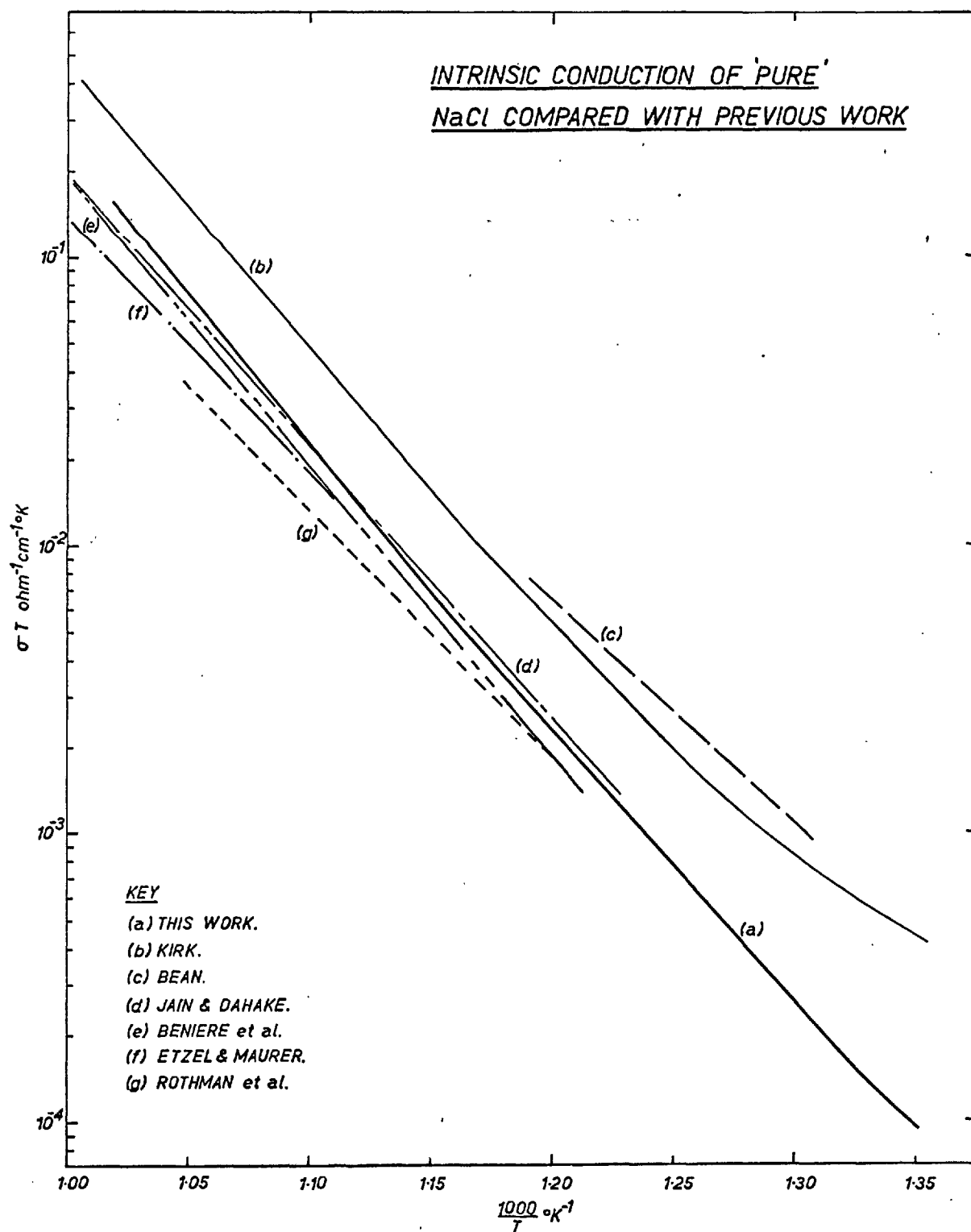


FIG.3.3.

for pure sodium chloride. Values ranging from 0.60eV to 0.85eV have been quoted in the literature. The values of the enthalpy of motion of cation vacancies obtained by different methods are not the same; d.c. conductivity and diffusion measurements give larger values whilst N.M.R. gives lower values. Several workers (69,60,56) have

also noted that the enthalpy of motion of the cation vacancy increases in impure crystals, although there is no apparent simple relation between the enthalpy and the physical characteristics of the impurity ion (69).

The enthalpy of formation of a Schottky pair can be calculated from the activation energy of the intrinsic region, since $Q_I = \frac{hs}{c} + \Delta h_c$, using the above mentioned values of Q_I and Δh_c^2 . The Schottky formation energy was found to be $2.36 \pm 0.04\text{eV}$, which is in good agreement with previous work (48,61).

The intrinsic conductivity of pure 'A' sodium chloride has been compared with diffusion data for anion motion (Laurance (76), recently re-calculated by Fuller and Reilly (88)) and cation motion (Dreyfus and Nowick (55)), as shown in fig.3.4. where:

$$\sigma_c T = 4.7 \times 10^8 \exp(-1.86/kT) \text{ ohm}^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{K}$$

for cation motion (55) and

$$\sigma_a T = 1.2 \times 10^9 \exp(-2.07/kT) \text{ ohm}^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{K}$$

for anion motion (88). The anion contribution was calculated from the diffusion data using the Nernst-Einstein equation

incorporating the appropriate correlation factor. Laurence⁽⁷⁶⁾ found that:

$$D_a = 22 \exp(-2.07 / kT) \text{ cm}^2 \text{ sec}^{-1}$$

and for sodium chloride

$\sigma_a T = 5.25 \times 10^7 D_a$, from the Nernst-Einstein equation.

The slope of the intrinsic region is in good agreement with the diffusion data although there is a small discrepancy in the pre-exponential factor; from the intrinsic region of crystal pure A,

$$\sigma T = 4.6(\pm 2.0) \times 10^8 \exp(-1.87 \pm 0.02 / kT) \text{ ohm}^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{K.}$$

The slope of region I' is considerably greater than that calculated from the previous data, that is 2.02eV compared with about 1.91eV. In fig.3.4. the enhanced conduction in region I', that is the difference between the conduction in region I and I', is also plotted. If this contribution is attributed only to the motion of anion vacancies a value of Ah_a of 1.20eV is found, compared with 0.89eV found by Laurence and Beniere et al. Thus it would appear that the slope of region I' cannot only be attributed to anion vacancy diffusion in the lattice.

Kirk⁽⁴⁸⁾ found that the enhancement in region I' increased in crystals doped with hydroxyl ions, but his results did not clearly show whether this was due to the

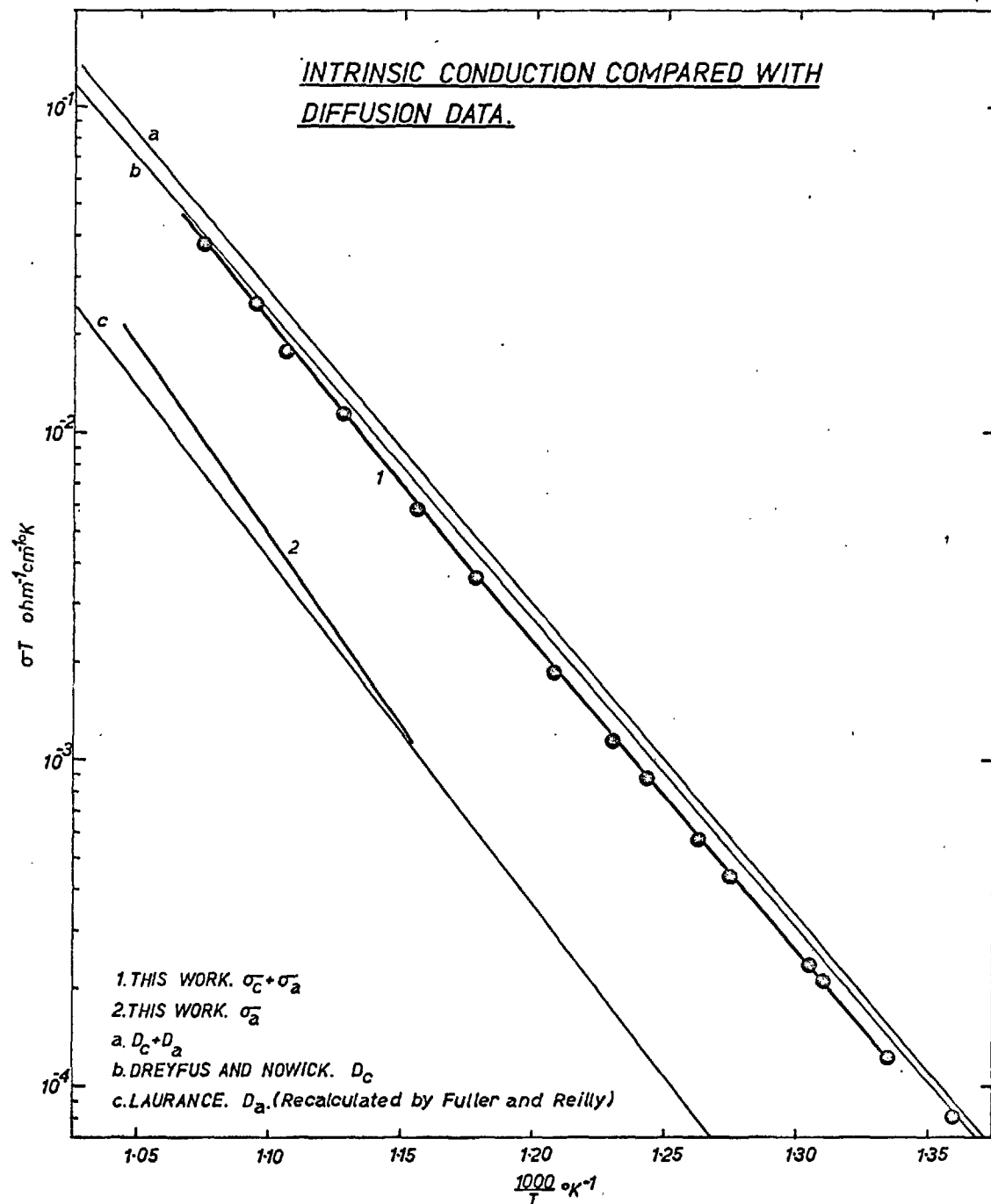


Fig. 34.

diffusion of hydroxyl ions or due to mechanical damage put into the crystal during its preparation. Recent work by Allen and Fredericks (162) on the diffusion of hydroxyl ions in potassium chloride has shown that the activation energy of diffusion of hydroxyl ions was 1.95eV, giving an enthalpy of motion of the hydroxyl ion of 0.79eV. The value of the pre-exponential term was in some doubt, but this work did show that the hydroxyl ion is very mobile indeed. This mobility, and ^{the} ease with which it forms relatively stable complexes with aliovalent impurities also explains the ease with which it can compensate cationic impurities. There is, therefore, a possibility that the enhanced conduction of region I' could also be due to the movement of hydroxyl ions in dislocations or sub-grain boundaries, since they are obviously very mobile. This would not necessarily explain the high activation energy unless the hydroxyl ion is complexed with other defects, although this possibility does not really seem likely at such high temperatures.

Kirk (48), in order to try to explain the existence of region I', has presented results of conductivity measurements on deformed single crystals. Similar tests have been carried out, using the technique employed by Kirk, and it was hoped that these tests would provide an explanation of the enhanced conduction in region I'. In heavily deformed and annealed crystals a sub-grain structure is present so it was thought that these results could be correlated with subsequent work on polycrystalline sodium chloride. The conductivity plots of deformed single crystals ^{*} are shown in fig.3.5.; it can be seen that the conduction in region I' is enhanced further by the deformation, although it is interesting to note that this enhancement decreases in crystals deformed

* Specimens were cut perpendicular to the [100] compression axis.

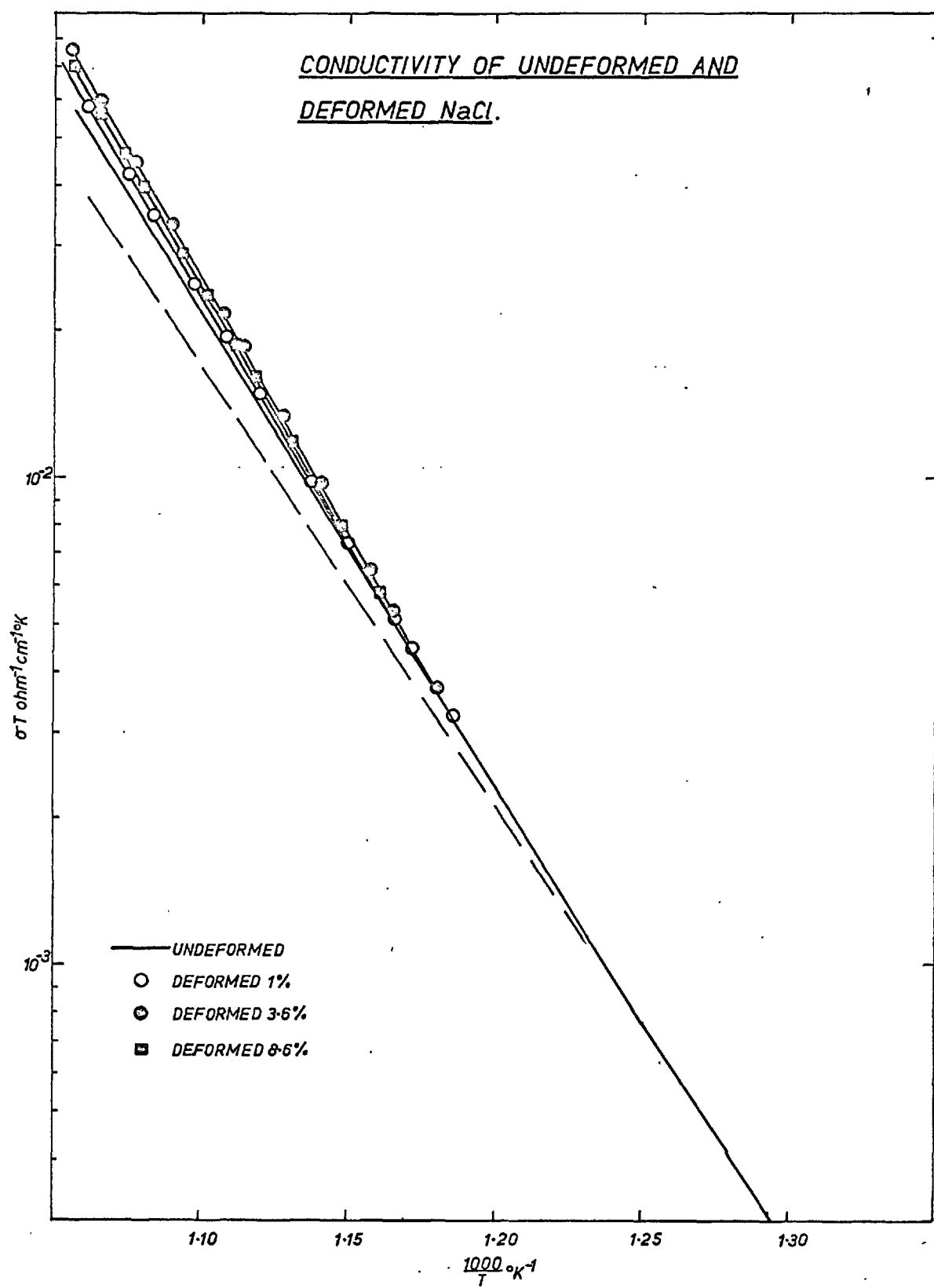


Fig.3.5.

more than 4%. With reference to work by Davidge and Pratt⁽¹⁶¹⁾ it would appear that the conduction is enhanced more in crystals deformed in stage I rather than in stage II of the stress-strain curve. The enhanced conduction is shown more clearly in fig.3.6; and it is apparent that these results agree very well with those of Kirk⁽⁴⁸⁾. Davidge and Pratt showed that the dislocation density rapidly increased in stage II, the distribution of dislocations being random in stage I (easy glide) but at higher deformation dislocation walls form. In these tests, of course, the dislocation structure at high temperatures is important. Davidge and Pratt showed that in a crystal compressed by 10% little change was seen in the structure of parallel dislocation walls below 670°K , the number of walls was reduced in specimens annealed at 770°K and at higher temperatures a sub-grain structure formed. They also noted that the work-hardening in stage II is connected with dislocation debris rather than dislocations themselves, this debris they found annealed out at about 520°K to 620°K .

Kirk showed that the enhancement of the conduction was reduced by prolonged annealing at 970°K and he associated this with the decrease in surface area of sub-grain boundaries, and that there was no enhancement in well annealed, undeformed crystals, where the sub-grain structure was absent. The present series of tests showed a similar decrease in the enhanced conduction after prolonged annealing of deformed specimens, but the enhanced conduction in undeformed crystals could not be reduced, even after an anneal of 60 hours at 970°K and then slowly cooled over 48 hours. Thus it would appear that the enhanced conduction in region I', in the undeformed crystals is not due to the damage

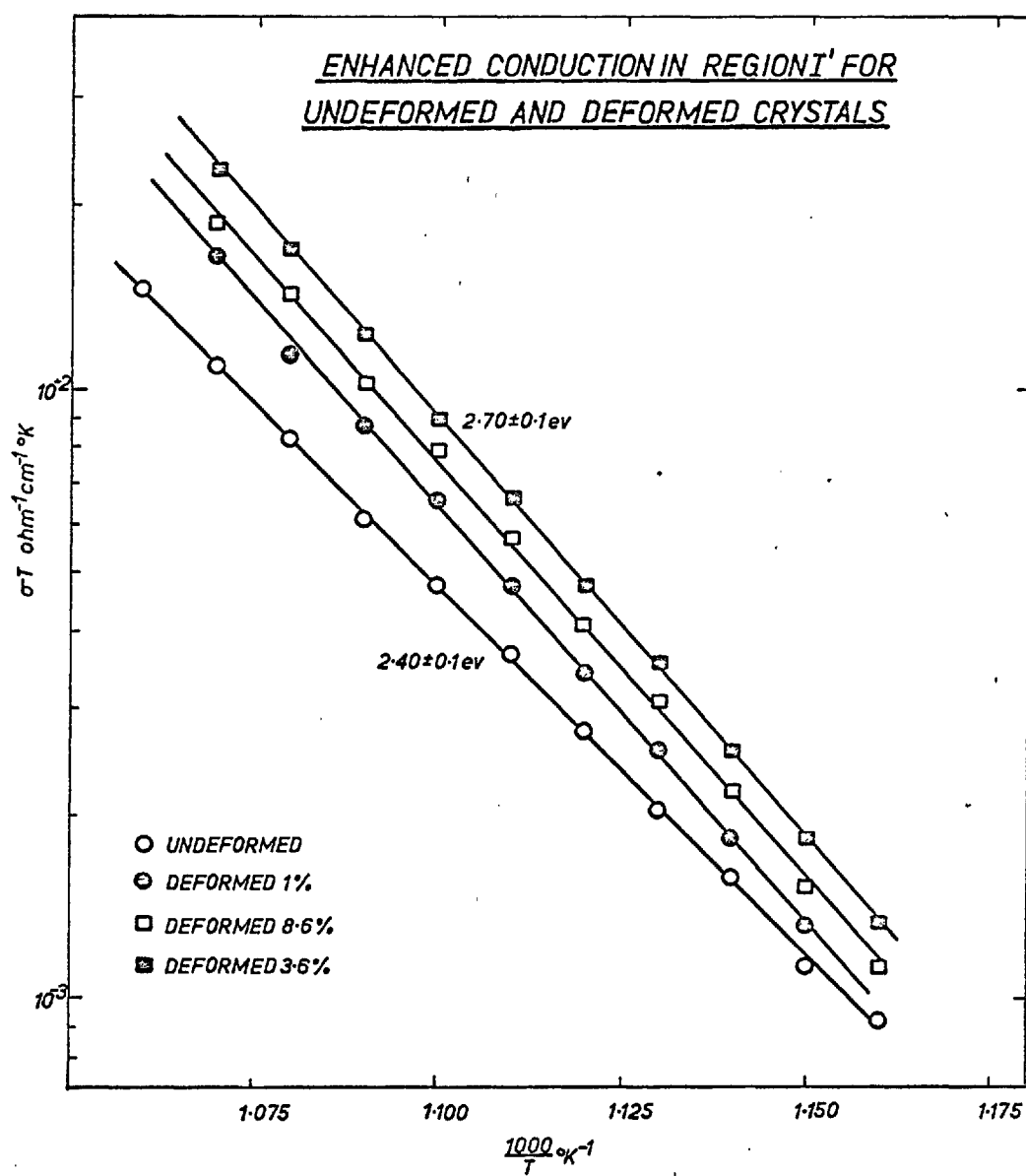


Fig.3.6.

caused by cleavage. The diffusion of either anion vacancies or impurities, such as hydroxyl ions, or both, down paths of easy conduction, would appear to be a tentative explanation of the enhanced conduction. The paths of conduction are the grown in dislocation structure in nondeformed crystals and the sub-grain structure in deformed crystals. It must be pointed out that although this crystal was not deliberately doped with hydroxyl ions some were very likely present, as will be shown later.

The production of a well-defined sub-grain structure in heavily deformed and subsequently annealed crystals resulted in no change in the conduction in region II of the conductivity curve. Results presented in Chapter 4 show that in polycrystalline sodium chloride the diffusion processes in region II are affected by the presence of grain boundaries. The lack of change in deformed crystals would appear to suggest that sub-grain boundaries do not affect the extrinsic conduction processes.

3.2.3. A.C. Conduction of manganese-doped Single Crystals.

The effect of divalent cation additions on the extrinsic conduction of sodium chloride is shown in fig.3.7. The curves correspond to crystals containing varying amounts of manganese ions, except pure B, which was grown from purified sodium chloride and grown in an inert atmosphere. The chemical analysis of this crystal revealed the presence of about 15ppm of copper ions which would account for its higher conduction in the extrinsic region. The curves shown

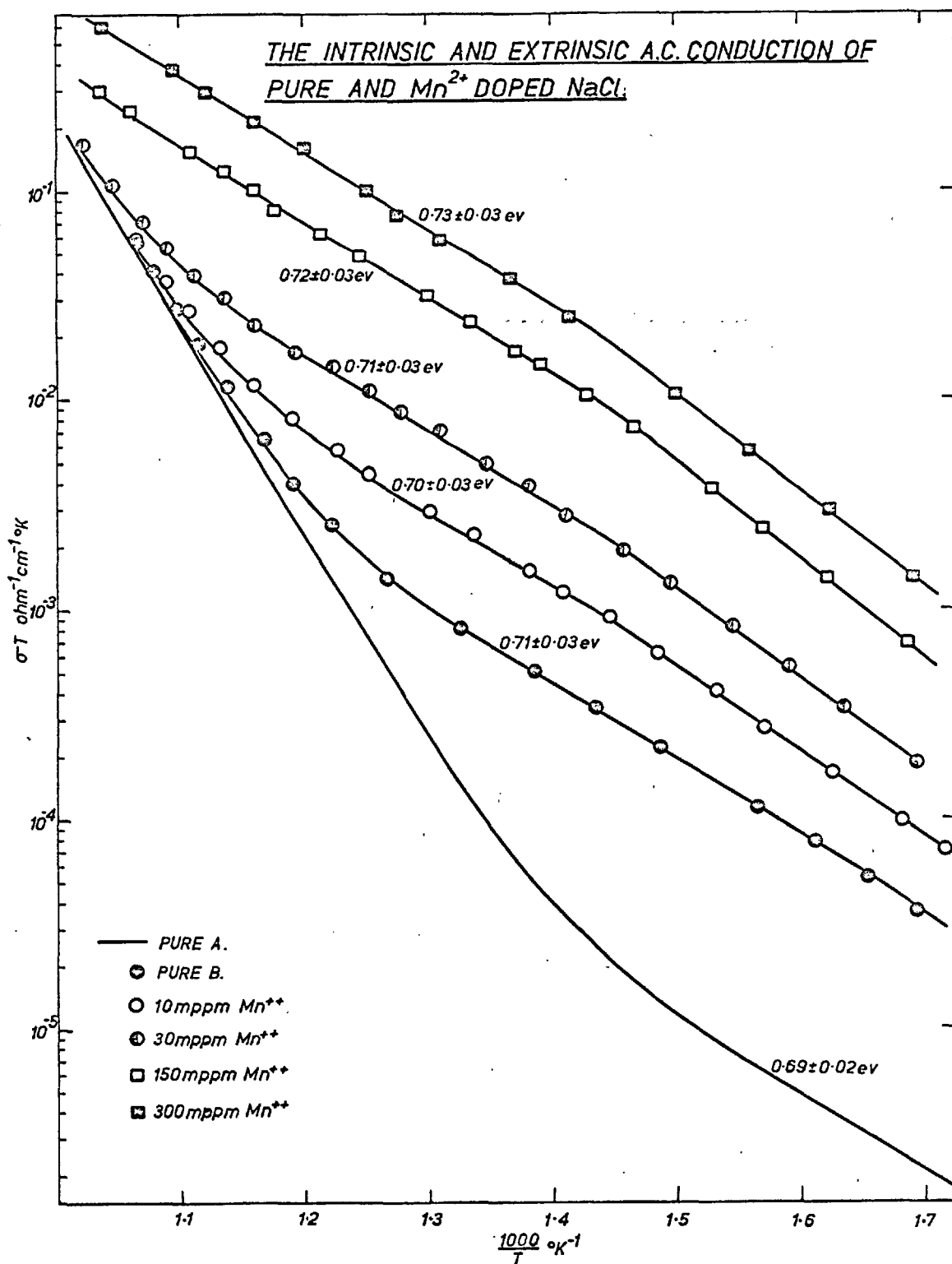


Fig.3.7.

in fig.3.7. are again the result of several tests on separate specimens cleaved from the same slice of the crystal. The points shown on the curves do not represent the total number of measurements used to calculate the slopes, many points have been omitted.

Previous work⁽⁴⁸⁾ has shown, from a consideration of conductivity isotherms, that in manganese ion doped sodium chloride a certain proportion of the impurity ions are complexed with anion impurities, this amount was found to be about 50ppm. Thus the effective divalent cation concentration which is affecting the extrinsic conduction is:

$$C_E = C - C_0 \quad 3.1.$$

where C is the total divalent cation concentration and C_0 is the concentration of divalent cations complexed with anion impurities.

Equation 3.2. shows that isotherms in the extrinsic region should be linear and pass through the origin, if the total divalent cation concentration equals the effective concentration, that is:

$$\frac{\sigma}{\sigma_0} = \frac{C}{x_0(1 + \phi)} \quad 3.2.$$

where σ_0 is the conductivity of a pure crystal and x_0 is the concentration of anion or cation vacancies in a pure crystal. For true extrinsic conduction a plot of σ versus C should be linear with a slope of

$$\frac{\sigma_0}{x_0} [1 + \phi]^{-1} \quad 3.3.$$

Kirk has shown that this is true for heavily doped crystals except that the line did not pass through the origin but cuts the concentration axis at $C = 50$ mppm. The isotherms shown in fig.3.8. show that the slopes of the isotherms decrease at low concentrations and do pass through the origin. This indicates that the value of C_0 is not fixed at low impurity concentrations. Thus it is not possible to estimate the effective divalent cation concentration from extrinsic isotherms, since C_0 is not constant for all values of C .

Another estimate of C_E could be obtained from the intrinsic-extrinsic 'knee' temperature. This temperature can be determined by extrapolating the extrinsic and intrinsic regions to the point where they meet, assuming that at this temperature the extrinsic cation vacancy concentration is equal to the intrinsic cation vacancy concentration. Then a plot of $\log n_c$ or $\log C_E$ against T_k^{-1} for different specimens should be a straight line as described by equation 1.23., that is:

$$C_E = \exp \frac{S}{2k} \exp - \frac{h}{2kT_k} \quad 1.23.$$

This approach must use a value of S_s which cannot be calculated from the extrinsic data since the effective concentration of divalent impurity is not known. A calculation using the total concentration of impurities gave erroneous values of ΔS_c and hence S_s . However, the value of $S_s/2 + \Delta S_c$ can be calculated from the intrinsic conductivity plot since C is not required in this calculation. The entropy term,

$$\frac{S_s}{2} + \Delta S_c = 4.5 \pm 0.5 \times 10^{-4} \text{ eV } ^\circ\text{K}^{-1}$$

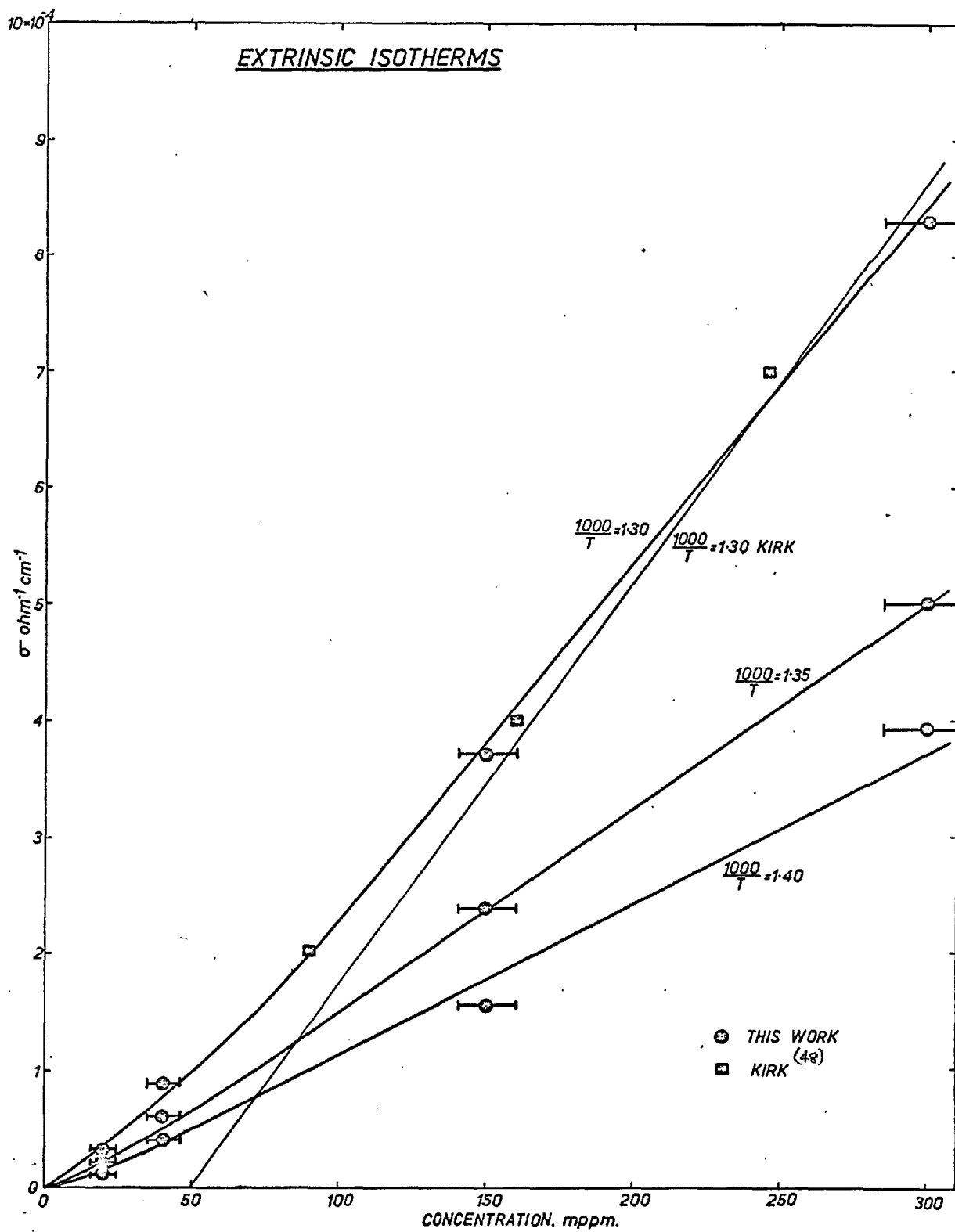


Fig.3.8.

using a value of ν_0 equal to the Debye frequency, where,

$$\nu_0 = 4.81 \times 10^{12} \text{ sec}^{-1}$$

In order to calculate S_g a value of ΔS_c must be assumed. Previously published values of ΔS_c are most probably suspect due to the difficulty of evaluating C_E . However, a value of $1.8 \times 10^{-4} \text{ eV}^\circ\text{K}^{-1}$ as found by Beniere et al.⁽⁶⁰⁾ is in good agreement with the value found by Kirk⁽⁴⁸⁾, who had considered the effect of anion impurities on the extrinsic conduction. If the above value of ΔS_c is considered to be reasonably good then, $S_g = 5.4(\pm 0.5) \times 10^{-4} \text{ eV}^\circ\text{K}^{-1}$. This value is in fairly good agreement with values calculated by previous workers^(48,60,71).

Using the calculated values of S_g and $h_{s_{are}}$ in equation 1.2.3. the values of C_E were calculated, and shown in table 8. The very small values of C_E appear to indicate that the crystals contain a relatively high concentration of anion impurities, which are complexing with the divalent cation impurity. The values of C_E would indeed appear to be unreasonably low compared with previous determinations⁽⁴⁸⁾. The reason for this lies in the form of equation 1.2.3. Small changes in S_g will markedly alter the value of C_E , for example at $1/T = 0.9 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$, a 10% increase in S_g increases C_E by about 50%. Thus it is apparent that the knee temperature cannot be used to provide a reliable estimate of C_E unless the entropy term can be calculated accurately. It may be possible to determine the free cation impurity from a careful analysis of the ultraviolet and infrared absorption peaks of hydroxyl and other anion impurities.

TABLE 8:

COMPARISON OF TOTAL DIVALENT CATION CONCENTRATION
AND EFFECTIVE DIVALENT CATION CONCENTRATION AS
CALCULATED FROM 'KNEE' TEMPERATURES.

CRYSTAL	MAX VALUE OF C ppm	C _E ppm
PURE A	10	0.1
PURE B	20	1
10ppm Mn ²⁺	20	4
30ppm Mn ²⁺	40	10
150ppm Mn ²⁺	160	30
300ppm Mn ²⁺	310	75

The presence of an absorption peak at 3600cm^{-1} in the infra-red spectrum of the 300ppm manganese doped crystal indicates that a considerable quantity of hydroxyl ions are present. Although peaks at 3600cm^{-1} were not detected in the other crystals the pure crystals did show a small band at 190μ , the absorption band of free hydroxyl ions⁽¹⁶³⁾ in the ultra violet region. The doped crystals did^{not} show an absorption at 190μ , this is presumably because the hydroxyl ions are complexed with the divalent impurity⁽¹⁶⁴⁾. Crystal pure 'B' showed further peaks in the infra-red which have been interpreted as being due to metaborate ions, introduced during the purification process. Thus the evidence does suggest that some of the crystals do contain a considerable concentration of hydroxyl ions and other anion impurities which can compensate for the divalent cation impurities.

To summarise, it is suggested that accurate values of entropies of formation of Schottky defects and motion of cation vacancies cannot be found unless the precise analysis of both anion and cation impurities are known, and the form in which anion impurities are incorporated in the lattice, that is as free ions or complexes.

3.3. INTERFACIAL POLARISATION IN SODIUM CHLORIDE.

3.3.1. D.C. Conductivity of Sodium Chloride.

Several previous workers have observed a high temperature polarisation phenomenon occurring in sodium chloride and potassium chloride. It has already been suggested that this

may give rise to anomalously low values of activation energy in region I if the polarisation is a function of temperature. In order to establish the nature of this polarisation phenomenon experiments have been carried out measuring the d.c. conductivity and deviation from Ohm's Law in pure and manganese doped sodium chloride. In a later section the a.c. conductance and capacitance as a function of frequency will be described.

This series of experiments was carried out to determine which carrier or carriers ^{were} being blocked and whether they were blocked at the electrodes or at other interfaces. Previous workers (5) have maintained that the polarisation is the result of the blocking of one charge carrier, the anion vacancy, at the electrode interface; the cation vacancy being able to discharge and so contribute to the conduction process.

Fig.3.9. shows the steady-state d.c. conductivity, σ_{∞} compared with the a.c. conductivity, σ_0 for crystals pure A and B. The field strength used was 5 volts cm^{-1} ; unless otherwise stated all the results in this section were obtained using this field strength. It is immediately obvious that the slope of region I is much less for the σ_{∞} curves due to the polarisation occurring in this region. The polarisation in the extrinsic region also increases with increase in divalent cation concentration. This effect is shown more clearly in fig.3.10. which shows the σ_{∞} curves for the manganese doped crystals. The activation energies for region II are shown to be inconsistent, varying from $0.69 \pm 0.03\text{eV}$ in the purest specimen to $0.60 \pm 0.04\text{eV}$ in the 300ppm manganese doped specimen. The activation energy of region I is reduced to $1.75 \pm 0.03\text{eV}$. Thus the

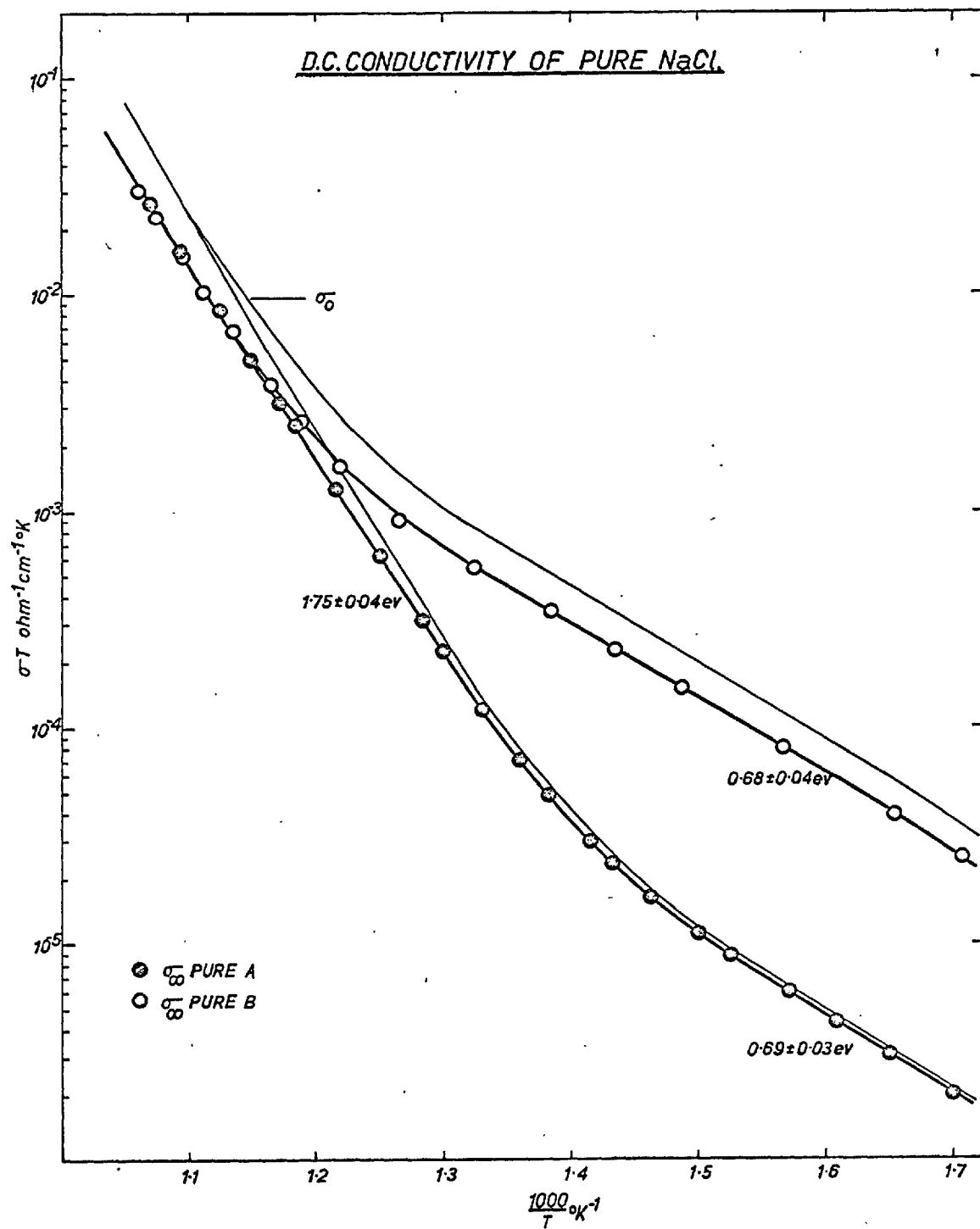


Fig.3.9.

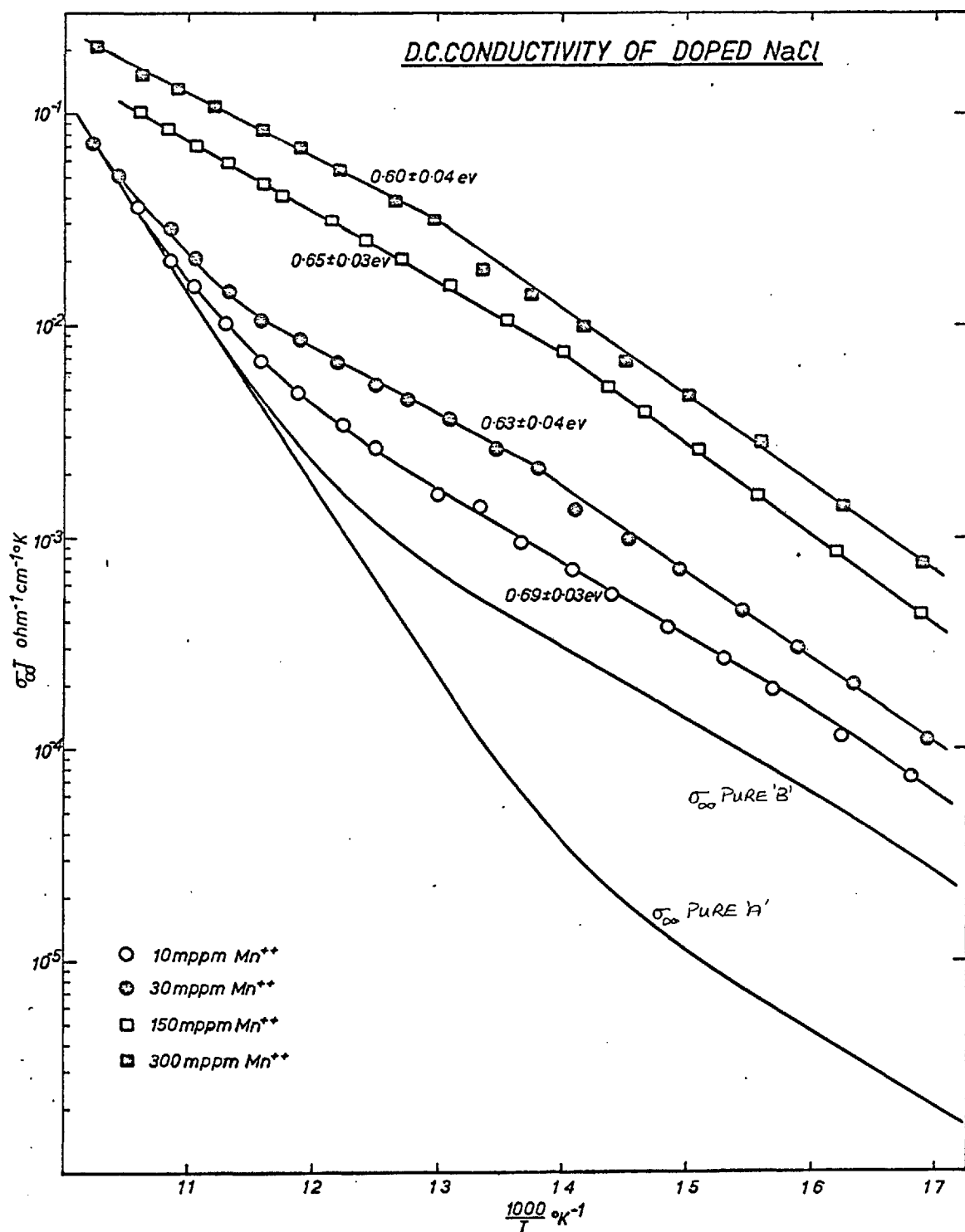


Fig.3.10.

values of Δh_c and h_g derived from high temperature d.c. conductivity or pulsed d.c. measurements may indeed be suspect.

The blocked conductivity, $\sigma_B = \sigma_o - \sigma_\infty$, as a function of temperature is shown in fig.3.11. The curves show a marked resemblance to a.c. conductivity curves except that the slopes of the intrinsic and extrinsic regions are increased, although the latter only slightly. The activation energy of region II is about $0.73 \pm 0.04\text{eV}$ compared with $0.69 \pm 0.02\text{eV}$ for σ_o curves. It would appear that σ_B is the result of blocking of cation vacancies in the extrinsic region. The difference in slopes between the σ_B and σ_o curves could be due to a decrease in the percentage of blocked carriers as the temperature decreases.

The activation energy of the intrinsic region of the σ_B curves is increased to $2.34 \pm 0.04\text{eV}$. This would suggest that either a carrier with an enthalpy of motion of 1.16eV is blocked or that the number of blocked carriers increases with increasing temperature. It is probable that both anion and cation vacancies are blocked at high temperatures. Since the magnitude of the blocked current is comparatively large and the degree of blocking varies with carrier concentration and temperature it is suggested that only partial blocking is occurring.

These results have been discussed assuming that the polarisation effect observed at these high temperatures is due to the blocking of charge carriers at interfaces or at the electrodes, that is space-charge polarisation. It is, however, possible that polarisation may be the result of a dielectric relaxation due to the time-dependent

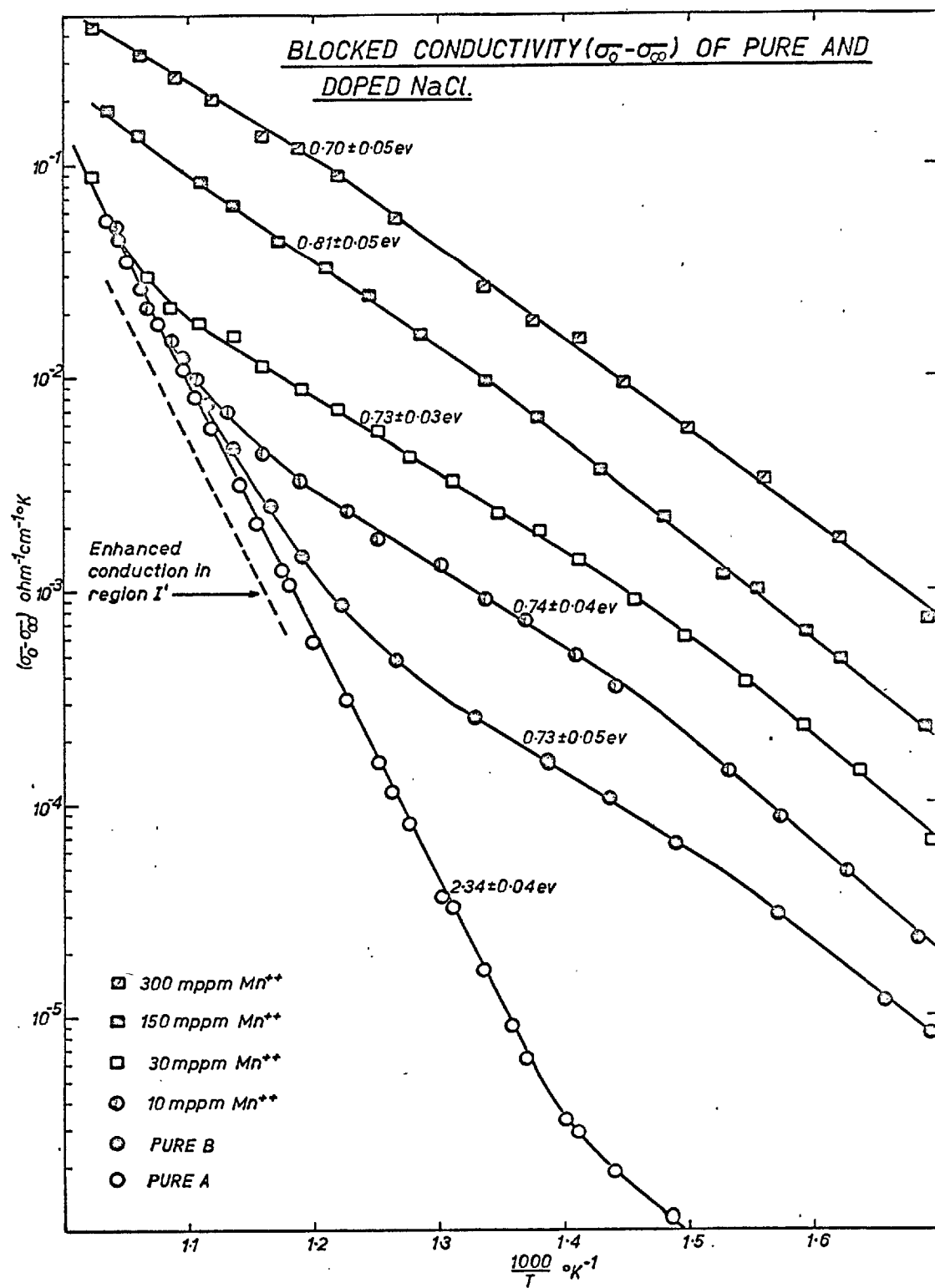


Fig.3.11.

formation of dipoles or the time-dependent reorientation of permanent dipoles existing in the material. Sutter and Nowick⁽¹³⁰⁾ have summarised the theories relating to both polarisation phenomena. If dielectric polarisation is occurring then Ohm's law will be obeyed, on the other hand if interfacial polarisation is occurring then Ohm's law will not be obeyed. Figs. 3.12 and 3.13. show typical voltage-current plots for pure and doped crystals. It can be seen that for the pure crystal Ohm's law is obeyed at temperatures where little or no polarisation is occurring. At higher temperatures there is a considerable curvature of the plot, especially at low voltages. Above an applied voltage of about 10 volts Ohm's law is apparently obeyed. The voltage-current curves for the manganese doped crystal show similar characteristics except that Ohm's law is not obeyed at all temperatures between 570°K and 970°K, for small voltages. The fact that Ohm's law is not obeyed suggests that the polarisation phenomenon is due to the build up of space-charge layers at interfaces or electrodes. These results also corroborate the conclusions from the σ_B plots, that is, that partial blocking of charge carriers occurs, since it is obvious that the amount of blocking is dependent on the magnitude of the applied field.

The current-voltage plots show a small ohmic region at applied voltages less than 0.1 volts. The reason for this is not clear but it is possibly due to the fact that at low voltages the space-charge layer is slow to build up and possibly the current was measured too soon after the application of the field. The voltage applied was increased from zero to 20 volts in as short a time as possible to make sure that temperature fluctuations were not too great during the measurements, the temperature was found not to

* Steady state current.

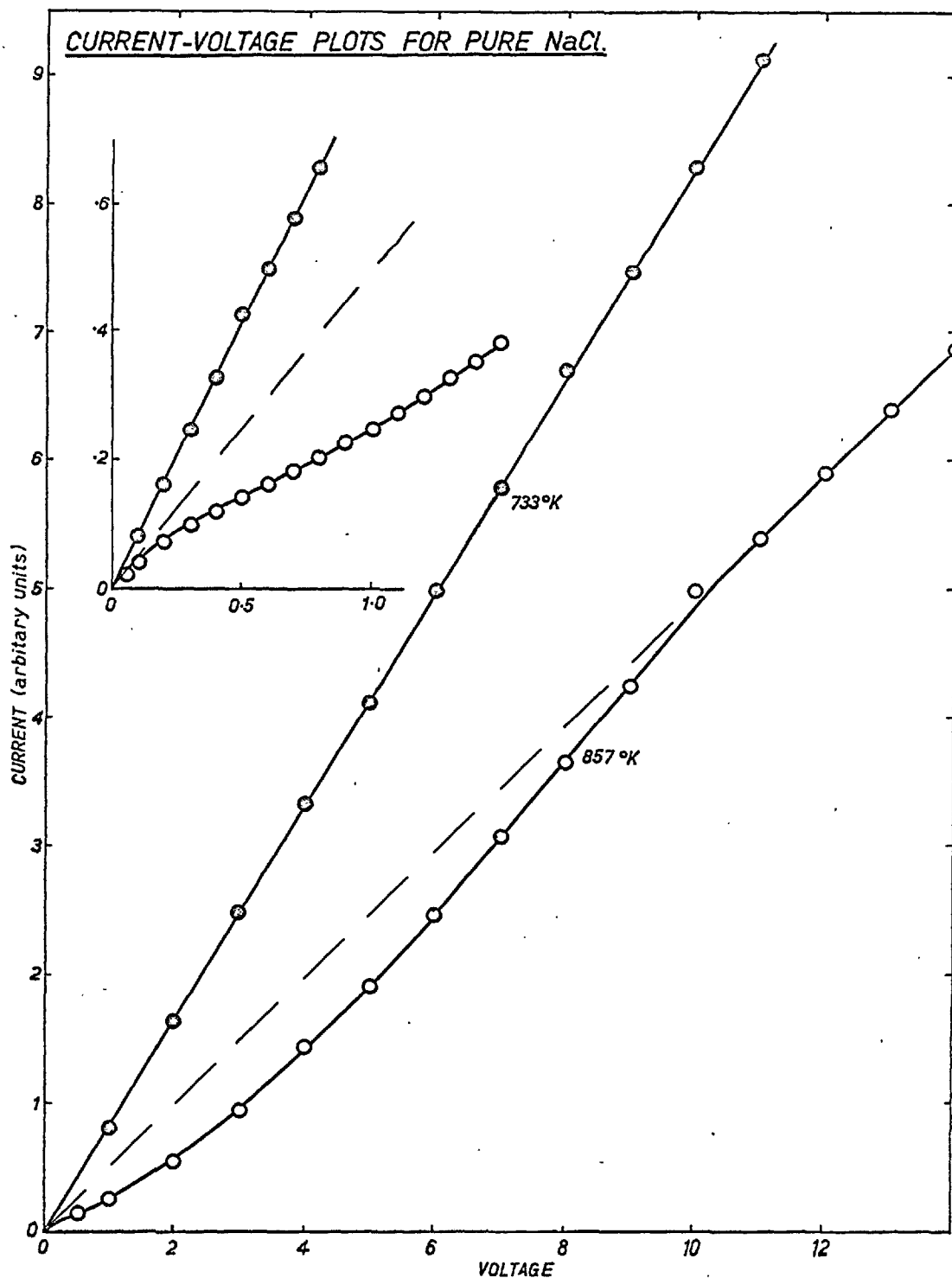


Fig.3.12.

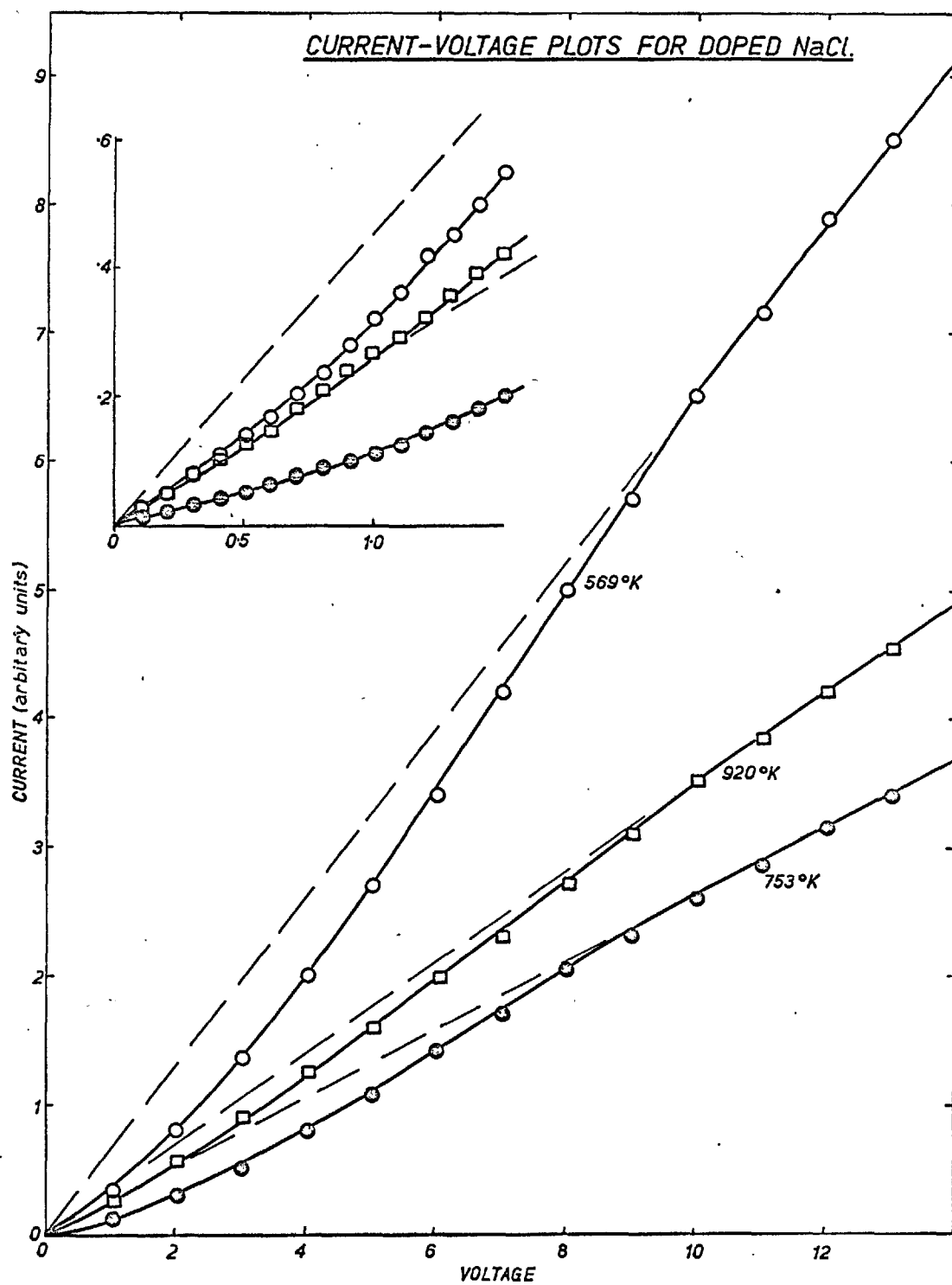


Fig.3.13.

vary by more than 0.5°K . It is also possible that at low field strengths the rate of discharge of the carriers is greater than the diffusion rate and hence no polarisation will occur.

Meycock ⁽¹³⁵⁾ found similar deviations from Ohm's law at high temperatures in potassium chloride. He found that the curves could be divided into a series of straight lines, as shown in fig.1.13. His explanation of the form of these curves would not appear to be applicable in pure and doped sodium chloride. He asserted that the steady state current for low applied fields was due to the conduction by electrons only. Since the conduction in sodium chloride is due to the motion of anion and cation vacancies, and even when maximum blocking is occurring the current flowing is still about 50% of the initial current, the residual current must be due to the discharge of a number of anion and cation vacancies. The results suggest that the electronic conduction is very small.

Optical scanning electron microscopy of electrode-crystal interfaces after fields of varying strength had been applied was tried to see if there were any obvious indications that anions or cations were being discharged or blocked at the electrodes. However, the results obtained were not conclusive and any features observed were not consistent.

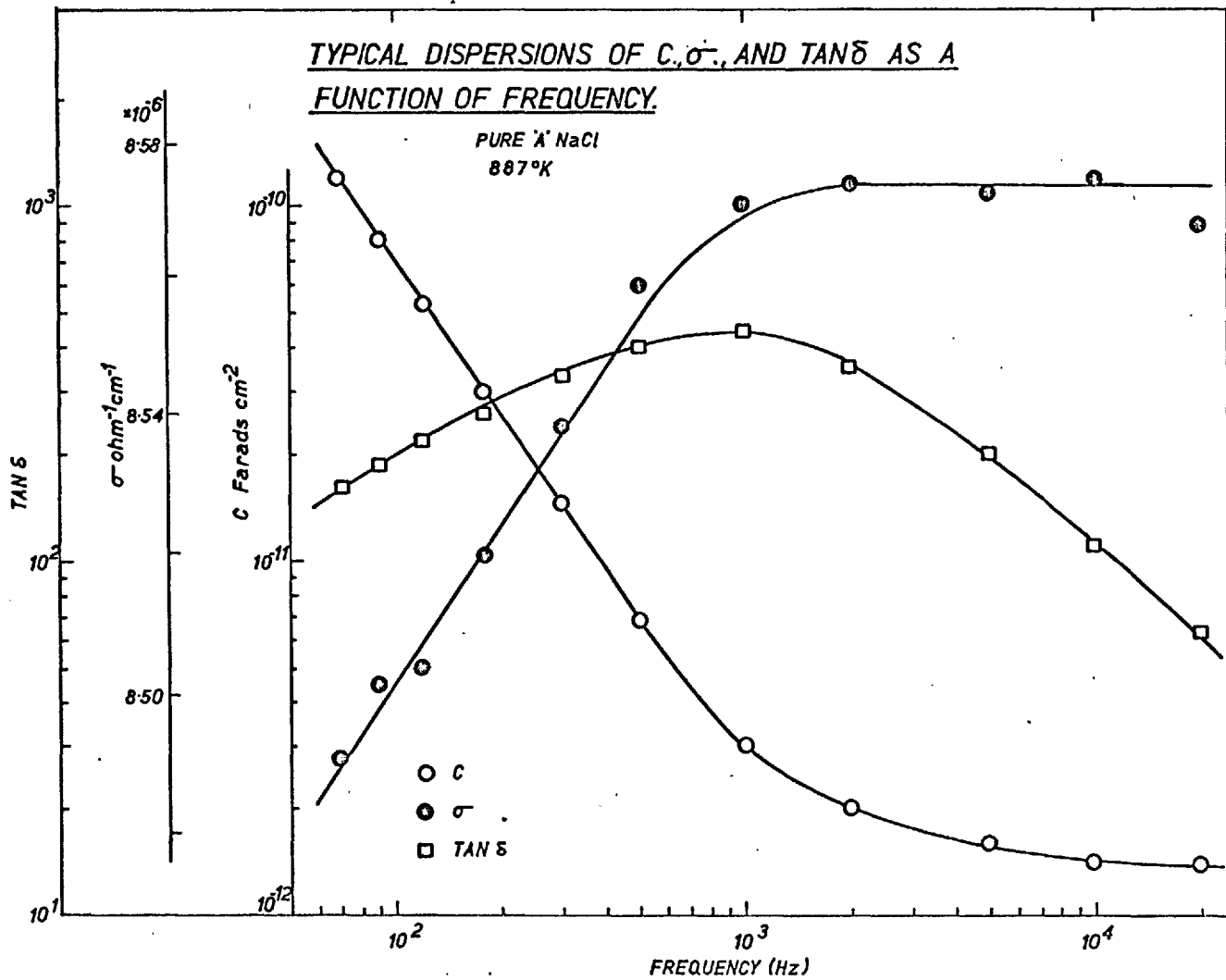
Parker ⁽¹⁶⁵⁾, and Parker and Schneider ⁽¹⁶⁶⁾ have suggested that the interfacial polarisation occurs at internal mosaic boundaries. The results described earlier would suggest, however, that the carriers are blocked at the electrodes, since it is difficult to envisage an internal interface which could block so many carriers. More recent work by Allnatt et al. ⁽¹⁶⁷⁾ has shown that the high temperature d.c.

polarisation of potassium chloride was the result of electrode blocking. Other workers (118,119,120) have shown that electrode polarisation also results in a frequency dependence of the a.c. capacitance. These results were not conclusive in establishing the blocked carrier. They found that the theory of Friauf (117) and MacDonald (116) was generally applicable for pure potassium chloride, that is one carrier only blocked. However, the results for strontium doped potassium chloride did not fit this theory and Beaumont and Jacobs (120) extended the theory for partial ionic discharge at the electrodes. However, as Raleigh (114) has pointed out there does not appear to be any thermodynamic justification for assuming partial discharge blocking for doped crystals and complete blocking for one carrier in pure crystals. The results presented in this work, as it has already been stated, suggest that the blocking is due to partial discharge of one or both carriers at the electrode-crystal interface, in both pure and doped crystals.

3.3.2. Frequency-dependence of a.c. Capacity

The frequency dependence of capacitance and conductance between 70 Hz and 20 kHz has been measured on pure and manganese doped sodium chloride. Fig.3.14. shows typical dispersions of log. capacitance, conductivity and $\log \tan \delta$ as a function of log. frequency, at constant temperature. Similar curves were found for manganese doped crystals. These dispersions are typical of interfacial polarisation and compare closely to those obtained by Tallon et al. (113). However, it must be pointed out that the increase in conductivity with increasing frequency is very small; it increases from $8.48 \times 10^{-6} \text{ ohm}^{-1}$

Fig. 3.14.



at 70 Hz to $8.57 \times 10^{-6} \text{ ohm}^{-1}$ at 20 kHz. Such small changes of conductance are difficult to measure at high temperatures since small fluctuations in temperature during the test will alter the conductivity considerably. Generally no consistent change in conductivity was noted and it was considered to be essentially frequency independent, within the limits of accuracy of the measurements. The conductivity curve shown in fig.3.14. was considered to be fortuitous and could be the effect of small temperature fluctuations in the rig.

Fig.3.15. shows the frequency dispersion of the total capacitance of the crystal for both pure and manganese doped crystals at 570, 770 and 870°K; the excess capacitance C_p , which is the total capacitance less the geometrical capacitance (the high frequency capacitance) is plotted against frequency in fig.3.16. It can be seen that C_p varies (on log. scales) linearly with frequency and the gradient of the lines are about - 2, if the frequency f is converted to angular frequency ω , by $f = 2\pi\omega$ and C_p is expressed in F cm^{-2} . This relationship between C_p and ω is in agreement with MacDonald's (116) theory, which is for blocking of both carriers. However, this theory predicts that C_p is proportional to $(2L)^{-2}$, where $2L$ is the specimen thickness, but no dependence of C_p on specimen thickness was observed. Likewise the dependence of $\Delta(1/R)$, where $\Delta(1/R) = 1/R_f - 1/R_\infty$, where R_f is the resistance at frequency f and R_∞ is the limiting resistance at high frequencies, on frequency, $\Delta(1/R) \propto \omega^2$ was not found. The results do not agree with the theory of Friauf (117) for blocking of one carrier only, which predicts that C_p is proportional to $\omega^{3/2}$.

The electrode charging phenomena has been studied in

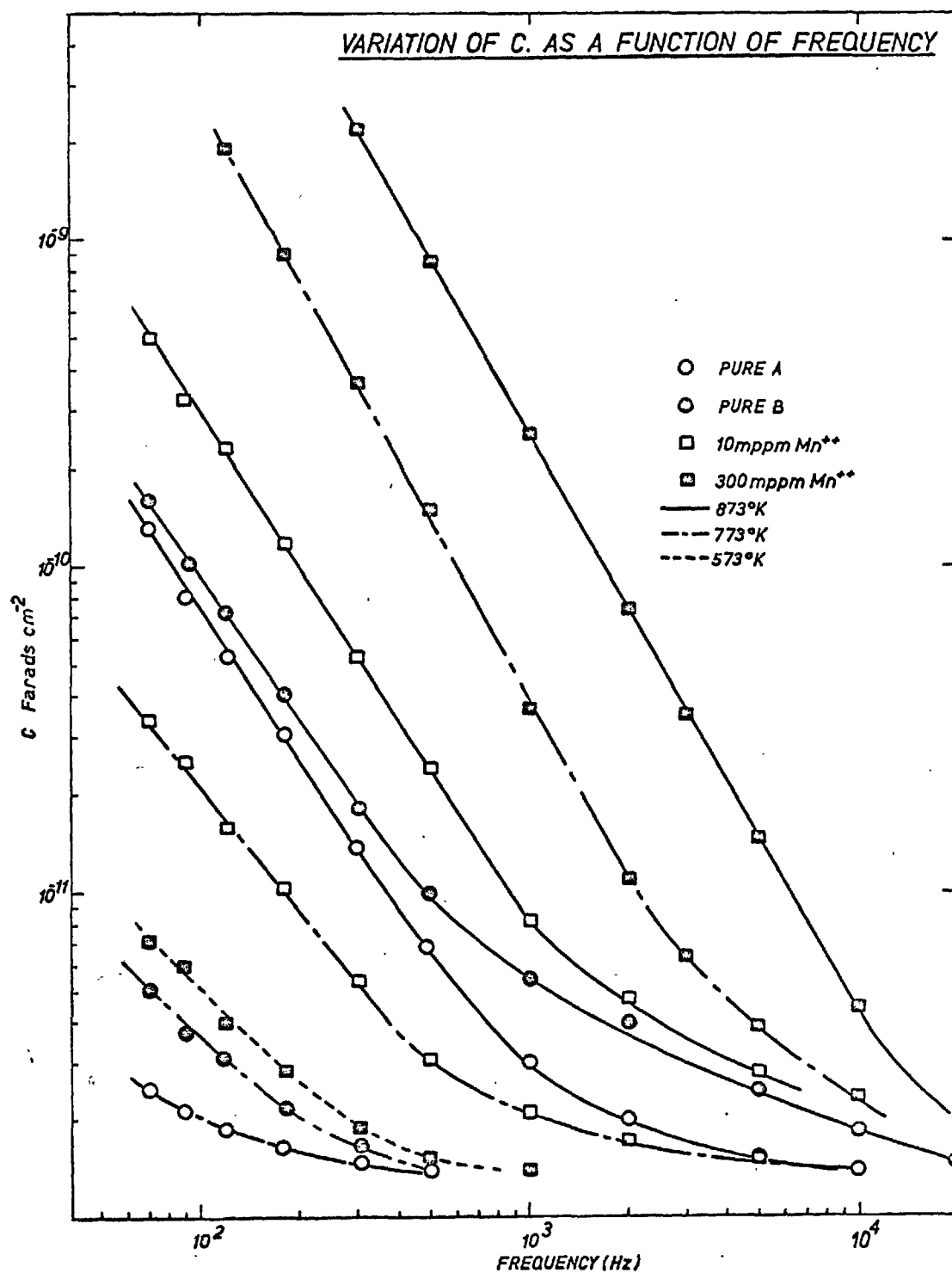


Fig.3.15.

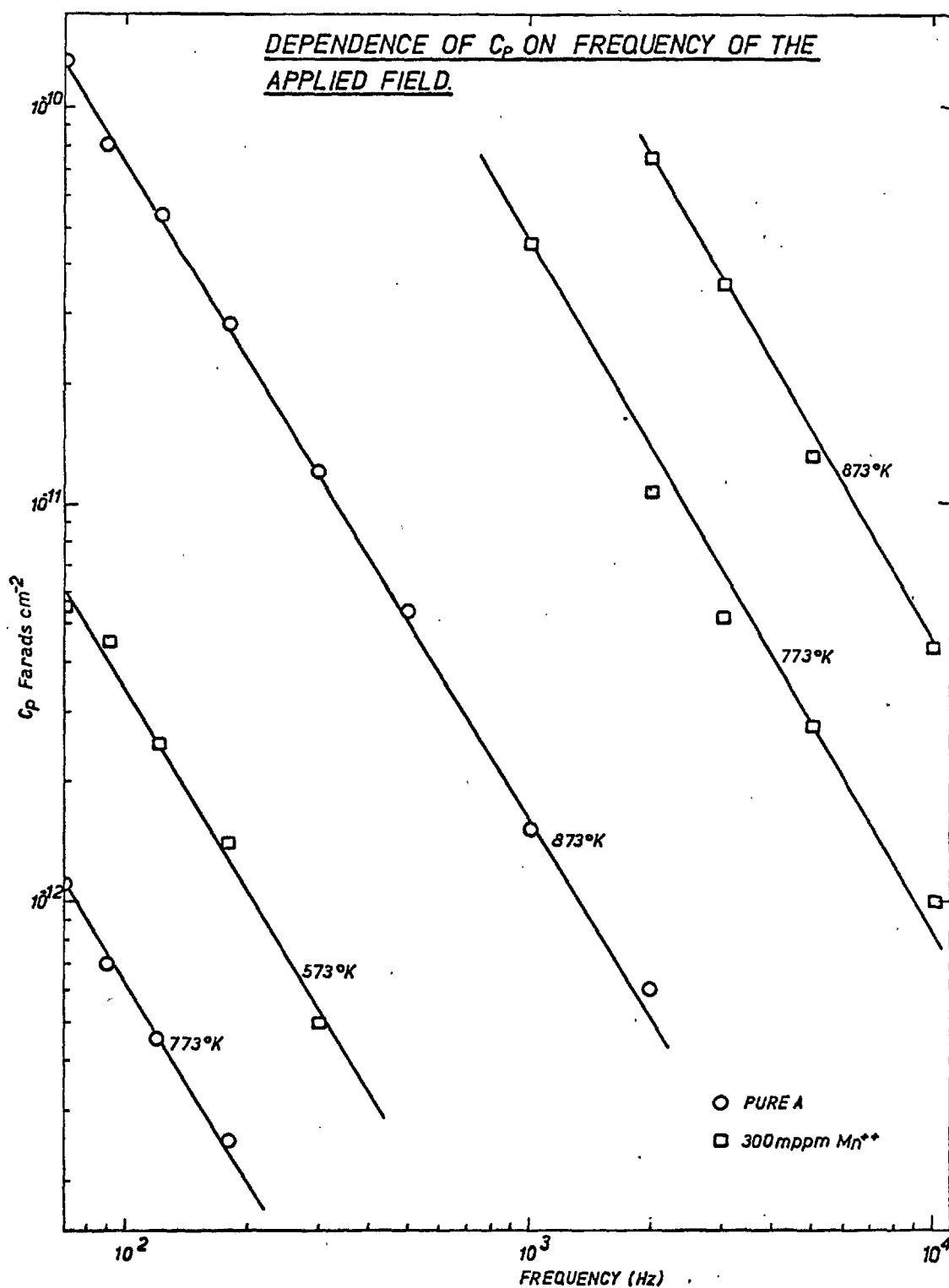


Fig.3.16.

greater detail. The temperature dependence of the loss factor $\tan\delta$, and the capacitance have been investigated. The results are summarised in fig.3.17., which shows that a maximum occurs in the $\tan\delta$ curves, and that this maximum moves to higher temperatures as the impurity concentration decreases. Fig.3.18. shows that the effective concentration of divalent impurity, C_E (values of C_E from Table 8) can be plotted against the reciprocal of $T_{\max}$, the temperature at which $\tan\delta$ is a maximum. This plot is a straight line and obeys the equation:

$$C_E = 10 (\pm 5) \times 10^{-9} \exp. (0.97 \pm 0.05)/kT$$

The kinetics of the charging processes may be more easily understood by measuring the change in $\tan\delta$ as a function of frequency, at different temperatures. Fig.3.19. shows the change in $\tan\delta$ for pure and doped specimens at 670°K and 870°K. Again the effect of divalent cation concentration can be observed on the frequency of $\tan\delta_{\max}$. The results of the $\tan\delta$ against frequency measurements can best be summarised by plotting the log. of the relaxation time, τ , at $\tan\delta_{\max}$ against $1/T$, as shown in fig.3.20. The relaxation time is related to frequency, $f_{\max}$, by the equation:

$$\tau = \frac{2\pi}{f_{\max}} \text{ secs, where } f_{\max} \text{ is in hertz.}$$

It can be seen that for pure and doped crystals the relaxation time can be expressed in the form:

$$\tau = \tau_0 \exp Q/kT \text{ secs,}$$

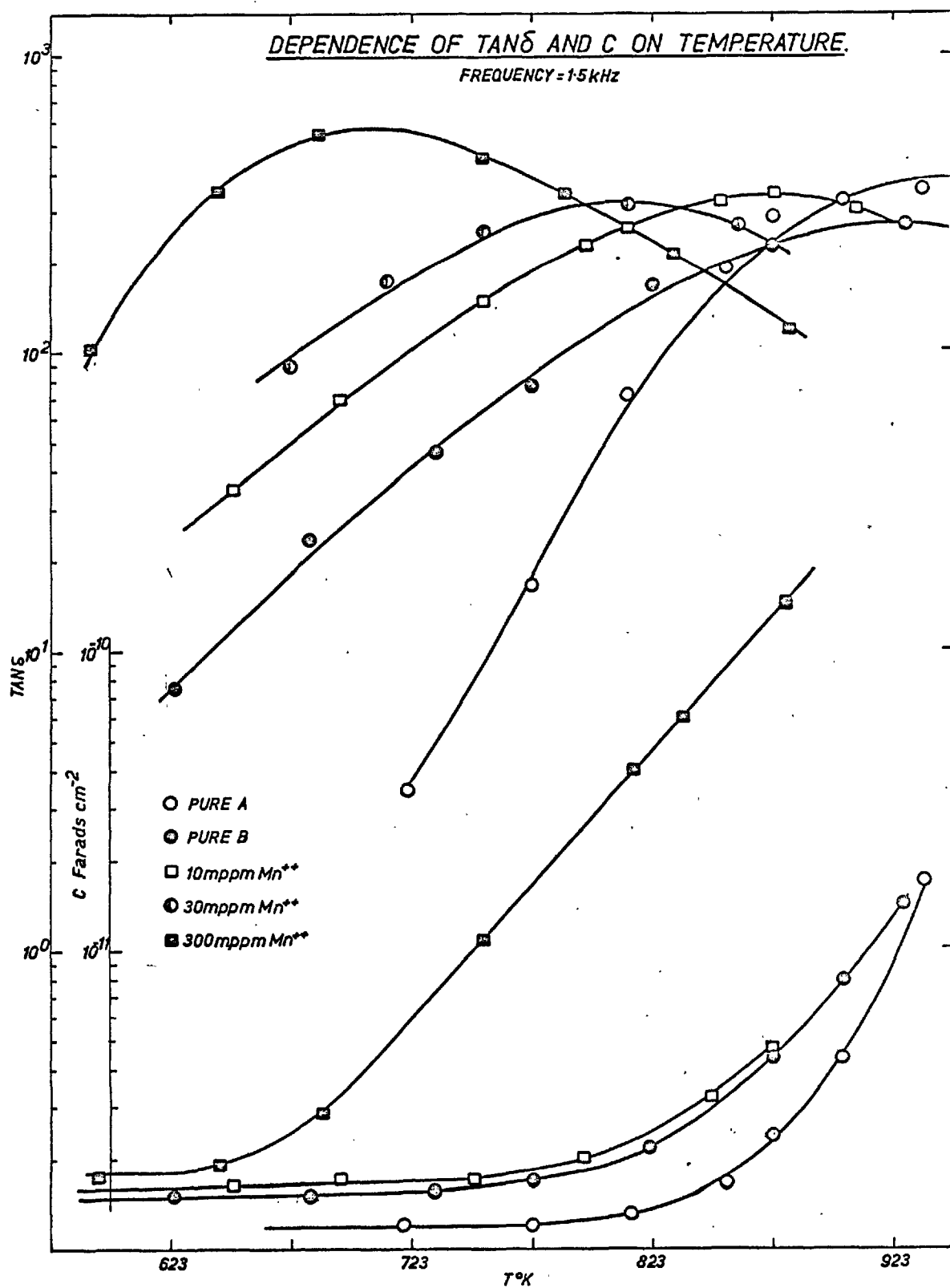


Fig.3.17.

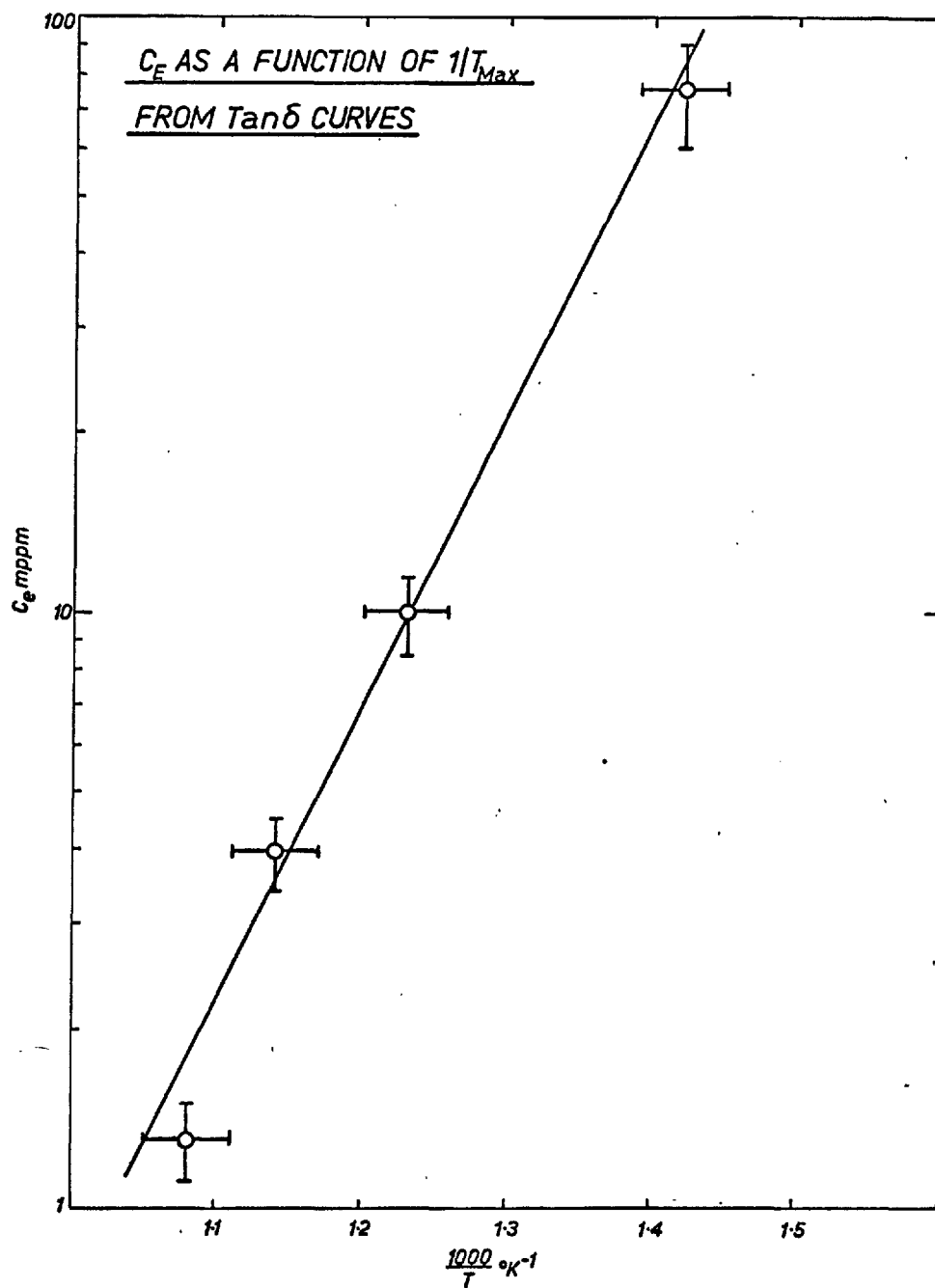


Fig.3.18.

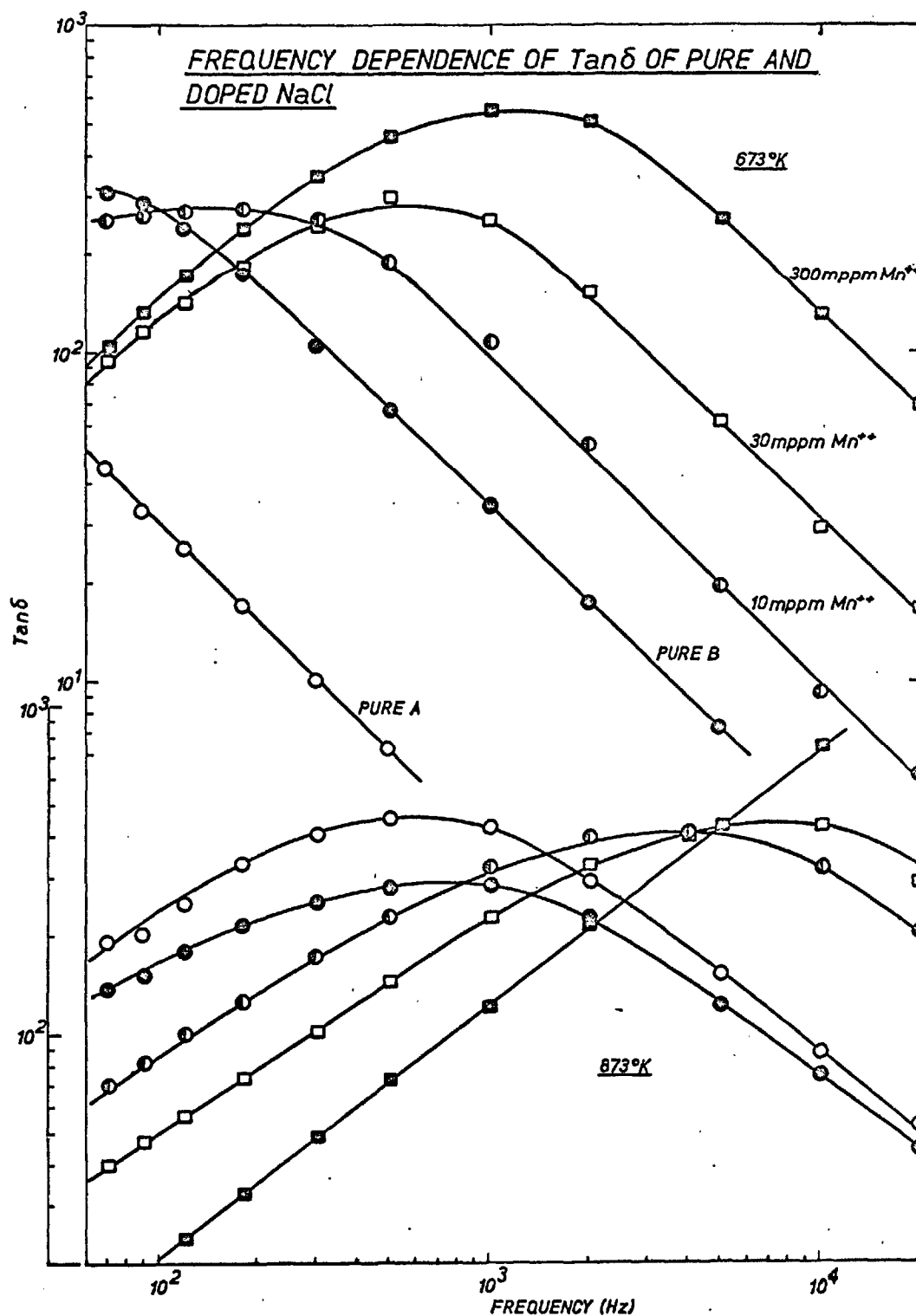


Fig.3.19.

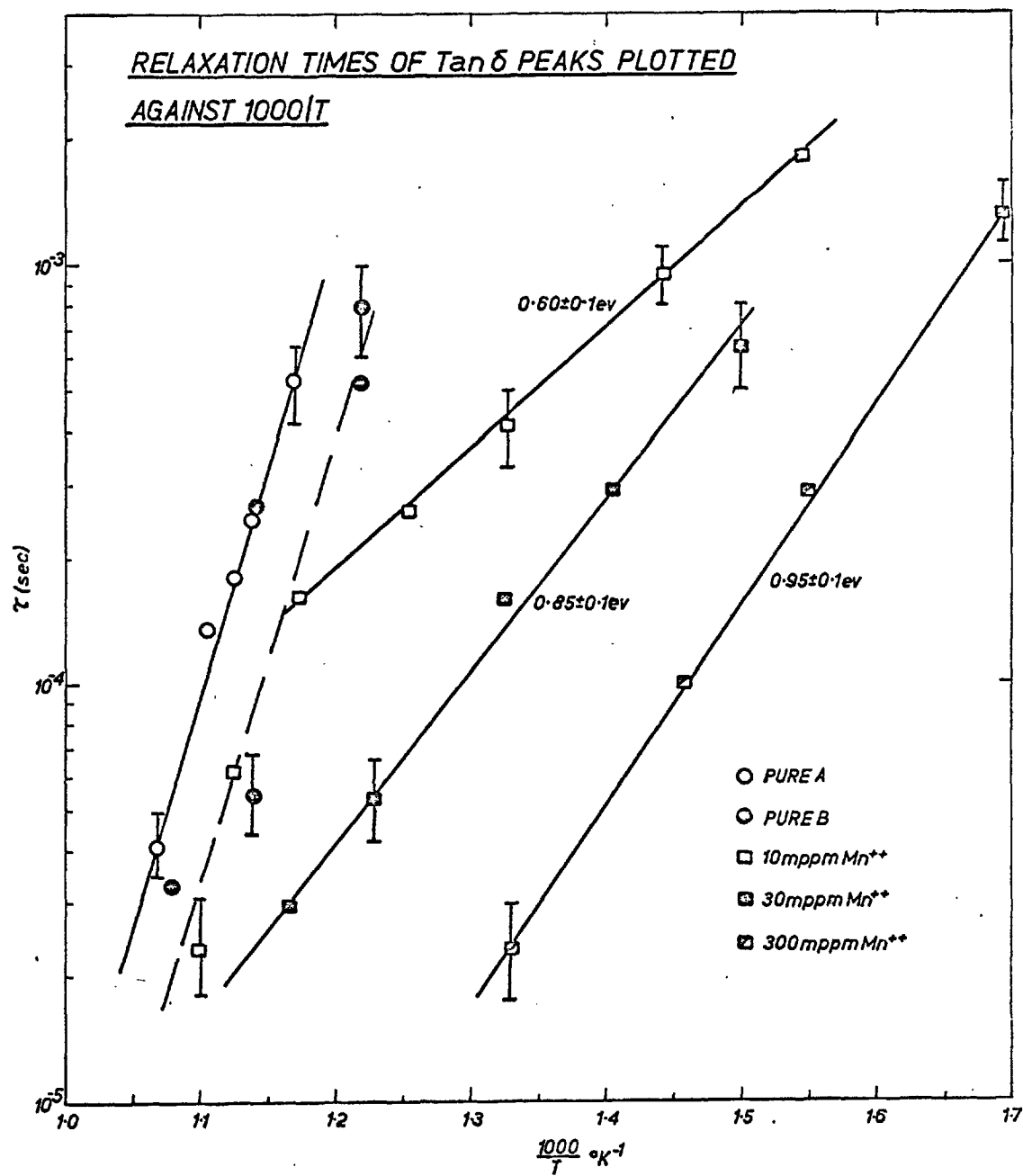


Fig.3.20.

where τ_0 is a constant and Q is an activation energy. The values of τ_0 and Q should give an indication of the relaxation processes which are occurring at the electrode, and it was hoped that this would indicate the rate-controlling process in the charge build-up.

The values of Q and τ_0 are shown in table.9. with the values found by Tallan et al.⁽¹¹³⁾ and Kao et al.⁽¹³⁴⁾. The values of Q and τ_0 for the 300 ppm manganese doped specimen compare fairly well with those obtained by Tallan et al. and the values of Q found by Kao et al. also show a close resemblance.

If the electrode blocking is controlled by the rate of charge build-up, then the value of Q should be related to the activation energy of the defects, as determined from the conductivity plots. Reference to the conductivity curves shows that the activation energy in the same temperature region is about 0.90 - 0.95eV, that is the association region of conduction, which is in agreement with the value of 0.95eV found from the a.c. data. The lower activation energies of the purest crystals would suggest that this energy is more appropriate to the extrinsic region of conduction, that is about 0.70eV. The variation of Q from 0.57eV to 0.85eV in the 10 and 30 ppm doped specimens could be due to experimental error in determining τ , since the $\tan \delta$ peaks are broad and $\tan \delta_{\max}$ is difficult to define. The pure crystals do not exhibit a relaxation time at low temperatures in this range of frequencies but they do show a peak at high temperatures. The activation energy is very much increased and can be attributed to the blocking of anion vacancies. If the energy can be written as $Q = h_g/2 + \Delta h$ then a value of $\Delta h =$

TABLE 9

VALUES OF Q AND τ_0 FROM TEMPERATURE DEPENDENCE OF $\tan \delta$ PEAKS
FOR PURE AND DOPED SODIUM CHLORIDE

Crystal	Q(eV)	τ_0 (secs)	Temp range °K	Source	Method
Pure A	2.14 ± 0.1	$5.6(\pm 1.0) \times 10^{-5}$	870 - 950	This work	A.C. $\tan \delta$
Pure B	2.14 ± 0.1	$2.0(\pm 1.0) \times 10^{-5}$	815 - 930	" "	"
10 mppm Mn ²⁺	0.57 ± 0.1	$7.0(\pm 1.0) \times 10^{-8}$	645 - 830	" "	"
" " "	2.14 ± 0.1	$2.0(\pm 1.0) \times 10^{-5}$	830 - 910	" "	"
30 mppm Mn ²⁺	0.85 ± 0.1	$3.5(\pm 1.0) \times 10^{-10}$	670 - 870	" "	"
300 mppm Mn ²⁺	0.95 ± 0.1	$10(\pm 1.0) \times 10^{-12}$	590 - 770	" "	"
NaCl	0.99	2.3×10^{-13}	> 616	(113)	"
NaCl (pure)	1.09		373 - 623	(134)	D.C. transients
NaCl Ca ²⁺	0.97		" " "	"	"
NaCl Ba ²⁺	1.00		" " "	"	"

$0.96 \pm 0.1\text{eV}$ is found. This is in good agreement with previous work for the enthalpy of motion of anion vacancies. Thus it would appear that the rate controlling process at high temperatures is the diffusion of anion vacancies, although, of course, this does not mean that cation vacancies are not also blocked. This is in agreement with the d.c. results.

Although it appears that the values of Q can be interpreted in terms of the diffusion processes occurring in the bulk of the crystal the processes occurring at the crystal-electrode interface are likely to be complex and affected by the nature of the interface. The variation between τ_c for pure A and pure B may be explained in these terms and the variation of Q for the low doped crystals may be related to electrode condition. Kessler and Mariani ⁽¹²⁵⁾ and Sano and Tomiki ⁽¹⁶⁹⁾ have noticed that the loss peaks due to interfacial polarisation are very much dependent on the state of the electrode-crystal interface.

This discussion has assumed that the relaxation peaks are due to interfacial polarisation. However, at the lower temperatures the peaks could be due to impurity-vacancy dipoles and at high temperatures the peaks could be the reorientation of vacancy pairs. However, dielectric loss and c.s.r. ⁽¹⁷⁰⁾ determination on the temperature dependence of impurity-vacancy dipole loss peaks indicate a pre-exponential factor in the order of 10^{-14} secs. Thus the value of τ_0 presented here is inconsistent with a dipolar relaxation mechanism at the lower temperatures. Likewise the high temperature relaxation of vacancy pairs ⁽¹⁸⁰⁾ is characterised by a value of τ_0 of about 10^{-14} sec. which is much smaller than that obtained in this work. Thus it would appear that it is justifiable to relate the relaxation

processes to the presence of electrode polarisation and not dipolar relaxations.

(112)

Volger has presented a review of the dielectric behaviour of material containing thin surface layers whose electrical properties differ from the bulk. He has proposed a two-layer model which could predict the thickness of the surface layer from the value of $\tan \delta$. He considered several different cases, but the one appropriate to this work was for a large capacitance dispersion but essentially no conductivity dispersion. In this case the surface layer would have a smaller resistance than the bulk but its resistivity would be greater. Volger's theory states that in the case mentioned the maximum value of the dissipation factor, $\tan \delta$ is related to the thickness of the surface layer and the bulk, d_1 and d_2 respectively;

$$\tan \delta = \left[\frac{d_2}{4d_1} \right]^{\frac{1}{2}}$$

The value of $\tan \delta_{\max}$ is approximately constant for all impurity concentrations at about 3×10^2 , at 670°K and 4×10^2 at 970°K ; the bulk thickness $d_2 = 0.25\text{cm}$. This gives values of about 10^{-6}cm at 670°K and $5 \times 10^{-7}\text{cm}$ at 970°K . These values are apparently small compared with those found by Tollen et al., that is $10\text{-}20\mu\text{m}$; and about an order of magnitude smaller than the value predicted for the space-charge layer found by Lebovec (92).

3.3.3. Series Representation of a.c. Capacitance and Conductance.

Raleigh⁽¹¹⁴⁾ has discussed the failure of both MacDonald's and Friauf's models, and the modification of these models by Beaumont and Jacobs⁽¹²⁰⁾, to account fully for the interfacial polarisation phenomena in terms of an ideal polarised electrode concept, first introduced by Graham⁽¹⁶⁸⁾. The ideal polarised electrode is an electrochemical concept, and is described as an electrode which has no chemical component in common with the adjacent electrolyte, and at which ionic discharge processes are prohibited for straight forward thermodynamic reasons. It has been suggested that such an electrode may be regarded as a simple capacitance in series with the resistance of the electrolyte. In such a system no dispersion of the series capacitance or conductance should be present. This concept differs from previous theories of electrode polarisation which consider the parallel capacitance and resistance, in which a dispersion will be present. A dispersion will be present in the series capacitance and resistance, however, if the charging of the electrodes is time dependent and if the time required for such a charge relaxation process is comparable to the frequency of the a.c. potential used. Raleigh⁽¹¹⁴⁾ has shown that the equations for the parallel capacitance and resistance C_p and R_p , from Friauf's⁽¹¹⁷⁾ theory are just the parallel capacitance and resistance of a frequency-independent capacitor and resistor in series. From this treatment, the dependence of C_p on $(2L)^{-2}$ and ω^2 and the frequency dependence of R_p is only a property of the parallel representation. Thus the lack of dependence observed of C_p on $(2L)$, and R_p on ω , in the results are

not inconsistent with electrode polarisation theories. Since C_p is approximately dependent on ω^{-2} it does indicate that C_s should be approximately independent of frequency, in agreement with the ideal model. Raleigh has pointed out that the series representation can only be a first-order theory and that deviation from the theory may provide useful information relating to the types of relaxation processes occurring in the Debye-layer charging. It is felt that if such information is to be obtained arrangements must be used where blocking is achieved in a thermodynamically well-defined manner. Raleigh has also pointed out that the microscopic nature of the electrode-electrolyte interface is very important. Recent work by Kessler and Mariani (125) and Sano and Tomiki (169) have illustrated the importance of electrode-electrolyte contacts.

CHAPTER 4

PRESENTATION AND DISCUSSION OF RESULTS II:

POLYCRYSTALS

4.1. DIFFUSION IN GRAIN BOUNDARIES IN POLYCRYSTALLINE SODIUM CHLORIDE.

4.1.1. Introduction.

Previous workers have studied the diffusion of monovalent cations in sodium chloride ⁽⁶⁾ and lithium chloride ⁽³⁹⁾ grain boundaries, using a conductivity probe technique. The effect of divalent cations on the grain boundary conductivity has not been studied, mainly because of their high diffusivity in the bulk which would make analysis of the results difficult. In this work the effect of grain boundaries on the bulk conduction, and the effect of divalent impurities in grain boundaries, has been investigated. Grahov et al. ⁽⁵⁾ have studied the a.c. and d.c. bulk conductivity of pure polycrystalline sodium chloride as a function of grain size, but their results, which showed an enhanced anion diffusion, were not compatible with the diffusion studies of Cabané ⁽³⁾; he found no enhanced diffusion of anions in carefully prepared polycrystals.

Cabané has shown that the preparation of the polycrystal is extremely important and a hot-pressing technique similar to that used by Cabané has been developed. The conductivity of pure polycrystals prepared by an extrusion technique developed by Stokes ⁽¹⁴⁷⁾ and Li ⁽¹⁴⁷⁾ has also been measured.

Microstructural studies of the polycrystals, both before and after annealing, have been made in order to establish the presence of pores, which might affect the conduction processes, and to evaluate the effects of grain

growth on the conduction.

The interfacial polarisation phenomena have been studied using both d.c. and a.c. conductivity techniques. The results have been compared with the results from single crystals so that the polarisation effects, if any, of the grain boundaries may be established.

4.1.2. Microstructure of Polycrystalline in Sodium Chloride.

The conductivity measurements were generally made on annealed polycrystals. The specimens were annealed at 870°K for one hour, followed by furnace cooling. The effect on the microstructure of such an anneal is shown in fig.4.1. and fig.4.2. Fig.4.1. shows the microstructure of an as pressed pure polycrystal, which had apparently a very small grain size. After annealing at 870°K the grain size apparently increased considerably and the grain boundaries became more distinct, fig.4.2. The structure of the unannealed polycrystal probably resulted from the heavy deformation undergone by the pellet during the hot-pressing; the apparently very small grain size resulting from the presence of sub-grains or possibly slip-bands within each grain. This heavily deformed structure could also result from the pressure exerted on the compact by the press body when it cooled after the pressing. This possibility was supported by the fact that the extruded polycrystals did not show this substructure in the unannealed state; the extrusion, of course, was not confined during the cooling period.

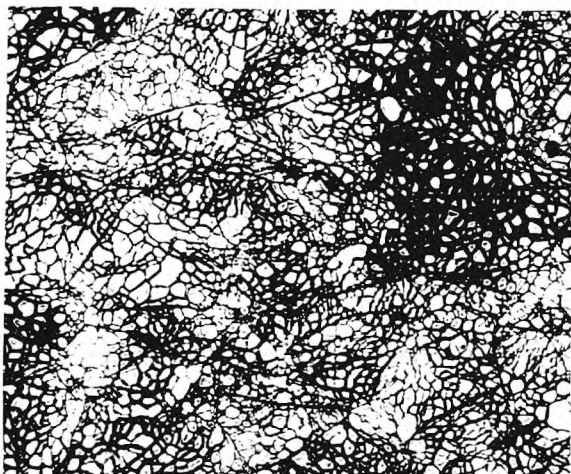


Fig. 4.1.

PURE POLYCRYSTAL.

AS PRESSED.

×50

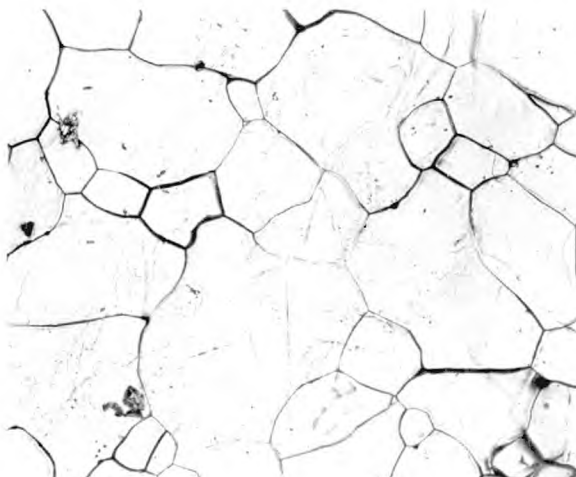


Fig. 4.2.

PURE POLYCRYSTAL.

ANNEALED AT 870°K FOR 1hr.

×50



Fig. 4.3.

LEFT: AS PRESSED

POLYCRYSTAL.

RIGHT: ANNEALED

POLYCRYSTAL.

CENTRE: SINGLE

CRYSTAL.

Throughout the microstructural examination of the polycrystals there was no detectable evidence of porosity. This is not really surprising since the polycrystals used for the tests were nearly as dense as single crystals of the same material.

The annealing of the pure polycrystals resulted in the appearance of a white colouration, the specimens being completely clear prior to annealing, as shown in fig.4.3. This whitish appearance of the polycrystals could be due to the formation of very small voids within the crystal. Coban⁽³⁾ noticed that the density of the compacts decreased significantly after annealing if the powder was not carefully predried. However, no such decrease in density was observed even after considerable periods of annealing at high temperatures.

The appearance of the white colouration occurred at fairly low temperatures, below about 500°K , and at the same temperature at which the sub-grain structure had largely disappeared. The extruded polycrystal always remained completely clear, even after annealing at high temperatures for long periods. Thus it would appear that the sub-structure within each grain and the white appearance of the polycrystal are connected. It is possible that the sub-structure was the result of stresses introduced during the cooling of the pellet in the press, and that the annealing of the pellet relieves the stresses within the pellet by the formation of very small pores on the grain boundaries. These pores are too small to be detected by optical microscopy and the density changes.

The whitish appearance could also be due to the precipitation of impurities at the grain boundaries. The

impurities, although present in small concentrations in the pure crystals, will tend to segregate at the boundaries and on cooling to room temperature could precipitate as chlorides. However, the low temperature at which the colouration appears, and the absence of colouration in the extruded polycrystals would tend to invalidate this process. It is possible that a sufficiently large amount of absorbed water was present in the pressed polycrystals to result in the formation of small pores, without noticeably decreasing the density; this effect has been observed by Cabané.⁽³⁾

The 870°K anneal for one hour was apparently sufficient to remove the sub-structure without causing too much grain growth. Figs.4.4 and 4.5 show the effects of prolonged annealing on the structure. The polycrystal shown in fig.4.4. had been annealed at 870°K for one hour and then furnace cooled; the grains were reasonably uniform in size. In fig.4.5 the polycrystal had been annealed at 870°K for 1 hour and then the conductivity had been measured up to 920°K and so had been annealed for a considerably longer period. The presence of considerably enlarged grains indicates that grain growth had occurred, the average grain diameter increased considerably.

This growth was not observed in any of the manganese doped polycrystals. Fig.4.6. shows the structure of an annealed manganese doped polycrystal, containing about 10ppm manganese. The grain size has apparently not increased from the original particle size of the powder. The brown colouration of the manganese doped polycrystals after annealing suggests that the manganese ions segregated at the grain boundaries where precipitation of manganese chloride occurred. The segregation inhibited the grain

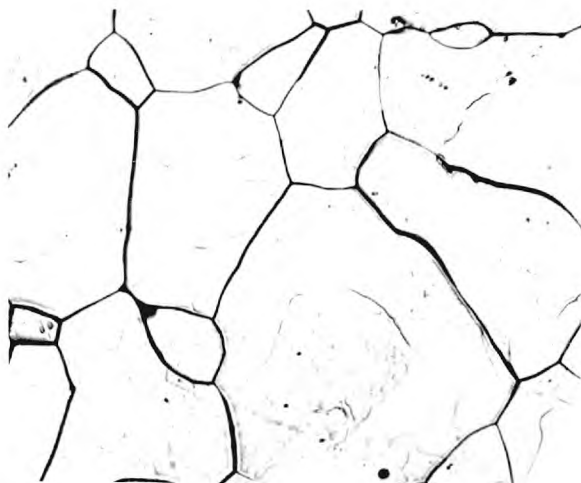


Fig. 4.4.

PURE POLYCRYSTAL
ANNEALED AT 870 °K FOR 1hr.

×50

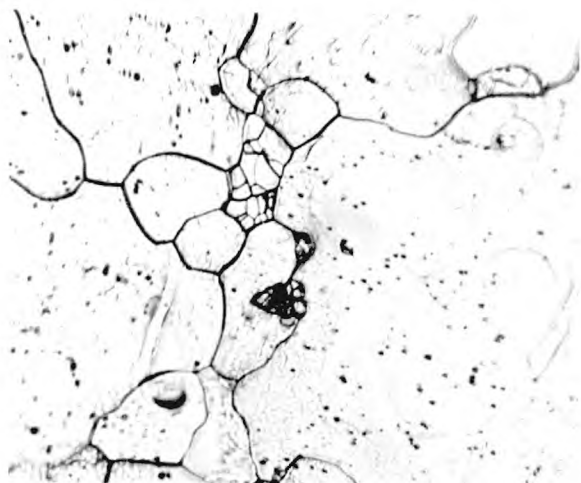


Fig. 4.5.

PURE POLYCRYSTAL
ANNEALED AT 870 °K FOR 1hr
+ CONDUCTIVITY RUN UP TO 920 °K.

×50

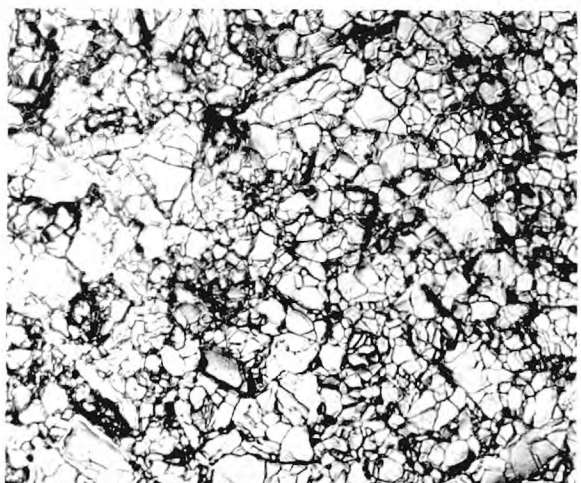


Fig. 4.6.

DOPED POLYCRYSTAL
ANNEALED AT 870 °K FOR 1hr.

×50

growth. This effect of segregation has been observed in many ceramic systems.

4.1.3. Conductivity of Polycrystalline Sodium Chloride.

The a.c. conductivity plot of an annealed polycrystal produced from pure 'A' material is shown in fig.4.7. The conductivity in the extrinsic region has increased by about one order of magnitude and the activation energy had increased from 0.69eV in the single crystal to $0.79 \pm 0.02\text{eV}$ in the polycrystal. This region, at high temperatures joins the intrinsic region of the single crystal in a long shallow curve. A straight-line region with an activation energy of 1.60eV can be drawn through the points in the transition region between the intrinsic and extrinsic regions in fig.4.8., it must be pointed out that this line could be a shallow curve and not a straight line as suggested. Fig.4.8. also shows that there was no grain size dependence of conduction over the range of $120\text{ }\mu\text{m}$ to $300\text{ }\mu\text{m}$ grain diameters. Attempts were made to test polycrystals with a wider range of grain sizes, from $40\text{ }\mu\text{m}$ to over $300\text{ }\mu\text{m}$, but it was found that grain growth during annealing and testing tended to even out the grain sizes of the different compacts. Fig.4.8. also shows that annealing in a wet nitrogen atmosphere had no pronounced effect on the conduction, the significance of this will be discussed later.

The conductivity of the less pure 'B' polycrystals is shown in fig.4.9. and fig.4.10. The a.c. conduction was not enhanced as much as in the purer polycrystals and

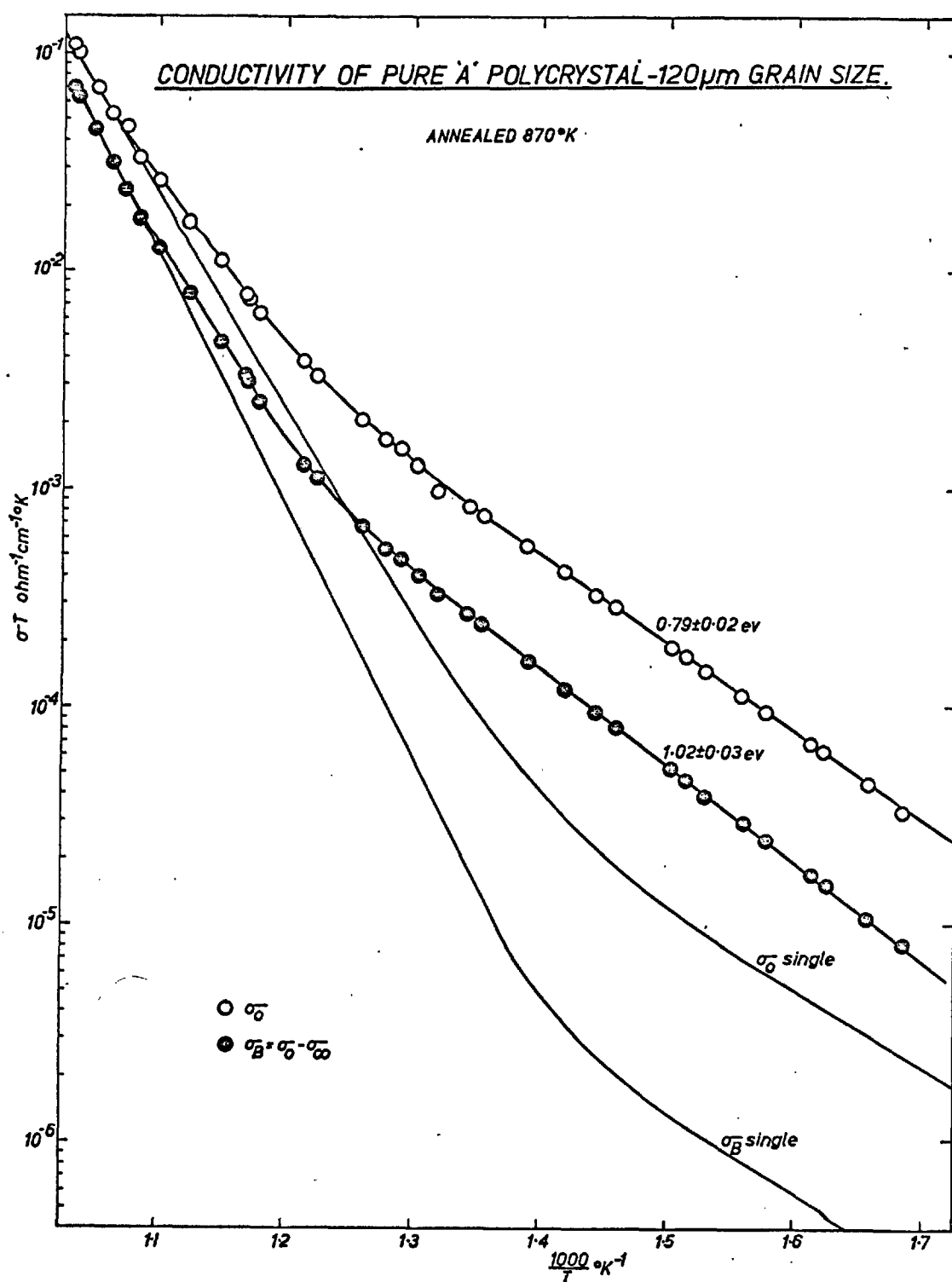
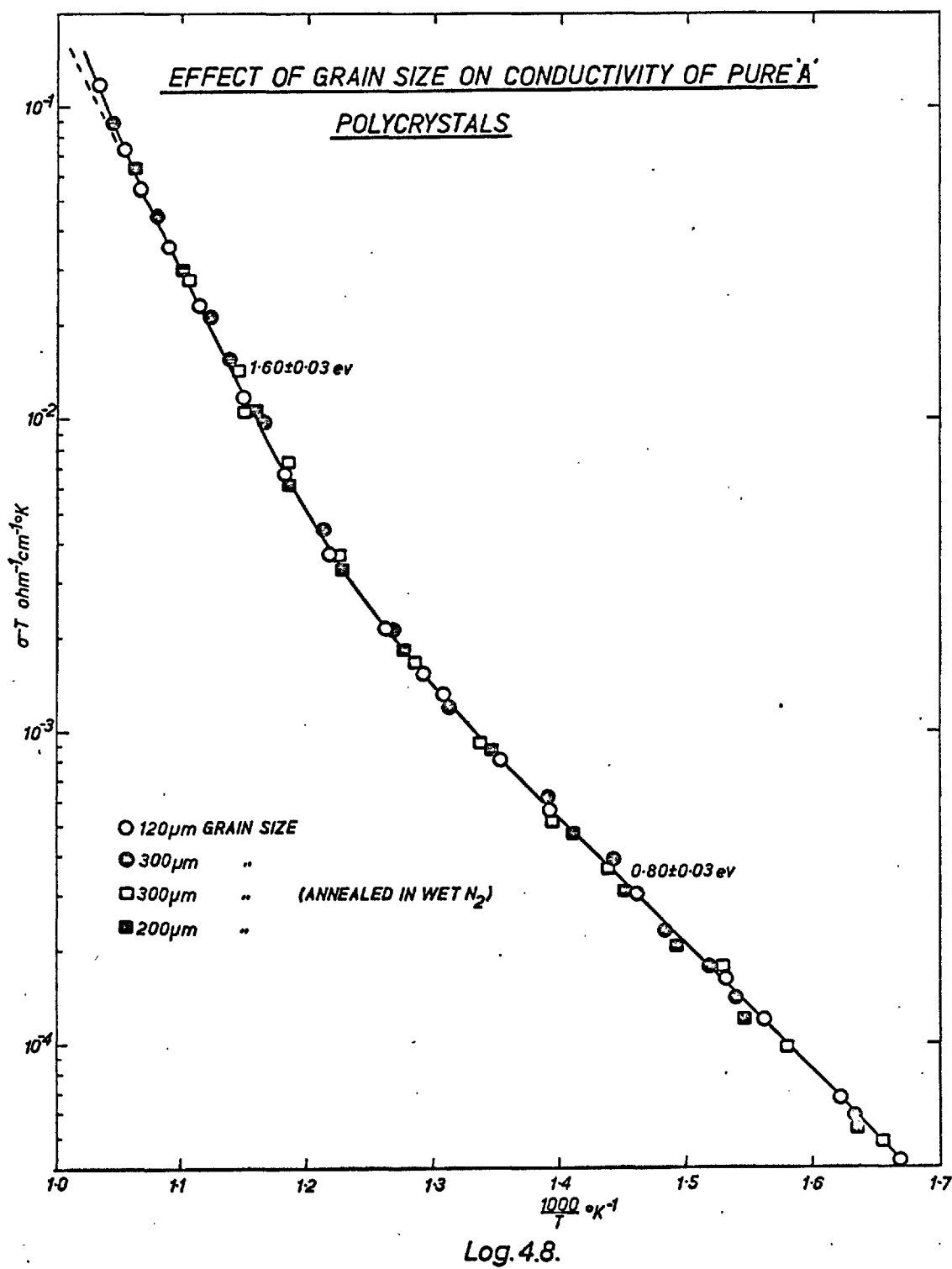


Fig. 4.7.



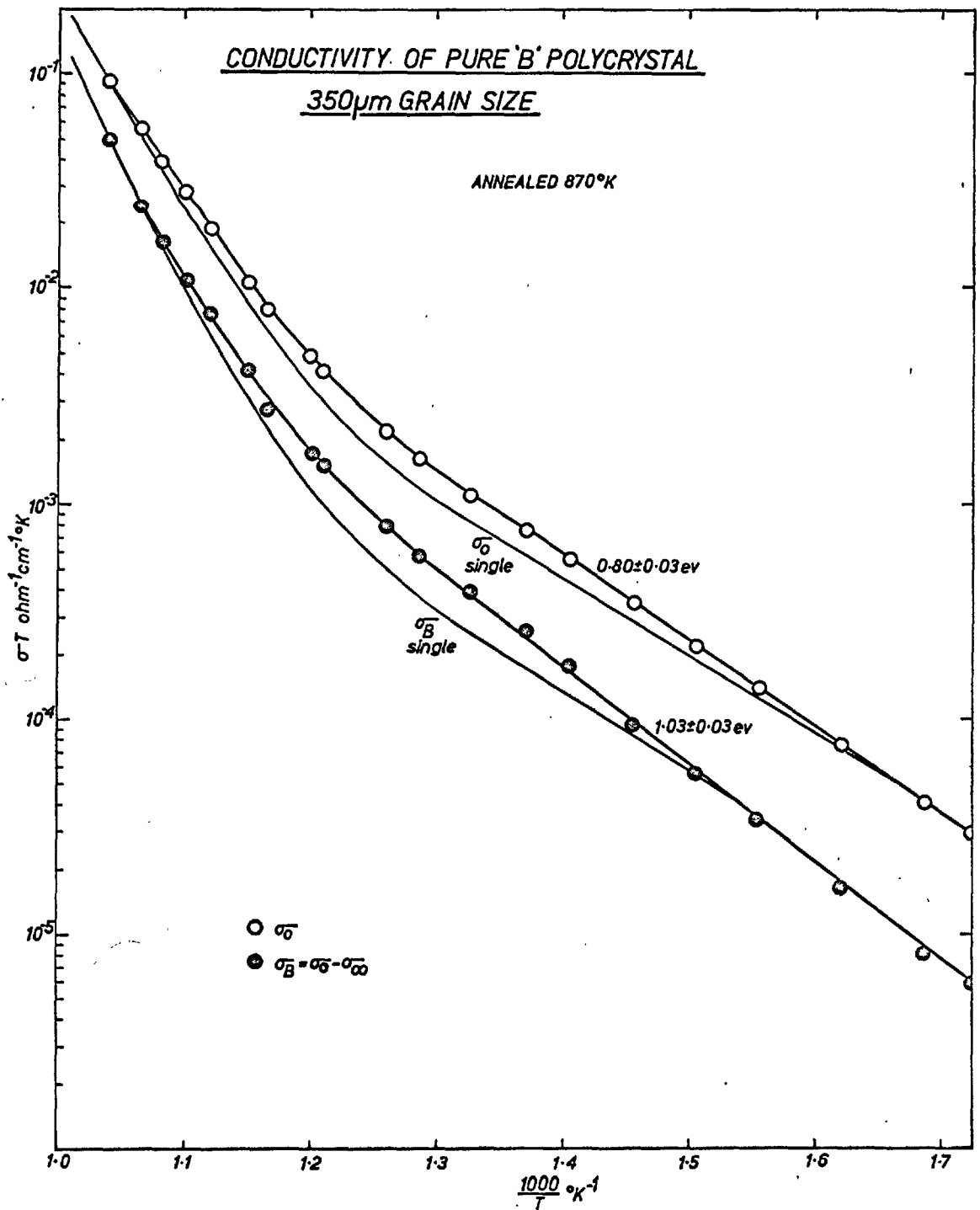
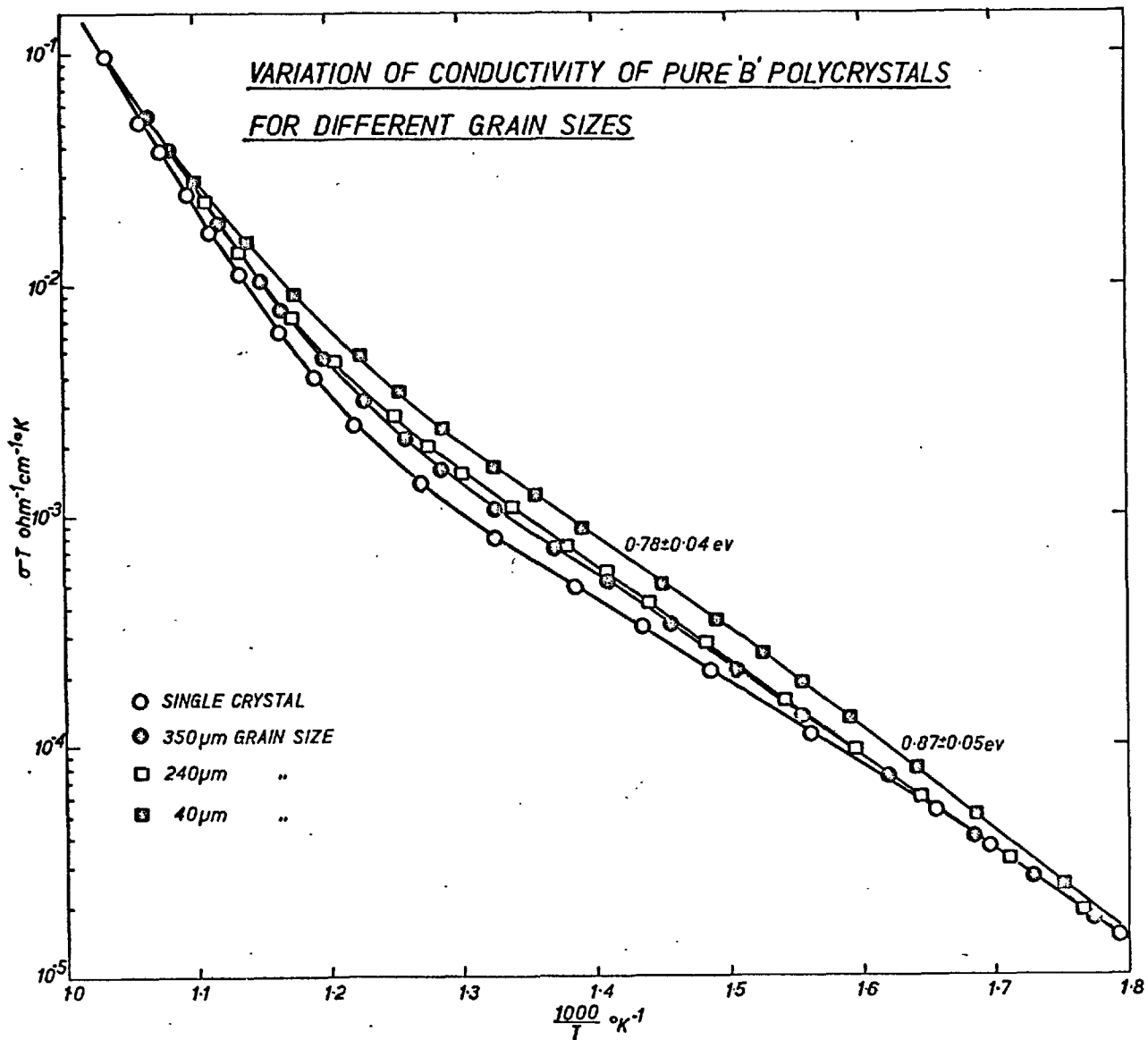


Fig.4.9.

Fig.4.10.



indeed at temperatures below 590°K a straight line region with an activation energy of $0.80 \pm 0.05\text{eV}$ was observed and it is interesting to note that this region exactly corresponds with similar region in the pure 'A' polycrystals. The line is described by the equation:

$$\sigma_T = 2.75 \times 10^2 \exp (-0.80 \pm 0.02) / kT \\ \text{ohm}^{-1} \text{ cm}^{-1} {}^{\circ}\text{K}.$$

Fig.4.10. shows that there was small grain size dependence of conductivity in the pure 'B' polycrystals. Apparently the 'knee' of the association region, that is the temperature at which the extrinsic region transforms into the association region, was shifted to higher temperatures as the grain size decreased.

The manganese doped polycrystals appeared to exhibit a similar behaviour to the pure B' small grained polycrystals, as it can be seen in fig.4.11

Region III of the single crystal conductivity curve was extended to much higher temperatures in the polycrystal. The activation energy of this region was $0.91 \pm 0.03\text{eV}$ which is in good agreement with the activation energies of region III in single crystals found in this work. The activation energy of region III can be written as:

$$Q_{\text{III}} = \Delta h_c + \frac{h_k}{2}$$

where h_k is the enthalpy of association of a divalent cation-vacancy complex. Thus the enthalpy of association is

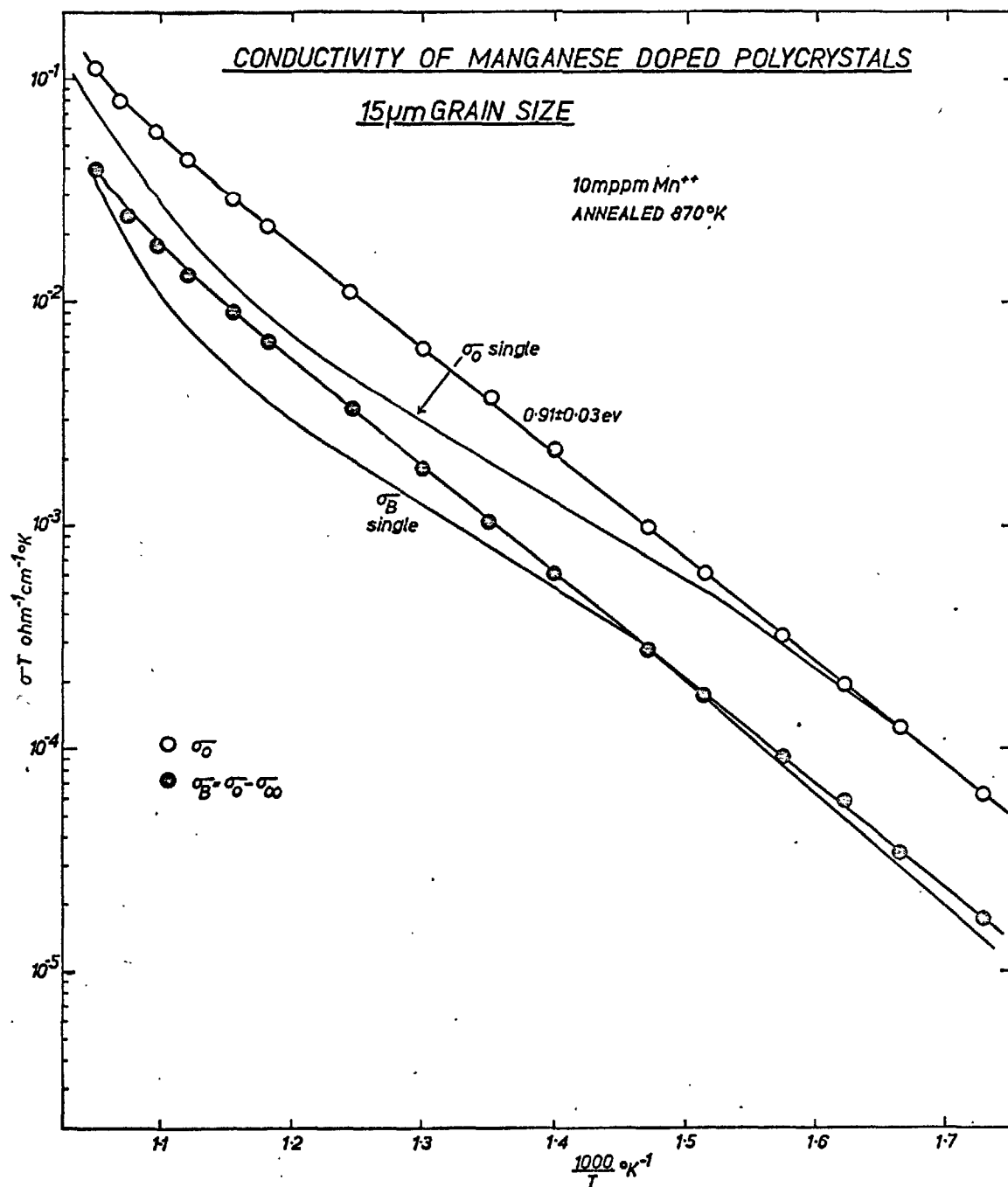


Fig.4.11.

calculated to be $0.44 \pm 0.03\text{eV}$ which is in good agreement with values obtained by Kirk (48) and Watkins (170).

Further work on more heavily doped polycrystals has not been presented here because of the considerable scatter of results. This was thought to be due to the precipitation of manganese chloride on the surface of the particles during the predrying procedure, and the subsequent loss of much of the manganese from the crystals by evaporation. This precipitation of the manganese on the surface also prevented the good adhesion between the particles during pressing and consequently the compacts tended to disintegrate during annealing. Attempts to extrude manganese doped single crystals also proved unsuccessful. It was not possible to produce a flaw free extrusion.

The effects described so far on the conductivity of polycrystalline sodium chloride could arise from the inclusion of impurities during the drying and hot-pressing procedure. For this reason the results of the conductivity of extruded pure polycrystals will be described. The conductivity plot is shown in fig.4.12 and it is evident that the conduction was very similar to the pure A polycrystals. Region II shows a considerable enhancement of conduction, although not nearly so great as the pressed polycrystals, and the activation energy was again $0.79 \pm 0.03\text{eV}$. The transition into region I of the single crystal curve was more sharply defined, and the lines for the polycrystal and single crystal were coincident in regions I and I'. The reduced enhancement of the conduction may be due to the very large grain size, that is about $800\text{ }\mu\text{m}$, present in this crystal. It was found that extruded polycrystals with smaller grain sizes could not be obtained.

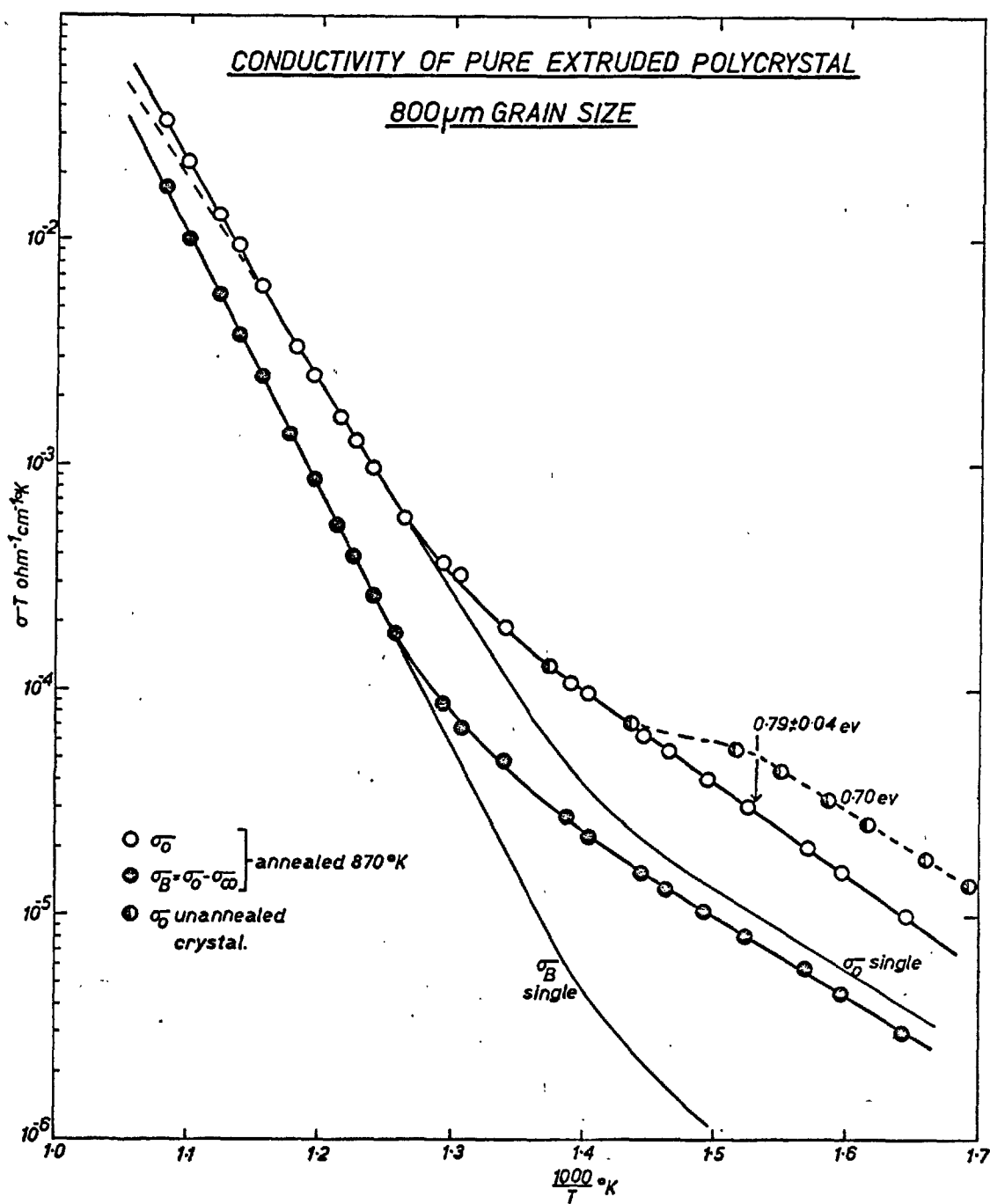


Fig.4.12.

The unannealed polycrystal also exhibited a considerably greater enhanced conduction at low temperatures, ^{and} at about 650°K the conduction of the unannealed crystal rapidly approaches the curve of the annealed crystal. The activation energy of the low temperature region of the unannealed crystal is $0.70 \pm 0.04\text{eV}$, which is the same as the activation energy of region II in single crystals. This transition from the unannealed to the annealed state was also apparent in hot-pressed polycrystals. The transition usually took the form of the curve shown in fig.4.13 where the unannealed conductivity curve gradually joined the annealed conductivity curve. In fig.4.14. the transition was rapid, as in the extruded polycrystal. The common features of the conductivity of unannealed polycrystals are that the conduction is greater at low temperatures than the annealed crystals and the activation energy of this enhanced region is about 0.70eV.

The enhanced conduction in region II of the pure polycrystals can be attributed to an increase in the number of charge carriers contributing to the conduction process, or to an increase in the mobility of the charge carriers, (present in the single crystal) in the grain boundary regions. The increased activation energy in region II would suggest that either the cation vacancies are no longer the predominant charge carriers or that the enthalpy of motion of the cation vacancies is increased in grain boundary regions.

McQuhac (6) found that the enthalpy of motion of sodium ions was significantly reduced in the boundary region, from about 0.70eV in the bulk to 0.35eV in the grain boundary. Cabané (3) also noticed a diffusion process in polycrystals

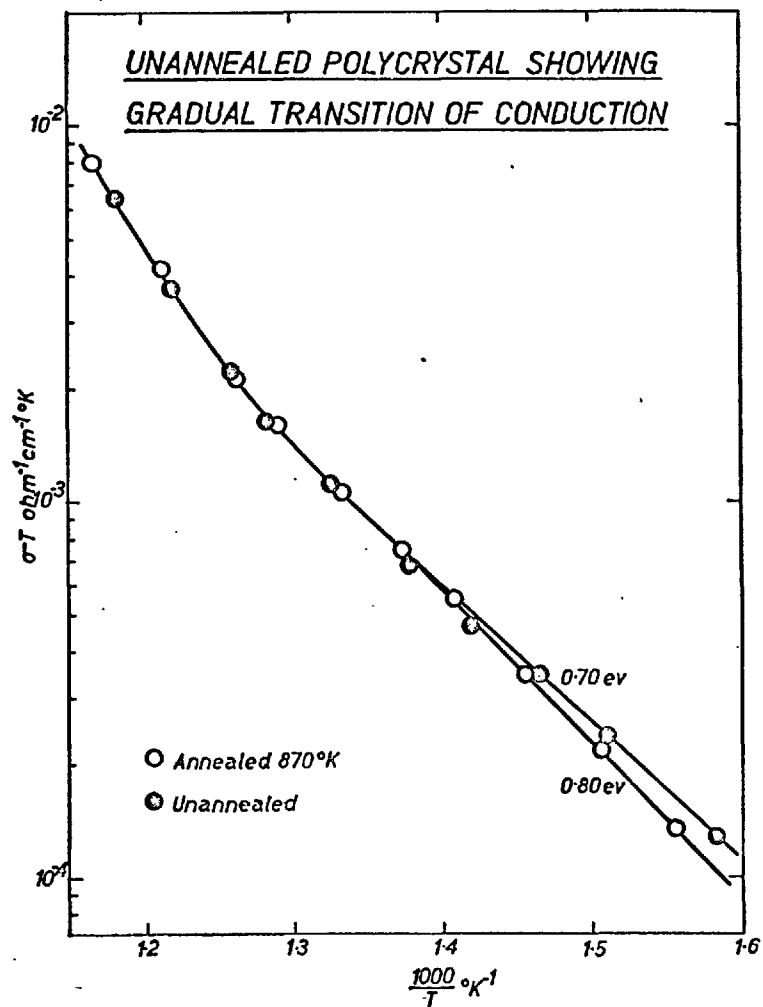


Fig.4.13.

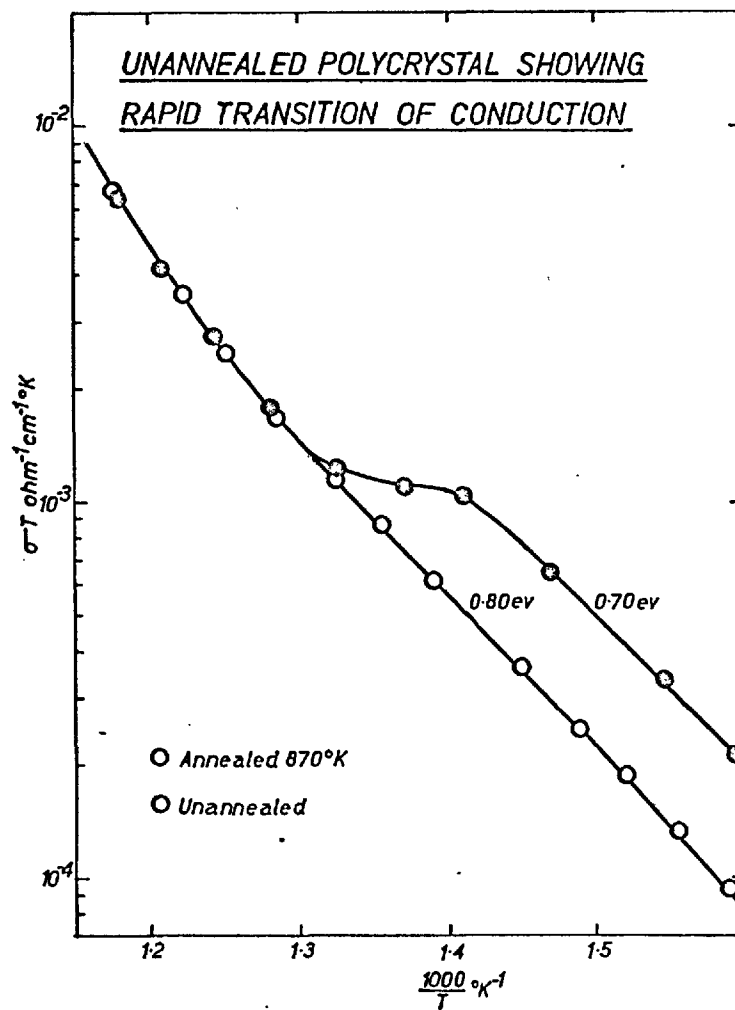


Fig.4.14.

at low temperatures which had a small activation energy. At higher temperatures both Laurent and Benard ^(1,2) and Cabané ⁽³⁾ noticed no change in the bulk diffusion of sodium ions in polycrystalline alkali halides. Thus it would seem unlikely

that the increased activation energy could be attributed to an increase in the sodium vacancy enthalpy of motion.

Graham et al. ⁽⁵⁾ have seen a similar enhancement of conduction in pressed sodium chloride which they attributed to the increased mobility of anion vacancies in grain boundaries. They also noticed that the enhancement was inversely proportional to grain size. In the pure crystals no grain size dependence was observed in the present work and only a very small dependence was noted in the less pure polycrystals. Cabané found that the enhanced chlorine vacancy diffusion was only present in undried polycrystals which were opaque. Graham et al. did not predry their powder before pressing.

If the explanation of the results presented in this work were in terms of enhanced diffusion of anion vacancies in the grain boundaries, it would be expected that two features in the conductivity plots would be apparent. Firstly it would be expected that the enhanced conduction is dependent on grain boundary volume, or grain size, as observed by Graham et al. and Laurent and Benard. Obviously the larger the grain boundary volume the greater the number of anion vacancies present in the grain boundary regions and hence increased conduction. However, it is apparent that the conduction is independent of grain size. Secondly if the motion of anion vacancies were increased then it would be expected that some enhancement of conduction would be apparent at high temperatures, in the intrinsic region.

This is apparently not present in any of the polycrystals. The close resemblance of the intrinsic conduction of both single and polycrystals is best observed in the extruded polycrystal. The polycrystalline and single crystal diffusion data of Laurent and Benard for anion diffusion has been compared with the high temperature conduction of pure polycrystals using the Nernst-Einstein equation. Fig. 4. 15. shows this comparison, and it is interesting to note that the high temperature conduction of the polycrystals is coincident with the single crystal data not with the polycrystal data of Laurent and Benard. This supports the suggestion that the anion vacancy diffusion is not enhanced in grain-boundary regions. This conclusion is supported by Cabané's work, since the polycrystals used for the present work are similar to those used by Cabané.

Since the enhanced motion of intrinsic charge carriers has been excluded from the explanation of the conductivity curves, the possible extrinsic carriers must be considered. The results from the manganese doped polycrystals suggest that the association region of the single crystal curve is continued to high temperatures in the polycrystals; up to 900°K in the 10ppm manganese doped $15\mu\text{m}$ grain size crystal and upto 690°K in the $40\mu\text{m}$ pure 'B' crystal. For this to occur the number of cation vacancies must increase, and this increase could arise from the presence of vacancies in the grain boundaries. The microstructural studies suggested that grain boundary segregation of impurities had occurred, and thus it would be expected that there will be a relatively high concentration of impurities close to the boundaries. It is also possible that the presence of relatively large numbers of divalent

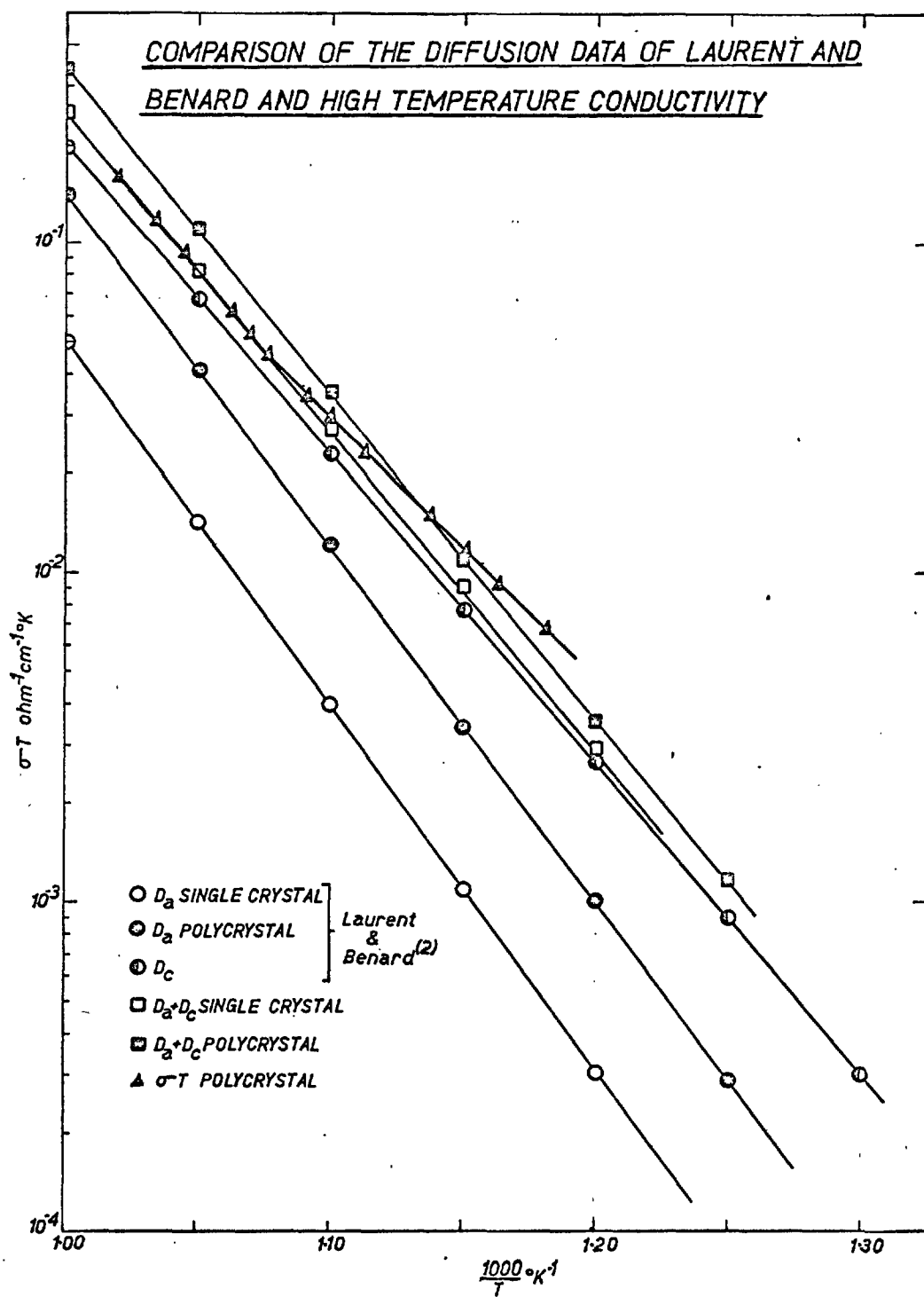


Fig. 4.15.

impurities and the vacancies present within the grain-boundary structure enable divalent cation-vacancy complexes to remain stable at much higher temperatures than they would in a single crystal.

The above discussion of the conduction in doped polycrystals is not applicable to the conduction in pure polycrystals since the activation energy of region II is too small. It is possible that the enhancement is the result of the diffusion of some other impurity. Allen and Fredericks⁽¹⁶²⁾ have found that the enthalpy of motion of hydroxyl ions is 0.79eV in the bulk of potassium chloride and that this ion is extremely mobile. Thus it would appear that a possible explanation could be the diffusion of hydroxyl ions in the grain boundaries. The high mobility of the hydroxyl ions can explain why no grain size dependence of enhanced conduction is observed. Only a relatively small number of carriers will be required to produce the enhanced conduction and these will be able to move equally rapidly in a small volume of grain boundary as in a larger volume. The magnitude of the enhanced conduction will then only depend on the concentration of the hydroxyl ions.

The origin of these hydroxyl ions is not clear since there are several mechanisms by which they can get into the crystal. Previous discussions have shown that the single crystals contain a small grown-in hydroxyl ion content. It is also felt that some adsorbed water must have been introduced during the hot-pressing, although it must be remembered that the extruded polycrystal exhibits a similar behaviour. It would also be possible for the crystals to pick up water vapour during the conductivity test, although

* It is felt that the wet-machining of the crystal prior to extrusion would not introduce significant amounts of hydroxyl ions into the bulk of the crystal.

the tests were done in high purity argon, and also a crystal annealed in wet nitrogen gas at 870°K for 6 hours showed no further enhancement of conduction.

The hydroxyl ions that originated from those present in the single crystal are probably complexed with divalent cation impurities and their associated vacancies. It is possible that the complex is "dragged" along to the boundary during the segregation process so that the vacancy associated with the complex can be annihilated. It may be possible that the conduction in the doped polycrystals is due to the motion of divalent cation-hydroxyl ion complexes.

The effects of segregation on the diffusion processes have been previously observed by Wuensch and Vasilos⁽¹⁰⁴⁾ in

magnesium oxide polycrystals. Geschwind and Machlin⁽¹⁰⁵⁾ have observed an enhancement of conduction in potassium chloride bicrystals which they attributed to water, present in the graphite dispersion used as electrode material, being drawn into the grain boundaries as either hydrogen or hydroxyl ions by the applied electric field.

The form of the conductivity curves of the unannealed polycrystals at low temperatures is not understood. It is tentatively suggested that at low temperatures the pressed and extruded polycrystals contain a very high dislocation density and that the easy diffusion of sodium ions along the dislocation could account for the enhanced conduction and the reduced activation energy. Davidge and Pratt⁽¹⁶¹⁾ showed that at about 670°K the dislocation structure of a deformed single crystal consisted of fairly well defined sub-grain boundaries. The work on the conductivity of deformed single

crystals showed that the sub-grain boundaries did not alter the conduction in the extrinsic region. Thus the annealing characteristics of the conductivity curves of the polycrystals could be due to the annealing of the dislocation structure into sub-grain boundaries which are not easy paths of conduction to sodium ions. It is also possible that the form of the unannealed conductivity curves could be connected with segregation process.

The results presented in this discussion would appear to indicate that grain boundary conduction is markedly affected by the presence of impurities. The ease with which these impurities can move in the grain boundaries suggests that they contain a high vacancy density and thus a coincident site or amorphous grain boundary structure would seem applicable rather than a dislocation model such as suggested for low angle boundaries.

4.2. High Temperature Polarisation in Polycrystalline

Sodium Chloride.

The results of the d.c. conductivity tests are shown in figs.4.7, 9, 11 and 12. The blocked conductivity, $\sigma_B = \sigma_o - \sigma_{\infty}$, curves are similar in form to the a.c. conductivity curves, as observed in single crystals. The slope of region II is, however, apparently increased to about 1.02eV.

Fig.4.16. shows the percentage of blocked d.c. conductivity ($\sigma_B/\sigma_o \times 100\%$) plotted against $\log \sigma_o T$ at $1/T = 1.5 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$. The percentage of blocked conduction in single crystals is proportional to $\log \sigma_o T$, and the blocked conduction in the polycrystals

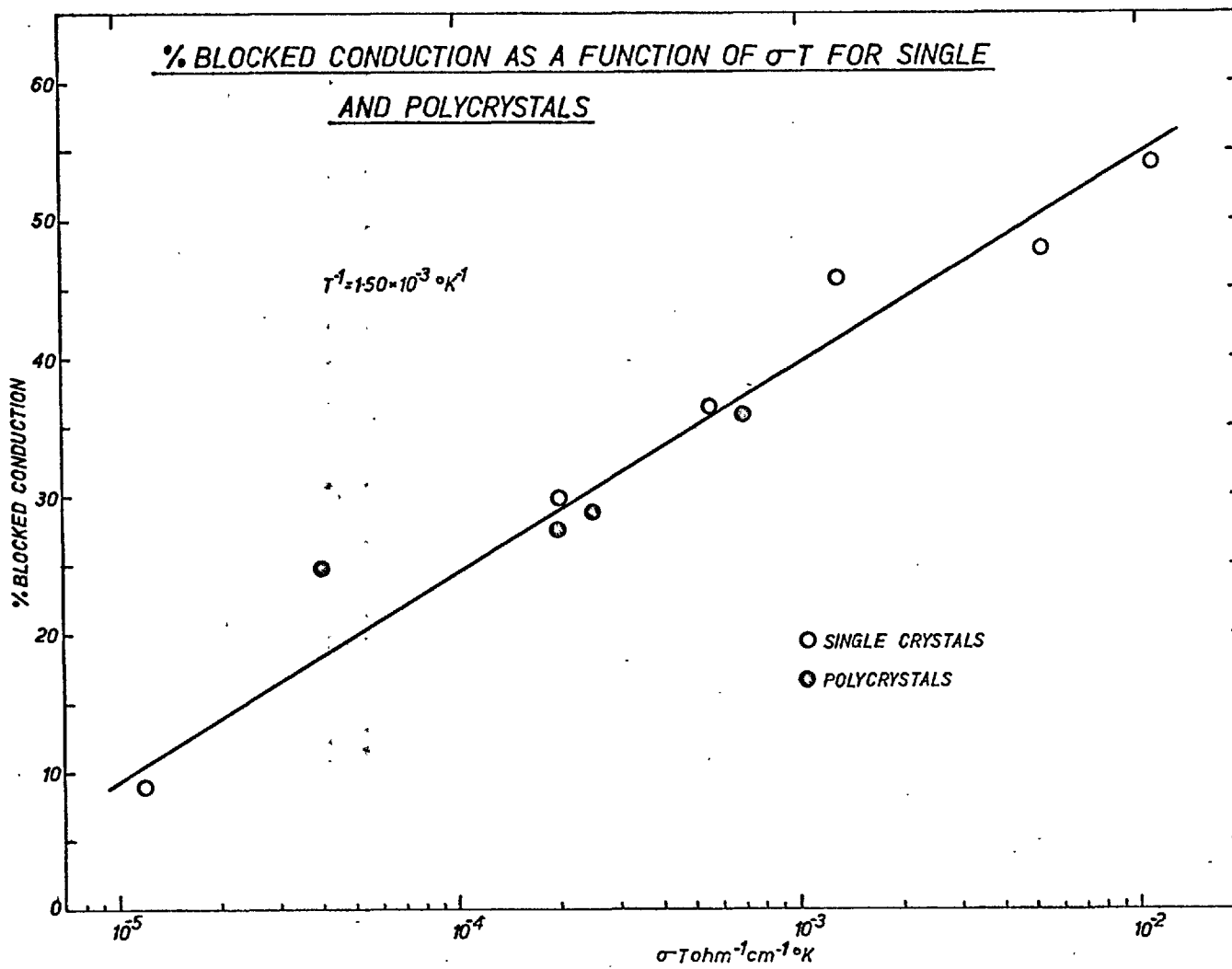


Fig.4.16.

is almost the same as in single crystals. This suggests that the grain boundaries are not contributing to the blocking and that all the blocking is occurring at the electrodes.

The grain boundaries may give rise to interfacial polarisation since they could behave like surfaces, particularly as the conductivity results could explain that the boundaries contain a high vacancy density. The d.c. conductivity is not an ideal method of discriminating between interfacial polarisation processes. The blocking of the carriers moving in the grain boundaries will mask any small blocking effects of the boundaries. The measurement of the dispersion of capacitance, resistance and loss factor as a function of frequency should discriminate between the blocking processes present in single and polycrystals. MacFarlane and Weaver (128) noticed a loss peak possibly corresponding to polarisation at boundaries with a different time constant to the electrode polarisation peak.

The results of the a.c. measurements are summarised in fig.4.17. where the relaxation time, τ , at $\tan \delta_{\max}$ is on a log. scale against $1/T$. The results of the polycrystals correspond closely with the results of the single crystals. No further loss peaks were found, with different time constants, that could be attributed to interfacial polarisation at grain boundaries.

The fact that the grain boundaries do not appear to block the charge carriers suggests that there is considerable continuity between two adjacent grains. This would suggest that the 'island' or coincident site models of grain boundary

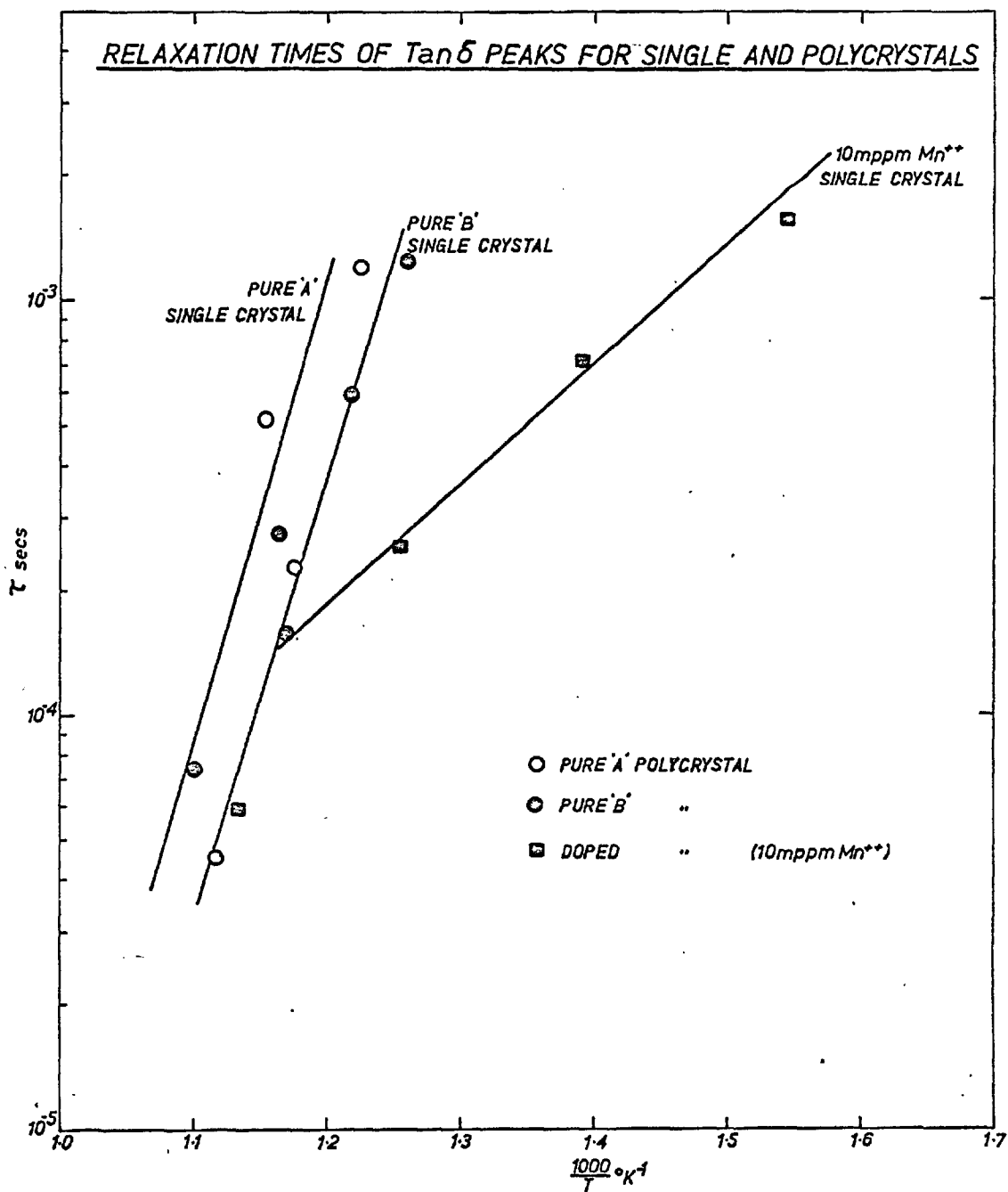


Fig.4.17.

structure would seem applicable. Both models would also account for the high vacancy density required for the conduction processes.

4.3. Microhardness of Grain Boundaries in Sodium Chloride.

4.3.1. Introduction.

The conductivity results on polycrystalline sodium chloride suggest that the effects of impurities in grain boundary regions are considerable. The use of an alternative technique would provide useful corroborative evidence and for this reason the microhardness technique has been developed for studying segregation of impurities at grain boundaries. It is also felt that this technique applied to the testing of bicrystals containing grain boundaries of different tilt angles could also provide useful information concerning the structure of the grain boundaries.

Preliminary tests have been carried out on nominally pure bicrystals containing 15° and 40° tilt boundaries. The results from microhardness traverses at room temperature will be cited in the following section.

4.3.2. Microhardness of 'Pure' Sodium Chloride Bicrystals.

The bicrystals were grown from 'pure' sodium chloride containing about 50ppm of divalent cations. The crystals

were annealed at 620°K for two hours and then air quenched. The crystals were cleaved in the indenter chamber, in a pure argon atmosphere.

The results shown in fig.4-18. indicate that the 15° bicrystal shows no hardening in the grain boundary region, whereas the 40° bicrystal exhibits considerable hardening for about 80 μ m either side of the boundary. These results are by no means conclusive and no attempt will be made to explain them, except to say that it is possible that the hardening effect is due to grain boundary segregation of impurities.

Further preliminary tests will be needed to make sure that the hardening effect is not due to other factors, such as the interactions of the grain boundary on the movement of the dislocations introduced by the indentation. It is possible to say that the technique is apparently effective in determining small changes of hardness over small areas.

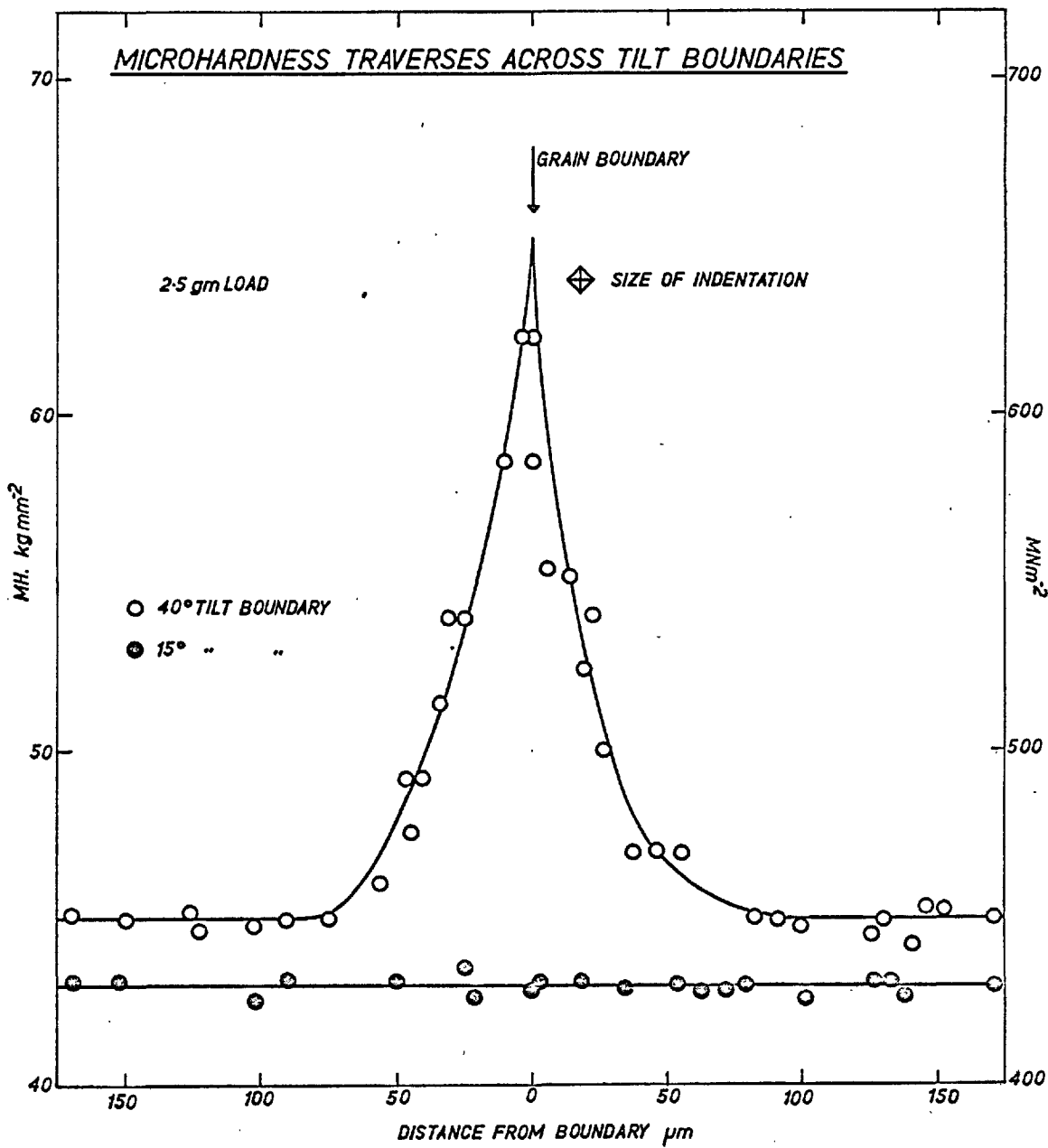


Fig. 4.18.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS
FOR FUTURE WORK.

5.1. CONCLUSIONS

5.1.1. Single Crystals.

The enthalpy of motion of cation vacancies was found to be $0.69 \pm 0.02 \text{ eV}$ and the enthalpy of formation of Schottky defects was found to be $2.36 \pm 0.02 \text{ eV}$. An estimate of the entropy of formation of Schottky defects was made; $S_g = 5.40 (\pm 0.10) \times 10^{-4} \text{ eV}^\circ \text{K}^{-1}$. The intrinsic conductivity was found to fit the equation:

$$\sigma T = 4.7 \times 10^8 \exp (-1.87 \pm 0.02 / kT) \text{ ohm}^{-1} \text{ cm}^{-1} \text{ }^\circ \text{K}.$$

The values obtained for the above parameters were compared and discussed with reference to previous work. It was concluded that the values were in generally good agreement with other work.

The enhanced conduction in region I' was discussed and was found to be sensitive to mechanical deformation, in agreement with previous work. The work suggest that the enhanced conduction could be the results of diffusion of anions or impurities in dislocation cores or sub-grain boundaries. No enhancement of conduction was observed in annealed deformed specimens at lower temperatures. This indicated that sub-grain, or low angle boundaries do not significantly alter the bulk diffusion processes. The enhanced cation diffusion in dislocations observed by other workers was not detected, probably because it was masked by the bulk conduction.

The conductivity of doped single crystals containing less than 300ppm manganese was measured. The extrinsic isotherms were found not to be linear at low manganese concentrations. This was thought to be due to the presence of hydroxyl or other impurity anions forming stable complexes with the manganese ions. The effective, or free, divalent cation impurity concentration was estimated from the 'knee' temperature and a value of the entropy of motion of cation vacancies of $1.8 \times 10^{-4} \text{ eV}^\circ\text{K}^{-1}$ was taken from previous work. This approach did not appear to produce a very reliable estimate of C_E , probably due to the uncertainty of the true value of the entropy term.

The d.c. conductivity results show that a temperature dependent polarisation phenomenon is present at high temperatures in pure crystals which results in a decrease in the slope of region I. The polarisation phenomenon is also present in the extrinsic region of the doped crystals giving rise to erratic values of the slope of region II. This explains the discrepancies in the literature between values of h_g and ΔS_c obtained by a.c. and d.c. techniques.

The d.c. conductivity results together with voltage - current plots indicating that Ohm's law is not obeyed, lead to the conclusions that the polarisation is the result of partial electrode blocking of both anion and cation vacancies. The frequency dependence of capacitance, resistance and loss factor tend to corroborate this. The interfacial blocking theories of Friauf and MacDonald failed to fit all the data, although the results did show the same ω^{-2} dependence of the parallel capacitance C_p . Raleigh has suggested that the failure of theories is due to the parallel representation

of the resistance and capacitance of the electrode-crystal interface. Raleigh suggested that the polarisation might better be represented in terms of a series network, in which case no frequency dispersions of capacitance or resistance would be expected. The results would seem to fit this model but it is felt that electrode-electrolyte systems which can be stabilised thermodynamically would have to be used to test the theory.

The results have fairly well established that the nature of the electrode-crystal interface is extremely important and can result in variations of the blocking behaviour. The time constants of the temperature shift of the loss peak indicate that the polarisation phenomena observed are not due to the rotation of impurity-vacancy dipoles or vacancy-pairs.

5.1.2. Polycrystals.

The conduction in pure and doped polycrystals prepared by hot-pressing or extrusion is thought to be influenced strongly by the motion of anion or cation impurities segregated at the grain boundaries. The extrinsic conduction of pure polycrystals is possibly due to the rapid diffusion of a small concentration of hydroxyl ions, their enthalpy of motion being about 0.80eV. This value is in good agreement with that found by Allen and Fredericks for bulk diffusion of hydroxyl ions in potassium chloride.

The high temperature extrinsic region in doped polycrystals is

thought to be due to the motion of divalent cation-hydroxyl ion complexes. The form of the conductivity plots also suggests that the association region is extended up to the intrinsic region. Thus it would appear that the complexes are very much more stable in grain boundary regions than in the bulk.

The absence of enhanced conduction at high temperatures and the lack of grain size dependence of the enhanced conduction at lower temperatures suggest that anion vacancy motion is not enhanced in grain boundaries. This is in agreement with the work of Cabane on well dried and carefully prepared polycrystals. The results of Laurent and Benard and Graham et al, who did not use carefully prepared and dried polycrystals, show that enhanced anion diffusion is present in 'dirty' grain boundaries.

The interfacial polarisation studies on polycrystals indicate that the blocking mechanisms are essentially the same as in single crystals. No dielectric loss peak was found within the frequency range used that would indicate blocking at grain boundaries.

The conductivity results indicate that the grain boundaries must contain a high vacancy density for the conduction to be enhanced to such an extent. This suggests that an amorphous grain boundary model would be applicable, but such a boundary may cause blocking of the charge carriers. Since no blocking by the grain boundaries was observed, the coincident site models where considerable lattice continuity, and a high vacancy concentration is present, might seem more applicable.

Preliminary microhardness traverses across tilt boundaries in pure sodium chloride bicrystals indicate that there is a hardened region at the boundary extending for $75\text{ }\mu\text{m}$ in a 40° tilt boundary. A traverse on a similar 15° tilt boundary showed no hardening. These results can possibly be explained in terms of grain boundary segregation in high-angle boundaries and not low-angle boundaries.

5.2. SUGGESTIONS FOR FUTURE WORK.

Considerable work has been done on both pure and doped sodium chloride but most of the work has not considered in detail the effects of anion as well as cation impurities. The study of the diffusion of hydroxyl and other anions such as oxygen ions in sodium chloride would be of considerable value. The association of these impurities with cation impurities would also be of interest.

A closer study of the diffusion processes occurring in region II' may lead to a greater understanding of diffusion in dislocations and dislocation structures such as sub-grain boundaries. Possibly further work using the conductivity probe technique would be of value.

The conductivity measurements on polycrystalline sodium chloride have indicated that impurity segregation is important in alkali halides. The study of this phenomenon using other techniques, in particular the microhardness technique, will provide much useful information, particularly if measurements can be made over the same range of temperatures

used in the conductivity tests. The extension of the conductivity results to lower temperatures to compare the aggregation and precipitation of impurities in single and polycrystals would also be of interest. Similarly the conductivity of polycrystals containing other impurities which might not be expected to segregate to the boundaries, calcium for example, needs to be measured. The measurement of diffusion, using tracer techniques, on polycrystals combined with the measurement of conductivity would provide the most useful information.

There is still much work to be done on interfacial polarisation. The effects of electrode contact, material and thermodynamic state must be investigated before the processes involved are clearly understood. The series representation of Raleigh may provide the best starting place for such work.

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REFERENCES.

1. J.F.Laurent and J.Benard. Comptes. Rendus de L'Academie des Sciences (Paris). 241, 1204, (1955).
2. J.F.Laurent and J.Benard. J.Phys.Chem.Sol. 7, 218, (1958).
3. J.Cabané. J.Chim.Phys. 59, 1135, (1962).
4. R.L.Moment and R.B.Gordon. J.Appl.Phys. 35, 2489, (1964).
5. H.C.Graham, N.M.Tallan and R.Russell. J.Am.Ceram.Soc. 50, 156, (1967).
6. K.G.McQuhae. Ph.D. Thesis. (London) (1969).
7. W.George. Colloquium on Surface Conductivity (unpublished) University of Leeds, (1969).
8. O.T.Ozkan. Colloquium on Surface Conductivity (unpublished) University of Leeds, (1969).
9. K.T.Aust, R.E.Hanneman, P.Neissen and J.H.Westbrook. G.E.Report No.67-C-297 (1967).
10. K.T.Aust, A.J.Peat and J.H.Westbrook. Acta.Met. 14, 1469, (1966).
11. J.H.Westbrook. Sci. of Ceramics. 3, 263, (1967).
12. Van Bueren. 'Imperfections in Crystals'. North Holland (1961).
13. P.Supitz and J.Teltow. Phys.Stat.Sol. 23, 9, (1967).
14. L.W.Barr and A.B.Lidiard. 'Physical Chemistry. An Advanced Treatise'. 10, (1970).
15. A.B.Lidiard. Handbuch Der Physik. 20(2), (1957).
16. R.W.Whitworth. Phil.Mag. 10, 801, (1964).
17. R.W.Whitworth. Phil.Mag. 11, 83, (1965).
18. R.W.Whitworth. Phil.Mag. 15, 305, (1967).
19. R.W.Whitworth. Phil.Mag. 17, 1207, (1968).
20. R.M.Turner and R.W.Whitworth. Phil.Mag. 18, 531, (1968).
21. J.E.Caffyn and T.L.Goodfellow. J.Appl.Phys. 33, 2567, (1962).

22. J.E.Caffyn and T.L.Goodfellow. Proc.Phys.Soc.
79, 1285 (1962).
23. J.E.Caffyn, J.C.DeFreitas and T.L.Goodfellow.
Phys.Stat.Sol. 9, 333 (1965).
24. J.E.Caffyn, T.L.Goodfellow and A.J.Hamdi.
Proc.Brit.Ceram.Soc. 9, 147 (1967).
25. R.W.Davidge. Phil.Mag. 8, 1369 (1963).
26. J.D.Eshelby, C.W.A.Newey. P.L.Pratt and A.B.Lidiard.
Phil.Mag. 3, 75 (1958).
27. T.M.McGee. Mats.Sci.Res. 2, (1965).
28. S.Amelinckx and W.Dekeyser. "The structure and Properties
of Grain Boundaries", in Solid State Physics, Advances
in Research and Application. 8, (1959) Academic Press.
29. W.T.Read. 'Dislocations in Crystals'. (1953) McGraw Hill
30. D.G.Brandon. Acta Met. 14, 1479 (1966).
31. M.L.Kronberg and F.H.Wilson. Trans.Am.Inst.Min.Metall.
Engrs. 185, 501 (1949).
32. W.T.Read and W.Shockley. Phys.Rev. 78, 275 (1950).
33. D.G.Brandon, B.Ralph, S.Ranganathan and H.S.Wald.
Acta.Met. 12, 813 (1964).
34. N.Fuschillo, M.L.Gimpl and A.D.McMaster. J.Appl.Phys.
37, 2044 (1966).
35. M.L.Gimpl, A.D.McMaster and N.Fuschillo. Mats.Sci.Res.
3, 259 (1966).
36. D.M.Martin, G.K.Fehr and T.D.McGee. Mats.Sci.Res.
3, 243 (1966).
37. M.L.Gimpl, A.D.McMaster and N.Fuschillo. J.Am.Cer.Soc.
51, 655 (1968).
38. N.F.Mott. Proc.Phys.Soc. (London) 60, 391 (1948).
39. R.L.Moment and R.B.Gordon. J.Appl.Phys. 35, 2489 (1964).
40. J.H.Westbrook. Met.Rev. 9, (36) 415 (1964).
41. J.H.Westbrook and D.L.Wood. Nature (London) 192,
1281 (1961).

42. J.H. Westbrook and D.L. Wood. J.Inst.Metals. 91, 174, (1963).
43. J.H. Westbrook and K.T. Aust. Acta.Met. 11, 1151, (1963).
44. K.T. Aust and J.H. Westbrook. 'Lattice Defects in Quenched Metals'. Academic Press. (1965).
45. P.J. Jorgensen and J.H. Westbrook. J.Am.Ceram.Soc. 47, 332, (1964).
46. J.H. Westbrook and P.J. Jorgensen. Trans.A.I.M.E. 233, 425, (1965).
47. H.G. Müller. Z.Physik. 96, 279, (1935).
48. D.L. Kirk. Ph.D. Thesis (London). (1968).
49. N.F. Mott and M.J. Littleton. Trans.Farad.Soc. 34, 485, (1936).
50. D. Mapother, H.N. Crooks and R. Maurer. J.Chem.Phys. 18, 1231, (1950).
51. H.W. Etzel and R.J. Maurer. J.Chem.Phys. 18, 1003, (1950).
52. F.G. Fumi and M.P. Tosi. Disc.Farad.Soc. 23, 92, (1957).
53. A. Taylor. Thesis, Birmingham Univ. (1958).
54. N. Bierman. Z.Physik.Chem. 25, 253, (1960).
55. R.W. Dreyfus and A.S. Nowick. J.Appl.Phys.Suppl. 33, 473, (1962).
56. S.C. Jain and S.L. Dahake. Ind.J.Pure Appl.Phys. 2, 71, (1964).
57. D.L. Kirk and P.L. Pratt. Proc.Brit.Ceram.Soc. 1, 215, (1964).
58. N. Brown and I.M. Hoodless. J.Phys.Chem.Sol. 28, 2297, (1967).
59. A.R. Allnatt and P. Pantalis. Sol.State Commun. 6, 309, (1968).
60. F. Beniere, M. Beniere and M. Chemla. J.Phys.Chem.Sol. 31, 1205, (1970).
61. E. Laredo and E. Dartyge. J.Chem.Phys. 53(6), 2214, (1970).
62. C. Bean. Thesis. Illinois. (1952).
63. H.W. Schamp and E. Katz. Phys.Rev. 94, 828, (1954).
64. F. Reif. Phys.Rev. 100, 1597, (1955).
65. R. Guccione, M.P. Tosi and M. Asdente. J.Phys. Chem.Sol. 10, 162, (1959).

66. K.Kobayashi and T.Tomiki. J.Phys.Soc.Japan. 15, 1982 (1960).
67. B.G.Lure. A.N.Murin and R.F.Brigewich Sov.Phys.Sol. State. 4, 1432 (1963).
68. B.Redfern and P.L.Pratt. Proc.Brit.Ceram.Soc. 1, 215 (1964).
69. K.C.Koo, L.J.Giles and J.H.Calderwood. J.Appl.Phys. 39, 3955 (1968)
70. H.L.Downing and R.J.Friauf. J.Phys.Chem.Sol.31, 845 (1970).
71. V.C.Nelson and R.J.Friauf. J.Phys.Chem.Sol. 31, 825 (1970).
72. H.Chenla. Ann.Phys. 1, 959 (1956).
73. D.Patterson, G.S.Rose and J.A.Morrison. Phil.Mag. 1, 393 (1956).
74. L.G.Harrison, J.A.Morrison and R.Rudhan. Trans.Farad. Soc. 54, 106 (1958).
75. J.Ewles and S.C.Jain. Proc.Roy.Soc. A423, 353 (1958).
76. N.Laurence. Phys.Rev. 120, 57 (1960).
77. L.W.Barr, J.A.Morrison and K.A.Schroeder. J.Appl. Phys. 36, 624 (1965).
78. L.W.Barr, I.H.Hoodless, J.A.Morrison and R.Rudhan. Trans.Farad.Soc. 56, 697 (1960).
79. A.E.Abey and C.T.Tomikuka. J.Phys.Chem.Sol. 27, 1149 (1966).
80. N.A.Economu and P.V.Sastry.Phys.Stat.Sol. 6, 135 (1964).
81. J.H.Becunent and P.W.M.Jacobs. J.Chem.Phys. 45 (5) 1496 (1966).
82. A.B.Lidford. Phys.Chem.Sol. 6 298 (1958).
83. P.V.Sastry and T.M.Srinivasan. Phys.Rev. 132, 2445 (1963).
84. H.S.Sack and G.C.Smith. J.Phys.Soc.Japan. 18 III (1963).
85. A.B.Lidford and K.Tharmalingham. Disc.Farad.Soc. 28, 64 (1959).
86. J.Rolfe. Can.J.Phys. 42, 2195 (1964).
87. J.Chandre and J.Rolfe. Can.J.Phys. 48, 412 (1970).

88. R.G.Fuller and M.H.Reilly. Phys.Rev.Letts. 19,113 (1967).
89. J.Auger, B.Fritz and F.Luty. Z.Physik. 174, 240 (1963).
90. T.G.Stoebe and P.L.Pratt. Proc.Brit.Ceram.Soc.
1, 181 (1964).
91. M.V.Pashkowski, N.A.Tsol' and A.D.Tkachuk.Sov.Phys.
Sol.State. 5, 853 (1963).
92. K.Lehovec. J.Chem.Phys. 21, 1123 (1953).
93. P.L.Pratt. "Defect in Crystalline Solids". Inst. of
Metals Monographs. (1957).
94. J.S.Kochler, D.Langreth and B. von Turkovich. Phys.
Rev. 128, 573 (1962).
95. L.M.Brown. Phys.Stat.Sol. 6, 585 (1961).
96. R.Tucker, A.Laskar and R.Thomson. J.Appl.Phys.
34, 445 (1963).
97. Ya.E.Geguzin and E.R.Dobrovinskaya. Sov.Phys.Sol.
State. 7, 2826 (1966).
98. E.W.Hart. Acta.Met. 5, 597 (1957).
99. R.Smoluchowski. Phys.Rev. 87, 482 (1952).
100. H.Kanzaki, K.Kido and S.Ohzura. J.Phys.Soc.Japan.
18, (III) 115 (1963).
101. R.T.Whipple. Phil.Mag. 45, 1225 (1954).
102. J.C.Fisher. J.Appl.Phys. 22, 74 (1951).
103. A.D.Le Claire. Brit.J.Appl.Phys. 14, 351 (1963).
104. B.J.Wuensch and T.Vasilos. Office of Naval Research.
Report No. NONR 4267 (00).
105. G.Geschwind and E.Machlin. J.Appl.Phys. 38, 900 (1967).
106. I.I.Frenkel. "Kinetic Theory of Liquids". Claredon
Press, Oxford (1946).
107. R.J.Schwensfeir and C.Elbaum. J.Phys.Chem.Sol.
26, 781 (1965).

108. I.M.Lifshits and Ya.E.Geguzin. Sov.Phys.Sol.State. 7, 44 (1965).
109. I.M.Lifshits, A.M.Kosevich and Ya.E.Geguzin. J.Phys. Chem.Sol. 28, 783 (1967).
110. K.L.Kliwer. Report No.1654. Institute for Atomic research and Department of Physics, Iowa State University, Ames. Iowa.
111. E.Nadgorni and A.Stepanov. Sov.Phys.Sol.State. 5, 726 (1963).
112. J.Volger. Progress in Semiconductors. 4, 206 (1960).
113. N.M.Tallon, H.C.Graham, and J.M.Winner. Mat.Sci.Res. 3, 111 (1966).
114. D.O.Rayleigh. J.Phys.Chem.Solids. 29, 261 (1968).
115. H.Chang and G.Jeffe. J.Chem.Phys. 20, 1071 (1952).
116. J.R.MacDonald. Phys.Rev. 92, 4 (1953).
117. R.J.Friauf. J.Chem.Phys. 22, 1329 (1954).
118. P.W.M.Jacobs and J.N.Maycock. J.Chem.Phys.39, 757 (1963).
119. A.R.Allnatt and P.W.M.Jacobs. J.Phys.Chem.Solids. 19, 281 (1961).
120. J.H.Beaumont and P.W.M.Jacobs. J.Phys.Chem.Solids. 28, 657 (1967).
121. H.J.Wintle and J.Rolfe. Can.J.Phys. 44, 965 (1966).
122. A.Kessler and E.Mariani. Czech. J.Phys. 14, 757 (1964).
123. A.Kessler and E.Mariani. Czech. J.Phys. 15, 407 (1965).
124. A.Kessler and E.Mariani. Phys.Stat.Sol. 8, K149 (1965).
125. A.Kessler and E.Mariani. J.Phys.Chem.Solids. 29, 1079 (1968).
126. J.M.Winner and N.M.Tallon. J.Appl.Phys. 37, 3728 (1966).
127. M.Kaderka. Czech. J.Phys. 13, 378 (1963).
128. J.C.MacFarlane and C.Weaver. Phil.Mag. 13, 671 (1966).
129. N.S.Parker. Thesis (Durham) (1954).

130. P.H.Sutter and A.S.Nowick. J.Appl.Phys. 34, 734 (1963).
131. J.S.Dryden. J.Phys.Soc.Japan. 18, III 129 (1963).
132. J.Quin. Thesis (London) (1967).
133. C.A.Bucci and S.C.Riva. J.Chem.Phys.Solids.26, 363 (1965).
134. K.C.Kao, W.Whitham and J.H.Calderwood. J.Phys.Chem. Solids. 31, 1019 (1970).
135. J.N.Maycock. Research Report R.I.A.S. October (1964).
136. G.Jaffe. Ann.Phys. 16, 217 (1933).
137. G.Jaffe and J.A.Rider. J.Chem.Phys. 20, 1077 (1953).
138. G.Jaffe and C.LeMay. J.Chem.Phys. 21, 920 (1953).
139. J.S.Cook and J.S.Dryden. Aust.J.Phys. 13, 260 (1962).
140. Y.Haven. Report of the Conference on Defects in Crystalline Solids, Phys.Soc.London (1955).
141. J.S.Cook and J.S.Dryden. Proc.Phys.Soc. 80, 479 (1962).
142. C.T.Butler, J.R.Russe, R.B.Quincy Jr, and D.E.Lavalle, J.Chem.Phys. 45, 968 (1966).
143. D.A.Otterson. J.Chem.Phys. 34, 1849 (1961).
144. L.W.Barr, E.P.Koffyberg and J.A.Morrison. J.Appl.Phys. 33, 225 (1962).
145. S.K.Argarwal and A.P.Kulshreshta. Ind.J.Pure Appl. Phys. 5, 535 (1967).
146. H.W.Elzel and D.A.Patterson. Phys.Rev. 112, 1112 (1958).
147. R.J.Stokes and C.H.Li. Mats.Sci.Res. 1, 133 (1963).
148. J.White. Proc.Brit.Ceram.Soc. 3, 155 (1965).
149. A.A.Ammar and D.W.Budworth. Proc.Brit.Ceram.Soc. 3, 185 (1965).
150. W.D.Kingery and M.Berg. J.Appl.Phys. 26, 1205 (1955).
151. A.A.Ammar and D.W.Budworth. Trans.Brit.Ceram.Soc. 66, 93 (1967).

152. T.Vasilos and R.M.Spriggs. Proc.Brit.Ceram.Soc.
3, 195 (1965).
153. J.D.McClelland and E.H.Zehms. J.Am.Ceram.Soc.
46, 77 (1963).
154. R.L.Coble and J.S.Ellis. J.Am.Ceram.Soc. 46, 440 (1963).
155. W.G.Johnson and J.S.Nadeau.G.E.Rept. ARL. 64-135 (1964).
156. A.R.C.Westwood. Mats.Sci.Res. 1, 114 (1963).
157. R.E.Honnenman and J.H.Westbrook. G.E.Research Report
67-C-367 October (1967).
158. A.R.C.Westwood. Phil.Mag. 7, 633 (1962).
159. D.A.Otterson. J.Chem.Phys. 38, 1481 (1963).
160. S.J.Rothman, L.W.Barr, A.H.Rowe, P.G.Silwood. Phil.
Mag. 14, 501 (1966).
161. R.W.Davidge and F.L.Pratt. Phys.Stat.Sol. 6, 759 (1964).
162. C.A.Allen and W.J.Fredericks. J.Solid State Chem.
1, 205 (1970).
163. J.Rolfe. Phys.Rev.Letter. 1, 56 (1958).
164. B.Fritz, F.Luty and J.Anger. Z.Phys. 174, 240 (1963).
165. N.S.Parker. Thesis, University of Durham (1954).
166. N.S.Parker and E.E.Schneider, Nature. 178, 326 (1956).
167. A.R.Allnatt, P.W.M.Jacobs, J.N.Maycock. J.Chem.Phys.
43, 2526 (1965).
168. D.C.Grahane. J.Am.Ceram.Soc. 68, 301 (1946).
169. R.Sano and T.Toniki. J.Phys.Soc.Japan.21, 1697 (1966) .
170. G.D.Watkins. Phys.Rev. 113, 79 (1959).
and Phys.Rev. 113, 91 (1959).
171. P.J.Jorgensen. Proc.Brit.Ceram.Soc. (1969). To be
published.