1969

Grain boundary self-diffusion in sodium chloride

Kenneth Ray Riggs

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GRAIN BOUNDARY SELF-DIFFUSION
IN SODIUM CHLORIDE
by
KENNETH RAY RIGGS, 1940-

A DISSERTATION
Presented to the Faculty of the Graduate School of the
UNIVERSITY OF MISSOURI - ROLLA
In Partial Fulfillment of the Requirements for the Degree
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING
1969
ABSTRACT

The diffusion of $^{22}\text{Na}$ and $^{36}\text{Cl}$ along tilt and twist grain boundaries in pure and calcium chloride doped sodium chloride bicrystals was investigated. No enhanced diffusion of $^{22}\text{Na}$ along the grain boundaries was observed. Between 400°C and 500°C the chlorine grain boundary diffusion parameter, $D'\delta$, is described by

$$D'\delta = (D'\delta)_0 \exp\left(-\frac{Q_b}{kT}\right),$$

where $(D'\delta)_0$ is approximately $10^{-7}$ cm$^3$/sec and $Q_b$ is $1.15 \pm 0.30$ eV. The grain boundary angle, the grain boundary character (tilt or twist), and the calcium chloride concentration appear to have no pronounced effect upon the observed chlorine grain boundary diffusion. The ionic movement is believed to occur in the grain boundary core region by the movement of "interstitial" type chlorine ions.
ACKNOWLEDGMENTS

The author wishes to thank Dr. Manfred Wuttig for the privilege of working with him during the course of this investigation.

The author is also indebted to Dr. Harry Weart, Chairman of the Metallurgy Department, for financial assistance of various kinds.

Finally, the author wishes to thank his wife, Sharron, for her continued encouragement and optimism throughout the course of his graduate studies.

This work was supported by the Advanced Projects Research Agency of the Department of Defense.
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1. INTRODUCTION

Self-diffusion in NaCl single crystals at high temperatures (above $0.7T_m$) has been studied extensively and the ionic mobility in this temperature range has been found to be due primarily to Schottky defects. Movement of anions and cations occurs independently on the ionic sublattices by the motion of single isolated vacancies.

At low temperatures the number of thermally activated defects is small and in this temperature range the Coulombic interactions between cation and anion vacancies and dissolved impurities play a substantial role in the movement of sodium and chlorine ions.

In commercially available high purity NaCl the predominant impurities are divalent cations. When these divalent cations are dissolved in NaCl they locate substitutionally on the sodium lattice sites. In order to preserve charge neutrality a sodium vacancy is produced for each divalent cation present. Although a fraction of the sodium vacancies reacts with the divalent cations forming neutral divalent cation-sodium vacancy complexes, the remaining sodium vacancies introduced with the divalent cations are free to contribute to the sodium ion diffusion. The variation of sodium single crystal diffusivity with temperature thus shows two distinct ranges with the activation energy for diffusion being smaller at low temperatures than at high
temperatures due to the predominance of the extrinsic sodium vacancy concentration at low temperatures.

The presence of divalent cation impurities in NaCl also influences the bulk or single crystal diffusivity of the chlorine ions. When thermally activated sodium and chlorine vacancies form simultaneously at a common source, the vacancy concentrations are given by

\[ n_+ n_- = \exp \left( -\frac{g_S}{kT} \right) = n_0^2, \quad (1) \]

where \( n_+ \) and \( n_- \) are the sodium and chlorine vacancy concentrations, \( g_S \) is the free energy of formation of a Schottky defect, and \( k \) and \( T \) have their usual significance. Thus, as first observed by Lidiard, the increase in the sodium vacancy concentration at low temperature due to divalent cation impurities should cause a corresponding decrease in the chlorine vacancy concentration. The chlorine self-diffusivity due to single vacancies should therefore exhibit high and low temperature ranges with the transition occurring at the same temperature as that of the "knee" in the cation diffusivity plot.

Since cation and anion vacancies have opposite virtual charges, it is energetically favorable that they locate at nearest neighbor cation and anion lattice sites. When this occurs, a neutral defect, a vacancy pair, is formed.

Although vacancy pair migration can contribute to the movement of both sodium and chlorine ions, comparison of the
enthalpies of motion for sodium vacancies and vacancy pairs (see Table I) shows that a measurable vacancy pair contribution to sodium diffusion is unlikely, particularly below the temperature of the diffusivity "knee." The possibility that vacancy pairs contribute measurably to the anion diffusion in alkali halides has, on the other hand, been the impetus for several investigations. The results indicate that vacancy pairs make an appreciable contribution to the anion diffusion in pure alkali halides and that they become the dominant diffusion mechanism when the divalent cation concentration exceeds 100 ppm.\(^{(4)}\)

In contrast to the situation for bulk diffusion, information concerning dislocation and grain boundary diffusion in alkali halides is meager.

Early work on polycrystalline alkali halides\(^{(7)}\) indicated that the activation energy for the diffusion of anions along grain boundaries was essentially the same as the activation energy for anion single crystal diffusion. Subsequent work on polycrystalline KI\(^{(8)}\) showed that when the quality of the samples increased—primarily through the exclusion of water vapor during sintering and annealing—the enhanced anion grain boundary diffusion occurred only at low temperatures and with an activation energy which was approximately half that in single crystalline material. There is also evidence\(^{(9,10)}\) of enhanced anion diffusion along individual dislocations in NaCl at low temperatures.
TABLE I

ENTHALPIES AND ENTROPIES OF FORMATION AND MOTION

OF VARIOUS DEFECTS IN SODIUM CHLORIDE

<table>
<thead>
<tr>
<th>DEFECT</th>
<th>ENTHALPY OF FORMATION (eV)</th>
<th>ENTROPY OF FORMATION (eV/°C)</th>
<th>ENTHALPY OF MOTION (eV)</th>
<th>ENTROPY OF MOTION (eV/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation Vacancy</td>
<td>1.07(11)</td>
<td>6.1 k(11)</td>
<td>0.80(13)</td>
<td>3.1 k(13)</td>
</tr>
<tr>
<td>Anion Vacancy</td>
<td>1.05(11)</td>
<td>0.1 k(11)</td>
<td>1.11(10)</td>
<td></td>
</tr>
<tr>
<td>Schottky Defect</td>
<td>2.12(13)</td>
<td>6.2 k(13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacancy Pair</td>
<td>1.27(10)</td>
<td>Cation Jump 1.46(10)</td>
<td>Anion Jump 1.27(10)</td>
<td></td>
</tr>
<tr>
<td>Divalent Cation-Cation Vacancy Complex</td>
<td>0.6(13)</td>
<td>Cation Jump 0.7(13)</td>
<td></td>
<td></td>
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</tbody>
</table>
Of those studies \(^{(7,8,14,15)}\), in which cation grain boundary diffusion in alkali halides has been investigated, only one \(^{(16)}\) has reported evidence of enhanced cation diffusion in the grain boundaries. This result would therefore seem to warrant little consideration--except for the fact that the samples investigated were bicrystals of exceptionally high purity.

Interpretation of grain boundary diffusion measurements is complicated by the fact that knowledge of the detailed structure of large angle grain boundaries is still incomplete. It is generally accepted that small angle grain boundaries in metals consist of stable arrays of individual dislocations and that these dislocations serve as high diffusivity paths for atom movements.\(^{(17)}\) No detailed atomic mechanism for this rapid movement has been accepted, but it is argued in a general fashion that since the dislocation cores are high energy locations in the lattice, atoms will experience a decreased restraint to movement while in the dislocation cores. A second distinct contribution to the increased diffusivity can arise if the point defects responsible for bulk diffusion tend to segregate to the vicinity of the dislocations due to their interaction with the dislocation strain fields.

Although the interactions between dislocations in high angle grain boundaries should tend to destroy their directionality, there are a number of investigations \(^{(18,19)}\)
which indicate that large angle grain boundaries are not isotropic and that they retain some characteristics of a dislocation structure even at maximum misorientation angles.

Considerations of dislocation and grain boundary structure in NaCl are subject to an additional complication not present in metals. Dislocations, grain boundaries, and external surfaces in NaCl can have an associated electrical dipole layer. The long range electrical fields arising from these charges can conceivably have a pronounced effect upon dislocation and grain boundary diffusion if the movement of the ions occurs by means of electrically charged defects.

The charge of dislocations in ionic solids has been investigated experimentally by measuring the current and potential that develops during mechanical deformation of single crystals. Although there was initial disagreement of published results, the weight of experimental evidence now indicates that edge dislocations in NaCl are positively charged at high temperature and negatively charged at low temperature, thus confirming theoretical predictions. In contrast to edge dislocations, screw dislocations in NaCl exhibit no indication of being charged. Internal friction studies of NaCl containing varying amounts of CaCl₂, showed that the isoelectric temperature varied with the divalent cation impurity concentration in a fashion that conformed to theoretical predictions.
As can be seen by the above discussion, there is only limited agreement among various investigations as to the nature of the self-diffusivities along grain boundaries in NaCl. One particular area of uncertainty concerns the influence of small amounts of impurity on the diffusivities. Also, there has been no attempt, to date, to determine the relationship between the electrical charge and self-diffusivities of the grain boundaries. Thus, a systematic investigation of the grain boundary diffusivities in NaCl was initiated in which the major objectives were:

1. To determine the anion and cation self-diffusivities along tilt and twist grain boundaries in high purity NaCl; and,

2. To determine, if possible, the influence of electrically charged impurities on the grain boundary self-diffusivities.
II. THEORY

A. Grain Boundary Charge

Frenkel\(^{(20)}\) first observed that when the free energies of formation of the two halves of a Schottky defect are different and when the two vacancies can form independently at a common source, the source will develop an electrical charge and the adjacent crystal lattice will contain a net charge of equal magnitude but opposite sign. Frenkel's original treatment of the problem has been extended by several investigators\(^{(21,22,23)}\) for a variety of assumed conditions. The most general treatment of the problem has been given by Kliewer and Koehler\(^{(24)}\) and their results are used as the basis of the discussion which follows.

The electrical dipole layer in pure NaCl forms in the following manner. Suppose that, as in NaCl, the energy necessary to form cation vacancies is less than that required for anion vacancies. Then, at any temperature, there will be a tendency for an excess concentration of cation vacancies to exist throughout the crystal. As these excess vacancies form and migrate into the crystal an electrical dipole layer is formed consisting of excess sodium ions on the vacancy sources and excess sodium vacancies in the adjacent bulk.

The energy required to form cation vacancies in the interior of the crystal is thus increased by the energy necessary to move them across the dipole layer. The energy to form anion vacancies in the bulk is reduced in exactly
the same manner and it can thus be seen that at equilibrium the dipole layer serves to adjust the free energies of vacancy formation such that the bulk of the crystal remains electrically neutral.

When divalent cations are present in the crystal they can influence the magnitude and nature of the dipole layer. At high temperatures, where the number of thermally activated vacancies is large, the divalent cation concentration has no effect upon the formation of the dipole layer. At lower temperatures, however, the number of thermally activated vacancies decreases and the relative concentration of divalent cations becomes appreciable. If the bulk cation vacancy concentration, and thus the dipole potential, were to remain unaffected by the presence of the divalent cations, the crystal would develop a net positive charge. This is prevented by an increase in the overall cation vacancy concentration and a corresponding decrease in the dipole potential. Physically, the divalent cations reduce the magnitude of the dipole potential by forcing a portion of the space charge to dissolve in the bulk.

As the temperature of the crystal is lowered the magnitude of the space charge and the potential of the dipole layer thus decrease and finally go to zero. The temperature at which this occurs is called the isoelectric temperature because it is here that the difference between the innate
cation and anion vacancy concentrations is equal to the concentration of divalent cation impurities.

Below the isoelectric temperature the chlorine vacancy concentration is negligible and no longer influences the crystal behavior. In this temperature range the crystal, in attempting to reach equilibrium on a thermal basis alone, will precipitate a fraction of those excess sodium vacancies, present due to the divalent cation concentration, which are near the linear and planar defects of the crystal. The result of this behavior is a low temperature electrical dipole layer in the vicinity of the vacancy "sinks" which consists of excess sodium vacancies on the vacancy sinks and a space charge layer in the adjacent lattice consisting primarily of divalent cation impurities.

For the interpretation of experimental grain boundary diffusion studies in alkali halides, the most important aspects of the theoretical development by Kliewer and Koehler are the predictions concerning the number and density of defects in the region of the grain boundary. In particular, for interpreting the results of the present investigation, it is necessary to know how the above quantities vary with temperature and divalent cation concentration.

The grain boundary region, as treated by Kliewer and Koehler, consists of two distinct parts—the core region, and the surrounding space charge region in the lattice.
The core region of the grain boundaries in NaCl, as in the case of metals \( (2\bar{8}) \) is assumed to be quite narrow—of the order of 2 to 3 unit cell edge lengths—and its width is assumed to be independent of both temperature and divalent cation concentration. The magnitude of the charge on the grain boundary core is given by the equation used by Kliewer and Koehler for the surface charge and changes with temperature and divalent cation concentration in the manner described above.

An expression for the density of charge in the space charge region is also available from the theoretical development. The sign of this charge varies with temperature and divalent cation concentration in exactly the opposite manner as that of the surface or grain boundary charge.

\( x_e \), the effective width of the space charge layer as defined by Kliewer and Koehler, remains essentially constant over an appreciable temperature range which includes the isoelectric temperature. The values of \( x_e \) in the range of the isoelectric temperature have special significance since they seem to indicate a basic deficiency in the theoretical development in a manner which will be discussed later.

**B. Diffusion Coefficients**

The single crystal diffusion coefficient for self-diffusion by a vacancy mechanism in a pure, face centered cubic substance, such as NaCl, is given by
\[ D = a_0^2 f \frac{n_v}{N} w, \]

(2)

where \( D \) is the diffusion coefficient, \( a_0 \) is the unit cell edge length, \( f \) is a correlation factor(29) introduced to account for the fact that successive jumps of the tracer ion are not random but are correlated, \( n_v \) is the number of vacancies in the crystal, \( N \) is the number of atomic or ionic lattice sites, and \( w \) is the jump frequency of the vacancy.

When the appropriate expressions for \( w \) and \( n_v \)(17) are inserted in the above equation, it can be written in the familiar form

\[ D = D_0 \exp \left(-\frac{Q}{kT}\right), \]

(3)

where \( Q \), the "activation energy," is the sum of the enthalpies of vacancy formation and motion.

In most investigations of grain boundary diffusion, the experimentally determined quantity is \( D'\delta \), the product of the grain boundary diffusivity and the grain boundary width. Since independent determinations of \( \delta \) are virtually impossible and since simultaneous calculations of \( D' \) and \( \delta \) by fitting experimental data to existing exact mathematical models requires excellent experimental results, the assumption usually made in interpreting the results of grain boundary diffusion measurements is that \( D'\delta \) obeys a relationship of the form
where $Q_b$ is now the "activation energy" of grain boundary diffusion.

In metals, existing experimental results indicate that the above assumption is justified. For alkali halides, however, published experimental results, to date, have not been of sufficient quality for this assumption to be tested and, as can be seen by the discussion in the previous section, an a priori assumption of this kind is certainly not justified in the case of alkali halides.
III. EXPERIMENTAL PROCEDURES

A. Growth of the Bicrystals

An NRC Model 2804A Czochralski type crystal growing furnace was used to grow the bicrystals using techniques which were essentially those of earlier investigators. (30) The growth crucible was high purity alumina which had been leached prior to use with molten high purity NaCl.

The source materials from which the bicrystals were grown were Harshaw optical grade NaCl (see Table II) and reagent grade anhydrous calcium chloride. The as-received single crystalline NaCl was prepared for use by washing individual pieces in deionized water and methanol using teflon coated tweezers, drying the pieces in a stream of hot air, and placing them directly in the pre-cleaned alumina crucible. The crucible and charge were then heated under vacuum in the crystal grower for approximately one hour at 400°C to remove residual water. Commercially available (99.996%) argon was then admitted to the growth chamber through heated turnings of an 88% Zr-12% Ti alloy which removed traces of O₂ and H₂O. A small positive pressure of argon was maintained during crystal growth.

After the charge had melted, the seeds were brought in contact with the bath surface and the temperature was raised to remove any initial polycrystalline overgrowth on the seeds. The temperature was then lowered and vertical growth of the bicrystal was started after the grain boundary had
**TABLE II**

**TYPICAL ANALYSIS OF HARSHAW SODIUM CHLORIDE**

<table>
<thead>
<tr>
<th>IMPURITY</th>
<th>CONCENTRATION (ppm)</th>
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<tbody>
<tr>
<td>Al</td>
<td>6</td>
</tr>
<tr>
<td>Ca</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
</tr>
<tr>
<td>Mg</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>2</td>
</tr>
</tbody>
</table>

15 ppm
formed. The temperature and pulling rate were adjusted such that the transverse size of the crystal increased slowly with vertical growth. The crystal and the crucible were both rotated during the growth of the bicrystals to assure a radially symmetric temperature gradient in the system. Upon termination of growth the bicrystal was raised slightly above the bath surface and the furnace was cooled at a rate of approximately \( 2^\circ \text{C} \) per minute.

Spectroscopic comparison of as-received NaCl and NaCl which had gone through the growth cycle showed that no detectable impurity was introduced by the growth procedures.

15, 30, and 45 degree tilt and twist bicrystals were grown from pure Harshaw NaCl. 30 degree twist and 45 degree tilt bicrystals were grown from a bath containing 400 ppm CaCl\(_2\). All the bicrystals were (100) type bicrystals.

**B. Sample Preparation and Acquisition of Data**

The tilt grain boundary samples and the single crystal samples were obtained by cleaving them from their parent bicrystals and the twist grain boundary samples were sawed from their parent bicrystals. The size of the samples was typically \( 3/8 \) in. \( \times 5/8 \) in. \( \times 1/16 \) in.

The sample treatment adopted for this study is the result of preliminary investigations of vapor deposition rates and isotope distribution, various sectioning parameters (crystallographic direction of cutting, knife adjustment,
sample alignment, temperature dependence of section thickness), and elimination of radioactive debris. The latter was of utmost importance since the presence of traces of radioactive material on the sides of the samples masked the grain boundary diffusion.

An A. O. Spencer Model 860 microtome was used to flatten the samples prior to the vapor deposition of the isotopes. The upper surface of a detachable sample mounting block was permanently aligned parallel to the plane of movement of the microtome knife edge so that the flattened samples could be vacuum coated, annealed, and remounted for sectioning with negligible misalignment. The samples were held on the mounting block using salol, and after flattening, the salol was removed by washing the sample in acetone and then toluene.

In this study, the self-diffusivities of both sodium and chlorine were investigated. $^{22}\text{Na}$ and $^{36}\text{Cl}$ were used as the radioactive tracers. The $^{36}\text{Cl}$ was received in the form of an aqueous $\text{H}^{36}\text{Cl}$ solution which was neutralized upon receipt to a pH of 8 using a concentrated NaOH solution. The $^{22}\text{Na}$ was received as an acid (HCl) solution of $^{22}\text{NaCl}$ and was used in this form except for one series of bicrystal samples whose sources contained $^{22}\text{NaCl}$ and NaOH.

Sample portions of the radioactive solutions were dried in a platinum evaporation crucible and the radioisotope was vapor deposited from the crucible using a tantalum heating coil in an NRC vacuum evaporator. The thickness of the
evaporated layer on the single crystal samples was about 2 microns while the layer thickness used for the bicrystal samples was approximately 16 microns. An X-ray examination of the evaporated layers using Laue back-reflection photographs revealed that at the low evaporation rates used, the layers formed epitaxially on the underlying material.

After the vapor deposition of the radioactive source, each sample was wrapped in platinum foil, encapsulated in a vycor ampule at a pressure of approximately $5 \times 10^{-6}$ torr, and then annealed. The long-time temperature stability of the annealing furnaces was always better than $\pm 1^\circ$C and the short-time temperature fluctuations were negligible. The spacial variation of temperature over the volume occupied by the sample was always less than $0.5^\circ$C.

Sample misalignment during sectioning was minimized by keeping the surface of the sample mounting block parallel to the plane of movement of the microtome knife edge. Under these conditions, if the pre-flattened sample suffered no deformation while being annealed, it could be repositioned on the sample holder such that its upper surface was exactly aligned with respect to the knife edge. Prior to sectioning, however, the sides of the sample were cleaved off to remove any surface diffusion effects and the deformation due to cleaving was then removed by grinding the back of the sample. The resulting misalignment of the sample surface during sectioning was always less than 4 microns per cm.
The sample sections were obtained by first painting the sample surface with a solution of Duco Cement in 2-pentanone, allowing the solution to dry, and then slicing off the sample surface with the microtome. The resulting sample section, consisting of a very thin layer of Duco Cement and the NaCl adhering to it, formed a compact, cigar-shaped roll which furnished a very reproducible counting geometry. The possibility of self-absorption within the sections was investigated by dissolving the sections of several previously investigated samples in water, drying the solutions, and remeasuring the activities of the sections. No error due to self-absorption within the sample sections was detected. Typical section thicknesses were 4 microns for the single crystal samples and 10 microns for the bicrystal samples.

The activities of the sections containing $^{22}\text{Na}$ were determined using a scintillation counter. The $^{22}\text{Na}$ spectrum between 0.7 and 1.5 MeV was counted and the background counting rate for this range was typically 230 cpm. The activities of sections containing $^{36}\text{Cl}$ was determined using a thin end-window, continuous gas flow geiger counter whose background counting rate was 15 cpm.

The samples—particularly the earlier ones—were examined autoradiographically while being sectioned to insure that the section activities consisted only of radioisotopes that had diffused into the sample either through the bulk or along the grain boundary. Figures 1 and 2 show the isotope
penetration profile and accompanying autoradiographs for a preliminary bicrystal sample.

C. Data Analysis and Estimation of Errors

The solution of the one-dimensional diffusion equation applicable to the single crystal source configuration applied in this work is

\[ C = \frac{C_0 h}{(\pi Dt)^{1/2}} \exp \left( -x^2/4Dt \right), \tag{5} \]

where \( C \) is the concentration in the single crystal, \( C_0 \) and \( h \) are the concentration and thickness of the source, \( x \) is the distance from the surface, \( t \) is the diffusion time.

In the single crystal samples the diffusion coefficient, \( D \), was thus obtained by assuming \( C \) to be proportional to the specific activity of a thin slice of crystal at a distance \( x \) from the surface of the crystal on which the radioisotope was originally deposited. A plot of the logarithm of the specific radioactivity versus \( x^2 \) gave a straight line of slope \( 1/4Dt \). Since the diffusion time was known, the single crystal diffusion coefficient could be calculated (see Figures 3 and 4).

Of the existing solutions to the grain boundary diffusion problem\(^{32,33,34}\) only the approximate one by Fisher can be used directly and with little difficulty; and, as Le Claire\(^{35}\) has pointed out, the application of this solution to grain boundary diffusion measurements made using a
Figure 1. $^{36}$Chlorine Penetration Profile Of An Undoped $30^\circ$
Twist Bicrystal Showing The Single Crystal And
Grain Boundary Diffusion.

Annealed $1.092 \times 10^6$ sec. at $428^\circ$C.

The numbered positions indicate locations at
which the autoradiographs of Figure 2 were
taken.
BULK DIFFUSION

GRAIN BOUNDARY DIFFUSION

ACTIVITY (Counts/Min)

X (Microns)
Figure 2. Autoradiographs Of The Bicrystal Diffusion Sample Of Figure 1 At Various Penetration Depths.

#1. Original evaporated surface

#2. Approximately 6 microns of NaCl removed from grain boundary entrance

#3. Approximately 26 microns from original sample surface

#4. Approximately 100 microns from original surface

The sample was misaligned approximately 15 microns from side to side as can be seen in autoradiograph No. 2. Also, the twist grain boundary in this particular sample was not symmetric; i.e., it was not parallel to the (100) planes of the adjacent single crystalline portions. The photographs are positive prints taken from original autoradiographic negatives.
Figure 3. A Typical $^{36}$Chlorine Single Crystal Penetration Profile.

Annealed $5.92 \times 10^5$ sec. at 524°C.
$D = (1.01 \pm 0.02) \times 10^{12} \text{ cm}^2/\text{sec}$
Figure 4. Normal And Anomalous $^{22}\text{Na}$ Bicrystal Penetration Profiles.

Lower plot:
This $^{22}\text{Na}$ sodium penetration profile was obtained from a bicrystal sample whose source contained no excess NaOH. The plot is typical of such bicrystal samples and is also typical of $^{22}\text{Na}$ single crystal diffusion samples. Annealed $1.15 \times 10^5$ sec. at $500^\circ\text{C}$.

Upper plot:
$^{22}\text{Na}$ sodium penetration profile in bicrystal sample whose source contained NaOH. Annealed $1.15 \times 10^5$ sec. at $500^\circ\text{C}$.
$D = 7.94 \times 10^{12} \text{ cm}^2/\text{sec}$

$D = 8.67 \times 10^{12} \text{ cm}^2/\text{sec}$
sectioning technique usually causes inconsequential errors in the measured activation energies of diffusion and small but correctible errors in the measured values of \( D'\delta \). For the present investigation the corrections to the measured values of \( D'\delta \) due to the application of the Fisher solution were within the limits of experimental uncertainty and, therefore, the data for the bicrystal samples were analyzed using the Fisher solution with no correction for formalistic error.

In grain boundary diffusion measurements made using a sectioning technique the total amount of tracer, \( \bar{C} \), present at a distance, \( x \), from the surface is the experimentally determined quantity and is given by the Fisher solution as

\[
\bar{C} = 4 \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}} C_0 \exp\left( -\frac{2^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} x \left[ \frac{1}{D'\delta} \left( \frac{D}{t} \right)^{\frac{1}{2}} \right]^2 \right). \tag{6}
\]

Thus, in the bicrystal samples the quantity \( D'\delta \) was obtained by assuming \( \bar{C} \) to be proportional to the specific activity of a slice of a bicrystal at a distance \( x \) from the bicrystal surface on which the radioisotope was originally deposited. A plot of the logarithm of \( \bar{C} \) versus \( x \) gave a straight line of slope \(-\frac{2^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \left[ \frac{1}{D'\delta} \left( \frac{D}{t} \right)^{\frac{1}{2}} \right]^2\). Since the diffusion time was known, the product of the grain boundary diffusivity and the grain boundary width, \( D'\delta \), could be found using the experimentally determined single crystal diffusion coefficient, \( D \) (see Figure 5).

The systematic error in the single crystal diffusion coefficient, \( D \), due to the finite section thickness, the
Figure 5. A Typical $^{36}$Cl Chlorine Grain Boundary Penetration Profile.

Annealed $1.90 \times 10^6$ sec. at 420°C.
\[ D'\delta = (1.08 \pm 0.08) \times 10^{12} \text{ cm}^3/\text{sec} \]
source thickness and the sample misalignment is given by (36)

\[ D_{\text{actual}} = D_{\text{experimental}} \left(1 - \frac{a^2 + 4b^2 + c^2}{24Dt}\right) \]  

(7)

where \( a \) is the section thickness, \( b \) is the source thickness, and \( c \) is the misalignment distance (the crystal width times the misalignment angle, for small angles). Using the above relationship it was found that the systematic error in the single crystal diffusion coefficients was always less than 1%.

When the logarithm of the section activity of a sample is proportional to \( x \), as is generally assumed to be true for grain boundary diffusion, an analysis of the type which led to equation (7) (37) shows that in grain boundary diffusion measurements there is no systematic error in the experimental values of \( D' \) due to section thickness and sample misalignment.

Error in the measurement of diffusion times arose from the time required to bring the sample from room temperature to the annealing temperature. Since the annealing times for the single and bicrystal samples ranged from \( 1 \times 10^5 \) to \( 2 \times 10^6 \) sec., it was possible to keep the heating and cooling times of any sample less than 1% of the total annealing time.

The precision of the temperature measurement, as determined by repeated examination of the temperature stability of the annealing furnaces, was always better than \( \pm 1^\circ \text{C} \) for
any sample. Also, the accuracy of the annealing temperature as measured by the chromel-alumel thermocouple used was ±1°C. Thus, the total uncertainties of the D and D'6 values due to errors in temperature measurement, as given by

$$\frac{dD}{D} = \frac{Q}{kT^2} dT,$$

were approximately 5% for the chlorine bulk diffusivities, 2% for the sodium diffusivities, and 2% for the grain boundary diffusivities.

The random fluctuations of section thickness due to variations in the microtome sample stage displacements were investigated using a Hewlett-Packard Model 7DCDT linear displacement transducer. By this method, the 95% confidence interval for the microtome sample stage displacements was found to be ±4% of the mean for 2 micron displacements and ±2% of the mean for 4 micron and larger displacements.

The accuracy of the section thickness (as given by the microtome stage displacement setting) was established by sectioning a single crystalline block of NaCl of known cross-sectional area. By weighing the sample and sample holder before and after sectioning, the total thickness of material removed could be calculated. The actual experimental section thicknesses were found to agree exactly with the microtome stage displacement settings within the estimated experimental error introduced by weighing and the initial determination of cross-sectional area.
Thus, except for those introduced by temperature uncertainties, the only appreciable errors in the diffusion measurements were the statistical errors in the individual section activities due to small counting rates.

Values of $D$ and $D^\prime \delta$ and their 95% confidence limits were obtained by fitting the single and bicrystal data to equations (5) and (6) by the method of least squares using a bivariate normal regression analysis. The random errors in the activities of the individual sample slices thus appeared as the calculated random errors in $D$ and $D^\prime \delta$. For the single crystal diffusivities the typical error was about ±5% while the uncertainties in the bicrystal diffusion coefficients, especially for the pure twist grain boundary samples, were larger and more variable.
IV. EXPERIMENTAL RESULTS

A. Single Crystal Diffusion Coefficients

The sodium and chlorine single crystal diffusion coefficients for Harshaw sodium chloride are shown as functions of temperature in Figure 6. The chlorine diffusion coefficient is well represented by

\[
D = (2890 \text{ cm}^2/\text{sec}) \exp(-2.45 \text{ eV/kT})
\]  

(9)

over the temperature range investigated. These results should be compared to those of Laurance\(^{(4)}\) for pure sodium chloride to which small amounts of calcium chloride had been added:

\[
D = (1280 \text{ cm}^2/\text{sec}) \exp(-2.49 \text{ eV/kT}).
\]  

(10)

The sodium single crystal diffusion was only investigated thoroughly below 510°C. In this temperature range, the sodium diffusion coefficient is also given by equation (3) with \(Q\) equal to 0.75 eV and \(D_0\) equal to \(5.12 \times 10^{-7} \text{ cm}^2/\text{sec}\). The high temperature sodium diffusion data are the result of an earlier investigation\(^{(1)}\) which also produced values of 0.77 eV and \(1.6 \times 10^{-6} \text{ cm}^2/\text{sec}\) for \(Q\) and \(D_0\) at low temperatures. The break or "knee" in the sodium diffusivity plot occurs at approximately 505°C. The temperature of the knee is the temperature below which the number of thermally activated vacancies becomes negligible in comparison with those introduced with the divalent cations. Thus,
Figure 6. Arrhenius Plots Showing The $^{36}$Chlorine And $^{22}$Sodium Single Crystal Diffusion Coefficients For Diffusion In Harshaw Sodium Chloride.

The 95% confidence limit for all values of $D$ is approximately ± 5%.

The high temperature data (dashed line) are those of Mapother, Crooks, and Maurer. (1)
this transition temperature was used in conjunction with the equation for the equilibrium number of thermally activated vacancies to calculate the divalent cation concentration. This calculation indicated the net aliovalent cation concentration was approximately 3 ppm.

B. **Grain Boundary Diffusion Coefficients**

For those bicrystalline samples which were prepared and annealed in the manner described above, i.e. using a pure or chemically neutral source and "clean" annealing conditions, there was no evidence of enhanced sodium ion diffusion along the tilt or twist grain boundaries in pure or calcium chloride doped sodium chloride.

Initially, there were positive indications of enhanced diffusion of sodium along the grain boundaries (see Figure 4) but these were eventually traced to the presence of relatively small amounts of sodium hydroxide in the radioactive source layer.\(^{(39)}\) It was found that enhanced diffusion of sodium along the grain boundaries occurred only when the concentration of sodium hydroxide in the source was greater than ten weight per cent, the solubility limit of NaOH in NaCl at the diffusion temperature, suggesting that the phenomenon consisted primarily of preferential attack of the grain boundary region by a partially molten source layer.

Within the limits of experimental error, the chlorine grain boundary self-diffusion coefficients were found to satisfy a relationship of the form
$\text{D'}\delta = (\text{D'}\delta)_0 \exp(-Q_b/kT).$ \hspace{1cm} (11)

The results of fitting the experimental values of $\text{D'}\delta$ to the above relationship are given in Figures 7 and 8 and a list of the resulting activation energies of chlorine grain boundary diffusion, $Q_b$, is given in Table III.

For the temperature range studied (420°C to 480°C), the values of $\text{D'}\delta$ were typically between $10^{-15}$ and $10^{-16}$ cm$^3$/sec and, except for the undoped 30° twist grain boundary samples, the activation energy for chlorine grain boundary diffusion in NaCl could be given as 1.15 ± 0.30 eV for all grain boundary types examined. The average value of $(\text{D'}\delta)_0$ was of the order of $10^{-7}$ cm$^3$/sec but the variation in the values of $(\text{D'}\delta)_0$ due to the range in values of $Q_b$ was so large that this figure should only be considered as qualitative. There seems to be no detectable systematic variation of either the grain boundary diffusion coefficients or the activation energies of grain boundary diffusion with any of the experimental parameters investigated, i.e. the grain boundary angle, the grain boundary type (tilt or twist), or the calcium chloride concentration.
Figure 7. Arrhenius Plots For Undoped Twist Grain Boundary Samples Showing The Variation Of The $^{36}$Chlorine Grain Boundary Diffusion Parameter, D', With Temperature.
PURE 45° TWIST BOUNDARY

PURE 30° TWIST BOUNDARY

PURE 15° TWIST BOUNDARY

$D' \delta$ (cm$^3$/sec)

$(1/T) \times 10^3$ (°K)$^{-1}$
Figure 8. Arrhenius Plots For $^{36}$Chlorine Grain Boundary Diffusion In Pure And Calcium Doped Tilt Boundaries And In Calcium Doped Twist Boundaries.

The error limit for all values of D'δ is approximately 10%.
| TABLE III.                        | ACTIVATION ENERGIES OF CHLORINE GRAIN BOUNDARY DIFFUSION |
| "PURE" BICRYSTALS               | 36 CHLORINE GRAIN BOUNDARY DIFFUSION (eV)                 |
|                                  | 15° TWIST BOUNDARY                                      | 1.19  |
|                                  | 30° TWIST BOUNDARY                                      | 0.38  |
|                                  | 45° TWIST BOUNDARY                                      | 0.91  |
|                                  | 45° TILT BOUNDARY                                       | 1.16  |
| CALCIUM CHLORIDE DOPED BICRYSTALS | 30° TWIST BOUNDARY                                     | 0.86  |
|                                  | 45° TILT BOUNDARY                                       | 1.45  |
V. DISCUSSION

For grain boundary diffusion in NaCl, the experimental observations which any proposed mechanism and/or diffusion path should account for are: the enhanced diffusion of chlorine along grain boundaries and dislocations; the absence of enhanced diffusion of sodium along the grain boundaries; and the observations that the grain boundary angle, the grain boundary character (tilt or twist), and the concentration of divalent cations in the crystal seem to have no significant effect upon either the magnitude or the activation energy of chlorine grain boundary diffusion.

The observed characteristics of grain boundary diffusion in NaCl may be either extrinsic, i.e. controlled by impurities present in the grain boundary region, or intrinsic in nature.

Because of the extensive effort made in this investigation to exclude water from the sample environment, it seems unlikely that the observed grain boundary diffusion is influenced by its presence. Furthermore, it seems unlikely that divalent cations contribute to the increased chlorine grain boundary diffusivities in NaCl since a hundred-fold increase of the divalent cation concentration in the present study caused no detectable change in the chlorine grain boundary diffusion.

Thus, since any predominantly intrinsic grain boundary
Diffusion mechanism will undoubtedly be related in some manner to the electrical dipole layer known to exist in the vicinity of the grain boundary, the results of the present study were analyzed using the theory of charged defects, as developed by Kliewer and Koehler. This analysis indicates that the rapid chlorine diffusion takes place in the grain boundary core region by the movement of the excess chlorine ions predicted to reside there. Since the number of "vacancies" which can coexist with the excess ions in the core is necessarily small, the ions are thought to move by an "interstitial" type mechanism in the relatively open region of the grain boundary core.

In order to decide what effect the electrical dipole layer has upon the grain boundary diffusion at any temperature, it is necessary to know the value of the isoelectric temperature for the material under investigation. The inherent difficulty in determining the isoelectric temperature is compounded by the fact that, although the energy of formation of a Schottky defect is a fixed property of the ionic solid, the manner in which this formation energy is divided between the anion and cation vacancies depends upon the vacancy source. Thus, the isoelectric temperatures for external surfaces, grain boundaries, and isolated dislocations are not necessarily the same.

The theory of grain boundary and dislocation charge, as developed by Kliewer and Koehler, predicts a grain
boundary isoelectric temperature of approximately 300°C for NaCl of the purity investigated in this work. Indirect measurements of the dislocation isoelectric temperature interpreted in terms of the charge cloud theory yielded a dislocation isoelectric temperature of approximately 400°C\(^{(11)}\) for similar material.

In contrast to the above results, direct experimental determination of the dislocation\(^{(12)}\) and grain boundary\(^{(40)}\) isoelectric temperatures in which the results were independent of the charge cloud theory gave values of 480°C and 630°C for the dislocation and grain boundary isoelectric temperatures in NaCl typical of the present investigation.

Thus, while the qualitative features of the theoretical development agree quite well with the observed behavior of dislocations and grain boundaries in NaCl, the theory does not adequately predict the experimentally determined values of the isoelectric temperature. This deficiency is thought to arise as a result of the restriction of the theory to space charge regions of limited extent.

It can be seen from the above discussion that in the temperature range of the present investigation, 400°C to 500°C, the grain boundaries were always below their isoelectric temperatures. Below the isoelectric temperature the grain boundary cores contain an excess of sodium vacancies—or equivalently, chlorine "interstitials"—and the positive
surrounding space charge regions consist primarily of divalent cations.

An examination of the expression for the chlorine vacancy concentration given by Kliewer and Koehler\(^{24}\) shows that below the isoelectric temperature the effective free energy of chlorine vacancy formation in the dipole layer is always greater than \(F^-\), the actual free energy of chlorine vacancy formation. Thus, if it is assumed that the free energy of motion of the anion vacancies is unchanged by their being in the dipole layer (a reasonable assumption for low defect concentrations), the activation energy for chlorine diffusion by a vacancy mechanism in the space charge region is always greater than \(1.12 + 1.11 = 2.27\) eV (see Table I). A comparison of this value with the experimentally determined activation energy of grain boundary diffusion, 1.15 eV, shows that the enhanced chlorine diffusion does not take place in the space charge region of the grain boundary by a vacancy mechanism.

Several investigations\(^{44,41}\) have indicated there is an appreciable contribution to chlorine ion diffusion in single crystals by vacancy pairs and although this mechanism may serve to move the chlorine in a direction normal to the grain boundary core, it can be ruled out as the mechanism of rapid chlorine movement along the grain boundaries by arguments similar to those above.
Thus, if the grain boundary diffusion is an intrinsic effect and if the grain boundaries conform to the predictions of the electrical space charge theory, the observed chlorine grain boundary diffusion probably takes place by the movement of the "interstitial" chlorine ions in the highly distorted grain boundary cores.

As pointed out by Poeppel and Blakely\(^{(25)}\), the magnitude of the excess charge and thus the magnitude of the dipole potential may be sharply reduced at high temperature if the number of surface sites where vacancies can form or precipitate is limited. This effect, however, will not appreciably alter the location of the isoelectric temperature and thus does not qualitatively alter the conclusions reached above.

All the samples except those of the pure, 30° twist bicrystal have grain boundary diffusion coefficients which are the same at all temperatures to within a factor of 3 and have activation energies which are within 25% of the mean value. A possible source of the unusual behavior exhibited by the pure, 30° twist bicrystal samples was the marked deviation from symmetry in these samples. The grain boundary was planar but inclined approximately 20° with respect to the (100) planes of the adjoining single crystal portions.

Although very little of a quantitative nature can be said concerning the movement of the ions in the highly distorted grain boundary core, it is surprising that those
parameters which should directly affect the structure of the core region; i.e., grain boundary type and angle, had so little effect upon the grain boundary diffusivities.

It has been pointed out\(^{42}\) that an electrical dipole exists even in the vicinity of electrically neutral surfaces in NaCl and the magnitude of this dipole has been calculated for (100) surfaces. This dipole results from the physical rearrangement of the ions in the surface of the crystal such that the chlorine ions are displaced out of the crystal and the sodium ions are attracted toward the interior of the crystal. This fact, plus the knowledge that the larger chlorine ion is much more easily polarized, also indicates that the chlorine ions should move in the highly distorted region of the grain boundary core by a sort of "interstitial" mechanism in which the polarizability of the ions plays an important role. This conclusion is supported by the fact that it explains the lack of sodium diffusion in the grain boundaries and on the surface. The conclusion is also strengthened by the observation of Laurent and Bernard\(^{7}\) that the larger anions move more rapidly along the grain boundaries in polycrystalline alkali halides.
VI. CONCLUSIONS

There is no measurable enhanced diffusion of sodium along pure or doped tilt or twist grain boundaries in NaCl. The diffusion of chlorine along the grain boundaries is described by the relationship

\[ D'\delta = (D'\delta)_0 \exp(-Q_b/kT), \]

(12)

when \((D'\delta)_0\) has a value of approximately \(10^{-7}\text{cm}^3\text{/sec.}\) and \(Q_b\) has a value of \(1.15 \pm 0.30\) eV. The grain boundary angle, the grain boundary character (tilt or twist), and the divalent cation concentration appear to have no pronounced effect upon the observed anion diffusion rates. The ionic movement is believed to occur in the grain boundary core region and to consist of the movement of "interstitial" type chlorine ions.
VII. BIBLIOGRAPHY

VIII. VITA

Kenneth Ray Riggs was born on July 31, 1940, in Malden, Missouri. He completed his primary and secondary education in Scott City, Missouri, and entered Southeast Missouri State College, Cape Girardeau, Missouri, in September, 1958. He graduated with honors from the University of Missouri, School of Mines and Metallurgy, Rolla, Missouri, in January, 1963, receiving a Bachelor of Science Degree in Metallurgical Engineering with a Nuclear Option. From May, 1963, to September, 1964, the author was employed by Mallinckrodt Chemical Works, Uranium Division, Weldon Springs, Missouri. The author has been a graduate student at the University of Missouri-Rolla, Rolla, Missouri, since September, 1964, and received a Master of Science Degree in Metallurgical Engineering from that institution in May, 1965. He is the author of two previous publications: "Effect of Alloy Additions on the Quench-Induced Texture of Alpha-Uranium", AEC Research and Development Report MCW 1491, 1965, and "Cation Grain-Boundary Diffusion in NaCl", to be published in the Journal of Applied Physics. Upon graduation, the author will be employed by Texas Instruments Inc., Houston, Texas.