GRAIN BOUNDARY MOBILITY OF KCl

by

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1970

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1971

Submitted in partial fulfillment of the requirements
for the degree of
DOCTOR OF SCIENCE
at the
Massachusetts Institute of Technology
February 1976

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MAR 10 1976
ABSTRACT

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by

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Submitted to the Department of Materials Science and Engineering on January 14, 1976 in partial fulfillment of the requirements for the degree of Doctor of Science.

Grain boundary mobilities of undoped and Sr-, Ca- and Br-doped KCl were measured by secondary grain growth experiments with hot deformed samples. The measured mobilities varied between $10^{-13}$ and $10^{-7}$ (cm/sec)(dyne/cm$^2$)$^{-1}$, over a wide temperature range, $0.45 \leq T/T_m \leq 0.95$. During the secondary grain growth, only the high angle boundaries are mobile, whereas the low angle subgrain boundaries remain immobile. The KCl grain boundary mobility is lowered by both monovalent and divalent dopants; however the grain boundaries in samples with 5 molar% Br are at least 10 times more mobile than those in samples with 50-100 molar ppm of aliovalent, Sr or Ca, dopant.

A grain boundary impurity drag model due to the electrostatic space charge interactions between grain boundary and impurity is formulated for ionic solids. The redistributions of the impurity and vacancy charge density associated in a moving grain boundary affect the space charge. However, numerical solutions show that the velocity dependence of the space charge potential is rather modest in the case of impurity limited grain boundary motion.

The three mechanisms which can influence the transport of divalent cation impurities in a space charge potential field are the electric field effects, the electric field gradient effects and the effects of a vacancy wind. The interactions between the impurity-vacancy dipole complexes and the space charge electric field are included in the analysis of the defect distributions in the grain boundary region. Numerical calculations show that the dipole-field interactions have a negligible effect on the space charge potential distribution. However, the dipole field interactions tend to polarize the distribution of impurity-vacancy associated complexes and cause a modest attraction of dipoles to the boundary.
Impurity distributions in a grain boundary with a steady velocity are calculated by numerical integration of the flux equation. The distributions are asymmetrical about the grain boundary. In the grain boundary region, Sr segregation at low temperatures and desorption at high temperatures are predicted. Furthermore, the magnitude of segregation and desorption decreases as boundary velocity increases.

The impurity drag is calculated and the boundary velocity is predicted for a given driving force. At the isoelectric temperature, the theoretical calculations, based on the space charge interaction alone, show a very high boundary velocity, limited only by the intrinsic mobility.

In addition to the space charge interaction potential, the strain field interaction between the impurity ions and the grain boundary also contributes to the impurity drag. Furthermore, the distributions of the charged impurity and the space charge potential are modified by the strain field interaction with the aliovalent ions. The impurity drag was calculated for the coupled effects of the electrostatic space charge and a ramp shaped strain field with an assumed magnitude and range. The predicted grain boundary velocities are within an order of magnitude of the experimental data in the low temperature range. However, the predicted high velocity for the breakaway grain boundaries are not in agreement with the experimental data in the high temperature range.

In the sample preparation, doped KCl single crystals were grown by the Czochralski method. The crystals were deformed, at homologous temperature ranging from 0.28 to 0.98, and with a normalized true stress, $\sigma/E$, varying between $2 \times 10^{-3}$ and $2 \times 10^{-4}$. The deformation microstructures show a uniform subgrain size and equiaxial grain shapes, but with a distribution of subgrain misorientation angles. An inverse relation between stress and subgrain size was found in which effects of temperature, alloying additions and crystal orientations are minor.

In addition, the contributions of the space charge cloud to impurity and self diffusion in the grain boundary region of an ionic solid are analysed.

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ACKNOWLEDGEMENTS

This author would like to thank his advisors, Professors H. K. Bowen and R. M. Cannon, Jr. for their encouragement and guidance. The discussions with Professors R. L. Coble and J. W. Cahn have always been stimulating and challenging. Professor R. J. Charles of General Electric is particularly helpful in the presentation of this work.

P. Kearney, A. Freker and W. Westphal are acknowledged for their assistance in the experimental work. M. Molnar has been particularly helpful in the use of computation facilities. The assistance of B. Baker, B. McDonald, D. Fellows, L. A. vanUitert and J. Mara are appreciated. This thesis could not be completed without the kind assistance of S. S. Goon.

Discussions with J. Drier, W. Gourdin and G. Wei in the space charge theory, W. Petuskey in grain boundary migration have been useful. T. Mason, J. Blendell, D. Reed, J. Blum, K. W. Cheng and T. Gattuso have contributed to my understanding in ceramics. Companionship of Kathy and Ace has been exciting.

This research was sponsored by ARPA order number 2055, contract number F19628-75-C-0191.
CHAPTER I  INTRODUCTION

Grain boundary mobility can often be an important factor in material processing, e.g. sintering, recrystallization and related processes, as well as in the microstructural stability at the operating temperatures.

However, the kinetics of the grain boundary migration process are not well understood; this is due in part to the lack of knowledge about the grain boundary structure. More importantly, the grain boundary migration phenomenon is related to other near boundary and boundary associated phenomena, Kingery (1974). In ceramics, grain boundary mobility is nearly always rate limited by extrinsic factors, e.g. solute segregation or second phase at a grain boundary.

In this thesis, the grain boundary mobility data of KCl are reported from the secondary grain growth experiments. Furthermore, an impurity drag model is proposed to account for the experimental data. The impurity drag mechanisms are identified as the space charge interaction potential and the mechanical strain interaction potential.
CHAPTER II LITERATURE REVIEWS

II - 1. GRAIN BOUNDARY STRUCTURE

A grain boundary can be considered as a minimum energy structure, constrained between two adjacent crystals. Some models of the grain boundary structure were concerned with the atomic arrangement in the boundary region to achieve the minimum free energy and satisfy the boundary condition of a periodic structure in the adjacent crystals. Other proposals were concerned with the invariants and theorems which must be satisfied in any boundary structure model.

Because of the periodicity of the adjacent crystals, the atomic arrangement of the boundary structure cannot be truly random. However, the transition from one crystallographic orientation to another in the boundary region is likely to bring about a certain degree of randomness. The conflicting views of the crystalline or amorphous nature of grain boundaries were compromised in recent computer calculations, e.g. Weins et al (1969, 70, 71), which showed that grain boundaries can be considered as a periodic combination of one or more structural units. However, the atomic arrangement within the structural units are related to the orientations and the relative orientation of the adjacent crystals.

An intuitive and geometric version of the minimum
energy grain boundary structure was proposed by Kronberg and Wilson (1949) based on their observations of the preferential occurrence of some specific misorientations between grains after secondary recrystallization. These specific misorientations were shown to result in the coincidence of some atoms of the adjacent lattices. By extending the concept of the coincidence lattice, Bishop and Chalmers (1968) and Chalmers and Gleiter (1971) showed that a boundary with an ideal coincidence orientation can lower the free energy by a relative translation of the adjacent lattices and by the removal and relaxation of certain atoms in the boundary. They also proposed that a grain boundary with a non-ideal coincidence orientation can be made up by mixing units associated with the adjacent ideal coincidence orientations in an appropriate proportion. These proposals were supported by the computations of Weins et al (1969, 70, 71) who assumed a truncated Morse potential as the interatomic potential and minimized the boundary free energy by lattice translations and atomic relaxations. Their computations showed two types of boundary structural units: "circular-" and "ledge-" type atomic arrangement of various periodicity.

Hasson et al (1972) used a similar energy minimization scheme to calculate the optimum boundary structure. Their calculations reaffirmed the models of Bishop and Chalmers
Several authors attempted to generalize the dislocation model of Read and Shockley (1950) for low angle boundaries and to elucidate certain invariant features governing the atomic arrangements in the grain boundary region. A boundary with a misorientation angle within a few degrees of a coincidence relationship was modelled by Brandon et al (1964) and Brandon (1966) as a superimposed dislocation network on a coincidence lattice. This dislocation approach was extended to the 0-lattice theory by Bollmann (1970, 1972) to describe the dislocation substructure in terms of the generalized coincidence lattice. Marcinkowski et al (1973) and Sadanada and Marcinkowski (1974) proposed a unified theory to bring the structural aspects associated with the low- and high-angle boundary into one framework. They showed that any grain boundary can be considered as some combination of crystal lattice dislocations associated with each one of the two grains comprising the boundary. Since the Burgers vector of a dislocation is independent of the precise nature of core relaxations, the Burgers vector of the grain boundary dislocation is an invariant feature and can be uniquely defined independent of atomic relaxations and of the choice of interatomic potentials in the boundary region. Electron microscope studies in metals by Schober and Balluffi (1969, 70), Schober
(1970) and Schober and Warrington (1971) gave experimental evidence on the dislocation structures in the boundary region.

There are few experimental and theoretical studies of boundary structures of ceramic materials. For twist boundaries in the clusters of MgO smoke particles, Chaudhari and Matthews (1970, 1971) have observed a remarkable preference for those angles corresponding to the coincidence orientations. However, the preferred existence of boundaries corresponding to the twist angle of $28.07^0$ was not observed despite the relatively high coincidence site density in this boundary. Calculations of Chaudhari and Charbnau (1972) suggested that the electrostatic contribution in the Born-Mayer potential raises the boundary energy and therefore diminishes the chance of the preferential occurrence of the boundary.

The faceted features observed in $\text{Al}_2\text{O}_3$, MgO and ferrite boundaries in the TEM studies of Paulus (1966), Tighe (1970), Tighe and Kreglo (1970) probably indicate the alignment of boundaries along the low energy path of a coincidence orientation, Kingery (1974).

Certain invariant features of boundary dislocations and the associated Burgers circuits proposed in the models discussed are applicable to metals as well as ceramics.
However the detail atomic arrangements in the boundary structural units are sensitive to the directionality of the atomic bonding and to the required alternating arrangement of the charged ions in the adjacent crystal lattices. So far as we are aware, there are no calculations of boundary structures in covalent or partially covalent bonding materials.
II - 2. SPACE CHARGE THEORY

The existence of space charge regions near lattice discontinuities (free surfaces, dislocations and grain boundaries) were first postulated by Frenkel (1946), and the charge distributions were formulated by Frenkel (1946), Lehovec (1953), Eshelby et al (1958) and Kliewer and Koehler (1965). The essential features of these formulations are that the system is in thermal equilibrium and that the point defects are free to redistribute spatially to achieve the minimum free energy and that the lattice discontinuities are infinite sources or sinks for vacancies of either sign without any significant change in the surface structures.

The space charge theory of Kliewer and Koehler (1965) for NaCl type crystals is considered in detail here. For a one dimensional crystal with surfaces at $X=0$ and $X=2L$, the space charge potential, $\varphi$, arising from the distribution of charged defects is symmetrical about $X=L$; and thus only the section of crystal from $X=0$ to $X=L$ need be considered. For the crystal section with $N_+(X)$ free cation vacancies, $N_-(X)$ free anion vacancies, $N_B(X)$ bound cation-anion vacancy pairs, $N_{if}(X)$ free divalent cation impurities, $N_{ib}$ impurity-vacancy complexes, the free energy, $F$, at temperature, $T$, is

$$F = \int_0^L dx \left\{ N_+(X)F^+ + N_-(X)F^- + N_B(X)(F^+_B + F^-_B) + N_{ib}(X)(F^+_B + F^-_B) + \frac{1}{2} \rho(X) \varphi(X) \right\} - TS_c$$

(II-1)
where $F^+$ and $F^-$ are the formation energies for the cation and anion vacancies respectively; $B$ is the binding energy between the free cation and anion vacancies; $B^+$ is the binding energy between the free cation vacancies and the free divalent cation impurity ions; and $S_c$ is the configurational entropy. The charge density, $\rho(X)$, is given by

$$\rho(X) = e(N_+(X)+N_{if}(X)-N+(X))$$

where $e$ is the absolute value of the electronic charge, and $\phi(X)$, the electrostatic potential is determined from Poisson's equation,

$$\nabla^2 \phi = -\frac{4\pi \rho(X)}{\epsilon}$$

(II-2)

where $\epsilon$ is the static dielectric constant.

By making a variation of the free energy, $F$, with respect to the five independent variables, the defect densities, $N_+(X)$, $N_-(X)$, $N_B(X)$, $N_{if}(X)$, $N_{ib}(X)$ under the constraints of impurity conservation,

$$\int_d^L dx(N_{if}(X)+N_{ib}(X)) = \bar{C}NL$$

(II-3)

where $\bar{C}$ is the average divalent cation impurity concentration, and $N$ is the density of anion and cation sites in the crystal, Kliewer and Koehler (1965) were able to obtain expressions for the defect concentrations for the approximations of low defect concentrations and of sufficiently large specimen size,

$$N_+(X)/N = \exp(-(F^+-e\phi)/kT)$$

(II-4a)

$$N_-(X)/N = \exp(-(F^-+e\phi)/kT)$$

(II-4b)

$$N_B(X)/N = Z_n \exp(-(F^++F^-+B)/kT)$$

(II-4c)
\[N_{ib}(X)/N = \tilde{c}(1-P_{\infty}) \exp(-(\varepsilon \varphi(X) - \varepsilon \varphi_{\infty})/kT)\]  
(II-4d)
\[N_{if}(X)/N = \tilde{c}P_{\infty}\]  
(II-4e)
\[P_{\infty} = \left\{1 + Z_{nn}^{-1} \exp((F^{+} - B^{+} - \varepsilon \varphi_{\infty})/kT)\right\}^{-1}\]  
(II-4f)

where \(\varepsilon \varphi_{\infty}\) is the potential in the bulk of the crystal, \(Z_{nn}\) and \(Z_{n}\) are the coordination numbers of the nearest and the next nearest neighbors respectively, and \(P_{\infty}\) is the probability of association for the divalent cations and the cation vacancies.

It was shown by Kliever and Koehler (1965) that the free energy of the system can always be expressed in terms of the potential difference at \(X\) and that at the surface, \(\varphi(X) - \varphi(0)\). Therefore, the choice of the surface potential, \(\varphi(0)\), is arbitrary and is assigned to be zero for simplicity.

With these expressions of defect concentrations, Poisson's equation, Eq (II-2), can be solved to obtain the space charge potential, \(\varphi(X)\), in terms of the reduced potential, \(Z\), as a function of the reduced distance, \(S\),
\[Z = 4 \tanh^{-1}\left\{e^{-S} \tanh(Z_{0}/4)\right\}\]  
(II-5)
where \(Z = (\varepsilon \varphi(X) - \varepsilon \varphi_{\infty})kT\)  
(II-6)
\[Z_{0} = -\varepsilon \varphi_{\infty}/kT\]  
(II-7)
\[S = X/\delta\]  
(II-8)
\[\delta = \left[\frac{\varepsilon kT}{8\pi Ne^{2}} \frac{1}{N_{+}(\infty)}\right]^{1/2}\]  
(II-9)
The Debye length, $\delta$, gives a measure of the characteristic length at which the space charge potential is more than $(1 - 1/e)$ or 63% of the bulk potential, $\phi_\infty$.

The bulk potential, $\phi_\infty$, is defined as the potential required to achieve the charge neutrality in the bulk,

$$\phi(X=\infty, e\phi_\infty) = eN\left\{\bar{c}(1-p_\infty) + \exp(-\mu+)kT - \exp(-\mu_-kT)\right\} = 0$$

(II-9a)

In the limits of intrinsic and extrinsic temperatures, the bulk potential, $\phi_\infty$, can be expressed as

$$e\phi_\infty = \begin{cases} 
\frac{(\mu^+ - \mu^-)}{2} & ; \text{ intrinsic temperatures} \\
\mu^+ kT \ln \bar{c}(1-p_\infty) & ; \text{ extrinsic temperatures}
\end{cases}$$

(II-9b)

The formation energies, $\mu^+$ and $\mu^-$ for the KCl as given in Dreyfus and Norwick (1962) are listed in Table II-1. The data of Fuller et al (1968) and Fuller (1966) were chosen, Table II-1, for Schottky formation energy and impurity-vacancy binding energy because they present a set of self consistent data from the same authors.

The bulk potential, $e\phi_\infty$, and the Debye length, $\delta$, were calculated from the defect formation and binding energies as a function of temperature and dopant level, Table II-2. The bulk potentials of 50 ppm Sr- and $\nu$-doped KCl were numerically calculated and shown in Fig. (II-1).
Fig. II-1: Bulk potential as a function of temperature in 50 ppm Sr- and O- doped KCl.
Table II-1

Data of KCl Vacancy Formation Energies, Impurity-Vacancy Binding Energies, and Cl Diffusion Activation Energies.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Enthalpy (eV)</th>
<th>Entropy (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-vacancy formation energy$^1$</td>
<td>0.84</td>
<td>3.2</td>
</tr>
<tr>
<td>Cl-vacancy formation energy$^1$</td>
<td>1.38</td>
<td>3.2</td>
</tr>
<tr>
<td>Schottky defect formation energy$^2$</td>
<td>2.49</td>
<td>7.64</td>
</tr>
<tr>
<td>Sr-impurity-K vacancy binding energy$^2$</td>
<td>-0.57</td>
<td>-1.88</td>
</tr>
<tr>
<td>O-impurity-Cl vacancy binging energy$^3$</td>
<td>-0.57</td>
<td>-1.88</td>
</tr>
<tr>
<td>Cl-diffusion by vacancy pairs$^4$</td>
<td>2.65</td>
<td>9.05</td>
</tr>
<tr>
<td>Cl-diffusion by Cl Vacancy in pure KCl$^4$</td>
<td>2.10</td>
<td>3.60</td>
</tr>
<tr>
<td>K-migration energy$^2$</td>
<td>0.76</td>
<td>2.56</td>
</tr>
<tr>
<td>Cl-migration energy$^2$</td>
<td>0.89</td>
<td>3.95</td>
</tr>
</tbody>
</table>

3. Assumed.
Table II-2

The Calculated Values of Bulk Potential, $e\varphi_\infty$, Debye Length, $\delta$, and Impurity-Vacancy Association Probability $P_\infty$, for Doped KCl.

<table>
<thead>
<tr>
<th>Impurity (concentration)</th>
<th>Temperature (°C)</th>
<th>$e\varphi_\infty$(ev.)</th>
<th>$\delta$(Å)</th>
<th>$P_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr (50 ppm)</td>
<td>700</td>
<td>-0.26</td>
<td>11.2</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-0.16</td>
<td>10.9</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.13</td>
<td>15.5</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.21</td>
<td>24.5</td>
<td>0.91</td>
</tr>
<tr>
<td>0 (50 ppm)</td>
<td>500</td>
<td>-0.48</td>
<td>11.1</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.67</td>
<td>15.5</td>
<td>0.72</td>
</tr>
<tr>
<td>0 (5 ppm)</td>
<td>500</td>
<td>-0.36</td>
<td>26.0</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.59</td>
<td>29.3</td>
<td>0.37</td>
</tr>
</tbody>
</table>
The isoelectric temperature, $T_0$, is the temperature at which the concentration of unbound cation vacancies at the surface is equal to the unassociated impurity concentration in the bulk and therefore no bulk potential, $\phi = 0$, is needed to maintain the charge neutrality,

$$\rho(\phi = 0, x) = 0 = eN\left[\mathcal{C}(1-P) + e^{-F^-/kT_0} - e^{-F^+/kT_0}\right]$$  \hspace{1cm} (II-10)

In the theory of Kliewer and Koehler (1965) and those of Frenkel (1946), Lehovec (1953) and Eshelby et al (1958), the effects of adsorbates and the energies of excess vacancies at the surfaces were neglected; Lifshitz et al (1965, 1967) noted that these surface properties would introduce a crystallographic orientation dependency in the potential and charge distributions in the space charge layer. Lifshitz et al (1965, 67) maintained that the number of positive and negative ion sites must be exactly equal and the surfaces become charged only because of a difference in the binding energies of vacancies to sites in the outer layer of ions on a flat surface.

Poeppel and Blakely (1969) and Blakely and Danyluk (1973) assumed the existence of a finite number of ionic surface sites which have a binding energy different from that of sites in the interior of a AgCl crystal. Fermi-Dirac statistics were used to treat the occupancy of the lattice and surface sites. As the surface sites become saturated
with defects at high temperatures, the sites at the surfaces and in the interior are physically indistinguishable and the space potential vanishes. The calculations of Blakely and Danyluk (1973) for AgCl with divalent cation dopants showed that the isoelectric temperature does not vary with the surface site density but decreases with increasing binding energy of the defects to the kink sites; the increase in the binding energy reduces the effective impurity level in the crystal.

Poeppel and Blakely (1969) and Blakely and Danyluk (1973) considered the surface site density as a parameter independent of temperature. However, the site density must be in thermal equilibrium and a function of temperature. For the case of a grain boundary in metals, structural transformations from a "tight" structure to a "loose" structure have been proposed by Gleiter (1970). The calculations of Hasson et al (1972) showed that the grain boundary entropy in aluminum is rather low and of the order of 0.2 erg/cm²°K. However, their calculations ignored the vacancy interactions with the boundary structure. The interaction of the charged defects in ionic materials with the grain boundary will probably increase the boundary entropy and bring about structural variations with temperature.

For a dislocation, Whitworth (1972) has made similar
proposals about the dislocation core as a sink and source of the lattice point defects. The binding energy of the defects to the dislocation core is assumed to be electrostatic in nature and the elastic interactions are ignored. Whitworth (1972) calculated the electrostatic energy for a continuous line of charges, with uniform spacing in the core and with a coaxial space charge cloud in the surrounding. The binding energy of a vacancy to the dislocation core is the change in the electrostatic energy resulting from adding one vacancy into the core. Furthermore, the space charge cloud is treated as a set of discrete point charges rather than a continuous distribution of the charge density.

Since the grain boundary structure of ionic materials is not well established, any simplifying assumptions about the boundary structure in the space charge theories are probably not correct in detail. Furthermore, the space charge phenomena are not treated explicitly in the grain boundary structure models. The coincidence models of Bishop and Chalmers (1968), Wein et al (1969,70,71), Hasson et al (1972) predicted that the effective range of the strain field from the boundary core corresponds to the periodicity of the boundary structural units. The periodicity is about 3-7 atomic spacings and is in the range of the Debye length as predicted from the space charge theory for a nominally doped crystal with 10-100 ppm
aliovalent cation dopants. It is very probable that the presence of a space charge cloud has significant influence on the boundary structure. On the other hand, the atomic arrangements in the boundary core have been shown to affect the space potential and defect distributions. The interrelated problem of the space potential and grain boundary structure can be approached by including the charged defects and their interactions with the ions near the boundary into the computer models of Chaudhari and Charbnau (1972) and Hasson et al (1972).

The experimental evidences of the charged dislocations have recently been reviewed by Whitworth (1975). However, most of the experiments failed to give a quantitative measure of the charged site density at a dislocation core.

The movement of a low angle tilt boundary, which consists of an array of edge dislocations, in an electric field has been observed in Schwensfeir and Elbaum (1965, 1967). Kingery (1974) reported the bowing of pinned high angle boundaries in the electric field direction. However, there is no agreement on the mechanism of the boundary movement in an electric field. Furthermore, Whitworth (1975) pointed out a major problem concerning the magnitude of the electric field within the crystal is due to the experimental conditions. Because of the high conductivity at high temperatures, a
charge redistribution or a current flow will occur in the crystal; thus the permanent field generated from the external circuit cannot be maintained.
II - 3. GRAIN BOUNDARY MIGRATION

Grain boundary migration has been reviewed in Gordon and Vandermeer (1966), Gleiter and Chalmers (1972) and Simpson and Aust (1972). The more prevalent theories of grain boundary migration are reviewed here. Besides, some relevant results of the boundary migration experiments in alkali halides are discussed in this section.

II - 3A. GRAIN BOUNDARY MIGRATION IN PURE MATERIALS

Turnbull (1951) has derived from the absolute reaction-rate theory an expression for the rate of grain growth, $V$, under a driving force, $\Delta F$, across the grain boundary width, $w$,

$$V = \frac{kT}{h} \cdot \frac{e^w \Delta F}{RT} \cdot \exp\left(\frac{S_G}{R}\right) \exp\left(-\frac{Q_G}{RT}\right)$$  \hspace{1cm} \text{(II-11)}$$

Where $Q_G$ and $S_G$ are the enthalpy and the entropy respectively of the migration process; $h$, Planck's constant; $\bar{V}$ is the molar volume; $kT$ and $RT$ have their usual meanings and $e$ is the base of Naperian logarithms.

Gleiter (1969) incorporated the effects of the grain boundary structure in the atomistic model for grain boundary migration. The migration process of an atom from a kink site in a step on the surface of a shrinking grain to a similar site on a growing grain can be separated into several kinetic processes:
(a) dissociation of the atom from the kink site.
(b) atomic diffusion along the step.
(c) dissociation from the step.
(d) diffusion on the surface and desorption into the grain boundary region.
(e) diffusion in the grain boundary and adsorption on the surface of the growing grain.

The grain boundary migration rate, \( V \), is given as

\[
V = \frac{kT}{h} \frac{1}{w^0} \frac{\Delta F}{RT} f \exp \left( - \frac{\Delta G}{RT} \right) \tag{II-12}
\]

where the activation energy, \( \Delta G \), of the boundary migration is treated as the sum of the activation energies in the dissociation and diffusion processes; \( w \) is the boundary thickness; \( b \) is the Burgers vector and \( 0 < f < 1 \), is a function of the step densities on both grain surfaces. For a coherent twin boundary parallel to the close packed planes and with a zero step density, the function, \( f \), vanishes and the boundary is immobile. As the step density increases, \( f \) approaches 1 and the boundary becomes more mobile, Gleiter (1969).

Although the relative step densities in various boundary orientations can be estimated, the absolute value of \( f \) and therefore the pre-exponential term of Eq (II-12) cannot be evaluated with certainty. Furthermore, the activation energy,
$\Delta G$, should be the activation energy of the rate limiting step among the proposed dissociation and diffusion processes instead of the sum of activation energies of all these processes.

These theories implicitly assume that the boundary structures remain invariant as the boundary migrates. This assumption may be justified by considering the kinetic energy of a boundary in motion; the energy increment due to the stress on a boundary; and the absorption of lattice defects into a boundary structure.

Since the boundary structure is already in the minimum energy state, and if the boundary motion is slow enough for the boundary core to re-establish the minimum energy configuration, the structural variation in a moving boundary is unlikely. Furthermore, since the boundary velocity is usually much lower than the sound velocity, the kinetic energy is only a small fraction of the total energy of a grain boundary.

For a boundary motion under a driving force, $2\gamma/R$, due to the boundary energy, $\gamma$, and the radius of curvature, $R$, the energy increment for the atomic movement of a lattice constant, $a$, across the boundary core, is $2\gamma a/R$. Since this energy increment is much smaller than the total energy of the boundary, the stress that initiates the boundary motion
is not likely to cause any significant structural variations.

Since the crystal in which a boundary migrates is not perfectly free of point defects and dislocations, the incorporation of these defects may probably change the boundary structure. For a lattice dislocation density of $N(\#/\text{cm}^2)$ and with a boundary modelled as a dislocation array, it can be shown that the maximum amount of dislocations the boundary can possibly absorb by moving through 1 cm of the lattice, may change the misorientation angle by $\Delta \theta = Nb$ radians, which is about 0.3 degree for a dislocation density of $10^5/\text{cm}^2$ and a Burgers vector, $b = 5 \times 10^{-8} \text{ cm}$. Whereas the change in misorientation angle may have a significant effect on the low angle boundaries which are relatively immobile, it has a small effect on the mobile high angle boundaries. Furthermore, $\Delta \theta$ may well be within the range of scatter in the experimental data of the misorientation angles.

Recently, Pumphrey and Gleiter (1975) prepared some non-equilibrium high angle boundaries formed at recrystallization fronts in a cold worked Ni alloy with 5% Al. The driving force was assumed to be $10^7 \text{ dynes/cm}^2$ from the boundary curvature, and the boundary motion resulted in absorption of the high bulk dislocation density. They observed that the temperature, $T_d$, at which the TEM images of the dislocations in these non-equilibrium boundaries became broadened and
eventually disappear, was $50^\circ - 100^\circ C$ lower than the corresponding temperature for the equilibrium boundaries. The lower temperature, $T_d$, of the dislocation spreading in non-equilibrium boundaries suggests that the mobility of the boundary atoms is higher in a non-equilibrium boundary than in an equilibrium boundary. Since the mobility of the boundary atoms is related to the boundary structure, Pumphrey and Gleiter (1975) concluded that the structures of non-equilibrium and equilibrium boundaries are different. However, their inference is rather qualitative and there is no obvious correlation between the difference in $T_d$ and the difference in atomic mobilities in these two types of boundaries. Furthermore, the driving force for the recrystallization front in the experiments of Pumphrey and Gleiter (1975) is about two orders of magnitude larger than that for the secondary grain growth during sintering. Nevertheless, the observations of Pumphrey and Gleiter (1975) should caution the use of equilibrium structures in the analysis of all boundary kinetic phenomena.

II - 3B. IMPURITY EFFECTS ON GRAIN BOUNDARY MIGRATION

Theory of Lucke and Detert (1957)

Lucke and Detert (1957) were the first to formulate a qualitative theory treating effects of impurities on grain boundary migration. Given that impurities segregate to grain
boundaries, Lucke and Detert (1957) proposed that before a critical combination of driving force and temperature is reached, the impurity atoms are bound to a grain boundary and migrate with it. The rate limiting step in this case is the bulk diffusion of solute atoms to maintain the impurity profile in the boundary region. Above this critical condition of driving force and temperature, the boundary breaks away from the impurity atmosphere and migrates in the same way as in an undoped crystal lattice where the rate limiting step is the atomic diffusion across the grain boundaries, i.e. grain boundary diffusion.

This theory assumes an abrupt break away of the grain boundary from the impurity atmosphere but there is no description of the transition from the low to high velocity regimes. In addition, the theory is applicable only to impurities which segregate to grain boundaries but not to those desorbed from boundaries. The experimental results of Rutter and Aust (1960) and Holmes and Winegard (1961) showed that under certain condition of driving force and dopant level, a solute with a larger diffusion coefficient exerted more drag on a boundary. This is contrary to the prediction of Lucke and Detert (1957).
Cahn (1962) attempted a more rigorous formulation of the impurity drag on boundary migration. The fundamental assumption of Lucke and Detert (1957), that the force exerted by an impurity atmosphere is responsible for the observed drag phenomena, was retained. An interaction energy between impurity atoms and grain boundary was included in the chemical potential of the impurity, from which the impurity flux equation is formulated. Solution of the flux equation gave the impurity distribution in the neighborhood of a moving grain boundary. The drag force on the boundary was then calculated from the impurity distribution profile and the interaction force between impurity atoms and the boundary. Simultaneously but independently of Cahn (1962), Lucke and Stuwe (1962) also treated the impurity drag problem in a similar way. For simplicity, only Cahn's theory is discussed here.

This one dimensional model is based on the following assumptions:

(a) A dilute solution of impurity in the matrix, thus the chemical potential for the impurity is, \[ \mu = RT \ln \chi C \] where C is the dopant concentration and \( \chi \) is the activity coefficient.
(b) There exists an interaction energy, $U$, between the dopant and the grain boundary which is assumed to have the following properties:

1. it is **not** a function of velocity;
2. it is **not** an explicit function of local dopant concentration; but
3. it is a function of the spatial coordinates in the frame of reference of the moving boundary.

(c) The Einstein relation between the diffusion coefficient and the mobility is assumed.

(d) Steady state velocity for the grain boundary,

\[ \frac{\partial C}{\partial t} = \nu \frac{\partial C}{\partial x} \quad \text{(II-13)} \]

where $\nu$ is the boundary velocity.

(e) The diffusion coefficient is a function of spatial distance from the moving boundary.

The chemical potential of the dopant species is given as,

\[ \mu = RT \ln C + U(x) + U_0 \]

where $U_0$ is an additive constant potential term. The impurity flux, $J$, as observed from the reference frame of the moving boundary is
\( \vec{J} = - \frac{DC}{RT} \nabla \mu \)

\[
\begin{align*}
\vec{J} &= -D \frac{dC}{dX} - \frac{DC}{RT} \frac{dU}{dX} \\
&= -D \frac{dC}{dX} - \frac{DC}{RT} \frac{dU}{dX} \\
&\quad \text{(II-14)}
\end{align*}
\]

With the equation of continuity,

\[ \nabla \cdot \vec{J} + \frac{C}{\partial t} = 0 \]

and the boundary conditions that at \( X = \infty \), \( \frac{dC}{dX} = 0 \), \( \frac{dV}{dX} = 0 \) and \( C(\infty) = C_{\infty} \). The impurity profile, \( C(X) \), is governed by the differential equation,

\[
D \frac{dC}{dX} + \frac{DC}{RT} \frac{dV}{dX} + V(C-C_{\infty}) = 0 \]

\[ \text{(II-16)} \]

Since an impurity atom will exert a force \( -\frac{dU}{dX} \) on the boundary, the total impurity drag, \( P_i \), due to the impurity profile, \( C(X) \), is given as

\[ P = -N_v \int_{-\infty}^{\infty} (C(X)-C_{\infty}) \frac{dU}{dX} \, dX \]

\[ \text{(II-17)} \]

where \( N_v \) is the number of atoms per unit volume. The impurity drag, \( P_i \), can be approximated to fit both the high and low velocity extremes as

\[ P_i = \frac{\alpha C_{\infty} V}{1 + \beta^2 v^2} \]

\[ \text{(II-18)} \]

where \( \alpha = 4N_v kT \int_{-\infty}^{\infty} \frac{dx}{D(X)} \sinh \frac{2U(X)}{2kT} \]

\[ \text{(II-19)} \]
Physically, \( \alpha \) is the impurity drag per unit velocity and per unit dopant concentration in the low velocity limit; and \( \beta^{-1} \) is the drift velocity for an impurity atom to move across the grain boundary region. As shown in Eq (II-19), a dopant with either an attractive or a repulsive interaction energy of an equal magnitude exerts the same drag on boundary motion.

Other than the impurity drag, a moving grain also experiences an intrinsic drag, \( P_0 \), due to the lattice resistance, which is proportional to boundary velocity, \( V \), Turnbull (1951),

\[
P_0 = \lambda V
\]

where \( 1/\lambda \) is the intrinsic boundary mobility.

The total drag force, \( P \), is the sum of intrinsic and impurity drag, Fig. (II-2),

\[
P = P_0 + P_i
\]

\[
= \lambda V + \frac{\alpha C_\infty V}{1 + \beta^2 V^2}
\]  

(II-22)

In the low velocity limit, \( V \ll 1/\beta \)

\[
V \sim \frac{P}{\lambda + \alpha C}
\]  

(II-23)

gives a linear relation between the velocity and the drag force.
Fig. II-2: A schematic diagram of the drag forces vs grain boundary velocity.
In the high velocity limit, \( V \gg 1/\beta \)

\[
V \approx \frac{P}{\lambda} - \frac{\alpha c_\infty}{\beta^2 P} \quad \text{(II-24)}
\]

or \( P \approx \lambda V + \frac{\alpha c_\infty}{\beta^2 V} \quad \text{(II-25)}\)

gives a non-linear relation between the velocity and the drag force. Since \( \alpha/\beta^2 \) is proportional to the dopant diffusivity, Eq (II-20), a dopant with a larger diffusivity exerts a larger drag on boundary motion in the high velocity limit. This is consistent with the experimental observations of Rutter and Aust (1960) and Holmes and Winegard (1962).

The drag force, \( P \), has a local maximum of \( P_{\text{max}} \approx c_\infty \alpha/2\beta \) at velocity, \( V_{\text{max}} \approx (1+4\lambda/c_\infty)^{\frac{1}{2}} \beta^{-1} \) and a local maximum of \( P_{\text{min}} \approx 2(\lambda c_\infty)^{\frac{1}{2}} \beta^{-1} \) at \( V_{\text{min}} \approx (c_\infty \alpha/\lambda)^{\frac{1}{2}} \beta^{-1} \). For an experimental driving force, \( \Delta F \), such that \( P_{\text{min}} < \Delta F < P_{\text{max}} \), there exist three possible velocity solutions for Eq (II-22). The intermediate velocity solution is unstable, Cahn (1962).

Theory of Lucke and Stuwe (1971)

Lucke and Stuwe (1971) revised the continuum model and attempted an atomistic model for the impurity drag theory for grain boundary migration. The conclusions drawn from the continuum model are essentially those arrived at in Cahn (1962) and Lucke and Stuwe (1962). The atomistic model considered
the kinetics of atoms in four adjacent lattice planes with
the central two planes as the boundary core. The difference
in the number of atomic jumps in both directions across the
boundary constitutes the boundary motion. The impurity drag
is the product of the interaction energy and the difference
in impurity concentration on one side of the boundary over
that on the other side. Similar to the predictions in the
continuum model, Lucke and Stuwe (1971) showed that in the
atomistic model the impurity drag increases with velocity
until a critical velocity is reached; then it declines with
increasing velocity. However, for a given interaction energy,
the atomistic model predicts a larger drag at low velocities
and a less likelihood of boundary breakaway from the impurity
atmosphere than is predicted from the continuum model. This
is probably because the impurity atoms are confined within
a limited space of four lattice planes, and therefore the
effective interaction energy may well be higher than that in
the continuum model.

Theory of Roy and Bauer (1975)

Roy and Bauer (1975) proposed a two dimensional model for
impurity-controlled grain boundary migration to account for
both the forward and lateral diffusion of impurities. Local
boundary shape and impurity concentration are interrelated
by the appropriate force balance and flux balance for a
boundary moving at a velocity, \( V \). For the force balance, the capillary force due to the boundary curvature, and the drag forces are included to balance the external driving force. For the flux balance, the convective flux of the dopant with a tangential component to the boundary and the diffusive flux due to the concentration gradient are included in the continuity equation.

Using perturbation methods, Roy and Bauer (1975) obtained two coupled equations for the fluctuations in the dopant concentration, \( \Delta C \), and in the boundary shape, \( \Delta y \). These equations together with the initial conditions of a periodic fluctuation in the concentration as well as in the shape, were solved by the appropriate mathematical transformations. It was found that the fluctuations will grow and the boundary shape and concentration profile are inherently unstable, if the boundary velocity exceeds a critical value, \( V_1 \),

\[
V_1 = \frac{4\pi \tau}{\lambda^L} \left( DD' \right)^{\frac{1}{3}} \tag{II-26}
\]

where \( \lambda^L \) is a characteristic wavelength limited by the specimen size in a bicrystal experiment and to the grain size in a grain growth experiment; \( D \) and \( D' \) are the dopant diffusivities tangential and normal to the boundary respectively.
However, when the boundary velocity exceeds another limit, $V_2$, the boundary breaks away from the impurity atmosphere and restores to a planar shape. The concept of abrupt boundary break-away from the impurity cloud, Lucke and Detert (1958), was implicitly assumed here. In Appendix F, we extend the analysis of Roy and Bauer (1975) to include the impurity drag term with a velocity dependence, Cahn (1962).

At the intermediate velocities, $V_1 < V < V_2$, both the boundary shape and impurity profile are unstable; dopant redistribution and clustering occur along the boundary. If impurity diffusion normal to the boundary is much greater than the tangential diffusion, the impurity profile fluctuates greatly but with only a slight variation in the boundary shape. However, if the tangential diffusion is much greater than the normal diffusion, the large shape fluctuation is associated with only a small dopant profile variation.

It was pointed out in Roy and Bauer (1975) that the fluctuations in the unstable boundary shape and concentration profile also affect the initiation of boundary breakaway. However, the perturbation analysis can only give the stability conditions, but as the fluctuations increase in magnitude, the model becomes unrealistic. Since the periodic concentration profile and boundary shape is out of phase by half the
wavelength, the forerunning part of the boundary is dopant depleted and this section will breakaway from the impurity atmosphere and lead to boundary fragmentation.

II - 3C. GRAIN BOUNDARY MIGRATION EXPERIMENTS IN ALKALI HALIDES

The experimental works of Muller (1935), Gibbon (1968), Sun and Bauer (1970a) and Kitazawa (1974) in the area of alkali halides (KCl and NaCl) grain boundary mobility are reviewed here.

Muller (1935) studied the recrystallization rate of NaCl crystals which had been deformed under varying stresses 650-4000 gm/mm² (920-5700 psi) at 400°C. After a certain nucleation incubation time, the recrystallization usually began at a corner of the hot deformed crystal. The recrystallization rate was measured as a function of temperature, ranging from 270-790°C, by hot-stage microscopy. However, there has been no estimate of the driving force for the recrystallization process in the experiments. The important conclusions are:

(1) The recrystallization rate decreases exponentially with the reciprocal temperature.

(2) There is a change in the activation energy for the recrystallization rates. The activation energy in the low temperature range is $17 \pm 3$
kcal/mole and without any systematic variation with the hot deformation stresses. However, the activation energy at high temperatures increases from 30 to 60 kcal/mole as the hot deformation stresses decrease from 4000 $gm/mm^2$ to 800 $gm/mm^2$. Furthermore, the transition temperatures increase from 385°C to 500°C as the deformation stress decrease from 1500 $gm/mm^2$ to 1000 $gm/mm^2$.

(3) An increase in the deformation stress increases the recrystallization rate and decreases the nucleation time.

Gibson (1968) measured the grain boundary mobility of a KCl bicrystal which was cut into a triangular prismatic shape with the grain boundary parallel to the rectangular base. The temperature range was 825-770°C and we estimate the driving force as about 550 dyne/cm². Furthermore, the boundary mobility activation energies, inferred from the experimental data, are 101 kcal/mole and 138 kcal/mole for 18° and 24° twist boundaries respectively. These are unexpectedly high for KCl.

Sun and Bauer (1970a) measured the mobilities of \{100\} tilt boundaries in NaCl bicrystal as a function of driving force, misorientation angle and temperature utilizing a novel method, Sun and Bauer (1970b), wherein hyperbola-like
boundary shapes are generated by capillary forces acting on a boundary originally subtending an acute angle with the free surface. The driving force ranged from $1.3 \times 10^4$ to $5 \times 10^4$ dyne/cm$^2$. Most of the data were limited in temperature range, 700-770$^\circ$C. Furthermore, thermal grooving at high temperatures may pin down the boundary in a thin platelet specimen of 1-2 mm thick. Besides, a significant impurity segregation to the grain boundary may occur during the bicrystal growth in an unprotected ambient atmosphere.

Kitazawa (1974) measured the boundary mobility of KCl by the method of Sun and Bauer (1970b) and reported an activation energy of 57 kcal/mole.

Schwensfeir and Elbaum (1967) measured the grain boundary mobility of NaCl bicrystals by observing the displacement of the low angle tilt boundaries under an electric field, at temperatures ranging from 640$^\circ$C to 600$^\circ$C, and obtained an activation energy of 87.4 kcal/mole. The driving force due to the electric field was estimated to be 75.6 dyne/cm$^2$ at 640$^\circ$C and 352 dyne/cm$^2$ at 600$^\circ$C.

Mobility data of the above mentioned experiments are compared with the current results in the next chapter, Fig. (IV-12).
II - 4. GRAIN GROWTH

Grain growth in a polycrystal can be viewed as simultaneous migration of grain boundaries leading to an increase in the average grain size at the expense of the grain number. Most of the reported grain growth data relate the average grain size, $D(t)$, after an anneal time, $t$, to the initial grain size, $D(t=0)$, by

$$D^n(t) - D^n(t=0) = K_1 t$$ (II-27)

where $K_1$ is a kinetic constant which is a function of temperature and other physical parameters and $n$ is the grain growth index.

Many researchers have attached great significance to the grain growth index, $n$. There have been many proposals of the grain growth mechanisms based on the $n$ values deduced from experimental data. Furthermore, the activation energies and other kinetic parameters of the proposed mechanisms can be extracted from the grain growth data only if the growth index is well established and remains constant throughout the experimental range of temperature and grain size.

However, the analyses of Simpson et al (1971), Chopra and Niessen (1973), Grey and Higgins (1973) showed that the grain growth index, $n$, is not constant over a wide range of grain size or over a wide temperature range even though the impurity drag is the unique rate limiting process for the
grain growth. The temperature and time dependencies of the growth index can be rationalized in terms of the nonlinear relationship between the boundary velocity and the driving force as predicted in the impurity drag theories of Cahn (1962) and Lucke and Stuwe (1962).

In a grain growth experiment, the statistical boundary velocity, $V$, is related to the rate of increase in the average grain size, $D$,

$$ V = \frac{dD}{dt} = \dot{D} \quad \text{(II-28)} $$

and the driving force, $F$, is due to the grain boundary curvature,

$$ F = \frac{\gamma_1}{D} \quad \text{(II-29)} $$

where $\gamma_1$ is a product of the grain boundary energy and a geometric factor.

With Eq. II-28 and II-29 in Eq. II-22, we get

$$ \frac{\gamma_1}{D} = \dot{D} \alpha + \frac{C_\alpha D \dot{\alpha}}{1 + \beta^2 D^2} \quad \text{(II-30)} $$

Solutions of Eq. II-30 in the limiting cases were obtained in Chopra and Niessen (1973). In the low velocity limit, $\dot{D} \ll 1/\beta$,

$$ D^2(t) - D^2(t=0) = K_2 t \quad \text{(II-31)} $$

where $K_2 = 2 \gamma_1 \alpha / (1 + \alpha C_\alpha \lambda)$.
In the high velocity limit, $D \gg 1/\beta$, 

$$D^2(t) - D^2(t=0) = K_3 \left\{ 1 - \exp(-2bt) \right\} \quad (II-32)$$

where $b = \alpha C_{\infty} / \beta^2 \gamma_1$ and $K_3 = \gamma_1 \lambda / b$

The initially small average grain size gives a relatively large driving force for the growing grain. As the grain growth proceeds, the driving force due to the grain curvature decreases and follows the locus of the driving force - velocity relationship. The nonlinearity of this locus gives the time dependence of the growth index.

Simpson et al (1971) observed four different stages of activation energies over a wide temperature range in the grain growth data of metals. The first two low temperature stages are probably due to the nucleation and recrystallization. The last two high temperature stages are normal grain growth in which the growth index is $n = 2$. The change in the activation energies in the last two stages was thought to be caused by structural transformation of the grain boundary. The concept of structural transformation was first introduced by Gleiter (1970) to account for the discontinuity in the measured grain boundary energy as a function of temperature. Similar behavior was also observed in the grain boundary migration of undoped and copper doped aluminum bicrystals, Demianczuk and Aust (1975).

The above discussions of the impurity effects in grain
growth have not accounted for the statistical distribution of grain sizes. However, grain growth cannot occur without a distribution of sizes. For the two dimensional case, Von Neumann (1952) and Mullins (1956) have shown that for a grain with radius, $R$, and $N$ sides, the grain growth equation is given as

$$\frac{dR}{dt} = \frac{M \gamma}{R} \left( \frac{N}{6} - 1 \right)$$

where $M$ is related to the boundary mobility and $\gamma$ to the grain boundary energy.

Hillert (1965) extended the concept of critical grain size to a three dimensional polycrystal. He showed that the grain growth equation for grains with radius, $R$, can be given as

$$\frac{dR}{dt} = M \gamma \left( \frac{1}{R_{cr}} - \frac{1}{R} \right); \quad R_{cr} = \frac{9}{8} \bar{R}$$

where $R_{cr}$ is the critical grain radius and $\bar{R}$ is the average grain size.

Hillert (1965) evaluated the grain size distribution and showed that the maximum grain size cannot exceed $2R_{cr}$. However, for a normal grain growth, the critical grain size can grow according to the rate equation,

$$\frac{dR_{cr}}{dt} = \frac{\gamma M}{R_{cr}}$$

Hillert (1965) introduced the concept of a defect pair which acts as a catalyst for the disappearance of grains.
The defect is composed of a pair of grains, one five-sided and the other seven-sided in a matrix of only six sided grains. He showed that the shrinking of an ordinary grain by means of the defect catalyst is the fundamental process of normal grain growth.

The presence of a second phase usually restricts the normal grain growth. Hillert (1965) showed that if the average grain size achieved by the normal grain growth is less than \( \frac{2}{3} \frac{r}{f} \), where \( r \) is the particle size and \( f \) is the volume fraction of the second phase, an abnormal grain growth can be nucleated by some grains with sizes much larger than the average.

Most of the grain growth experiments in ceramics are complicated by the presence of pores and second phase. Since these other phases are relatively immobile, their presence will generally retard grain growth. The rate limiting transport mechanism for the motion of pores at boundaries dictates the boundary mobility, its activation energy and its dependence on the pore size. It was shown in Shewmon (1964) that the pore mobility, \( M_p \), due to the transport mechanisms of volume diffusion, surface diffusion and vapor transport can be expressed in the form,

\[
M_p = \frac{k_4}{r^m} \exp (- \frac{Q}{RT}) \tag{II-36}
\]
where \( r \) is the pore radius; \( Q \) is the activation energy for the rate limiting mechanism; \( m \), the pore size index, ranges from 2 to 4 according to the nature of the transport mechanism and \( k_4 \) is the pre-exponential factor and is a characteristic of the individual transport mechanism.

It is probable that more than one transport mechanism are operative and each mode of transport has an approximately equal contribution towards the pore motion. In ceramics, the grain boundary and surface diffusivities of the anion are generally larger than those of the cation, whereas the bulk diffusivity of the cation is usually larger than that of the anion. Analogous to the case of ambipolar diffusion, the pore migration in an ionic solid may be rate limited by the slower diffusing species along its fastest path.

Following the assumption of Kingery and Francois (1965) that the average pore size is proportional to grain size, \( r \propto D \), Nichols (1966) derived the grain growth equation as a function of time, \( t \),

\[
D^{m+1}(t) - D^{m+1}(t=0) = t k_4 \exp \left( - \frac{Q}{RT} \right) \quad (II-37)
\]

A cubic rate behavior i.e. \( m+1 = 3 \), is generally observed for ceramic compacts, e.g. \( \text{UO}_2 \) and \( \text{Al}_2\text{O}_3 \). This growth behavior corresponds to the vapor transport mechanism for the pore motion, Nichols (1966).

The maximum driving force necessary for a grain boundary to
break-away from the pore of radius, \( r \), is \( \gamma_{gb} \pi r \), where \( \gamma_{gb} \) is the grain boundary energy. This driving force is supplied by the local curvature at the intersection region between the pore and the grain boundary. After the boundary breaks away from the pore, it moves rapidly until it is stopped by another pore. Pore coalescence at the grain boundary may occur by sweeping up the pores in the matrix and by connecting the existing pores at the boundary by diffusion mechanisms. Pore annihilation can be achieved by vacancy diffusion from pores to grain boundaries which serve as vacancy sinks.

The impurity solubility in ceramics is usually small, e.g., solubility of MgO in Al\(_{2}O_{3}/2\) is about 100 ppm at 1530°C with a solution enthalpy of about 91.5 kcal/mole, Roy and Coble (1968). Since the impurities tend to segregate to grain boundaries, dopant precipitation at grain boundaries as a second phase may occur. The second phase precipitation at grain boundaries also retards the grain growth. However, recently Johnson and Coble (1974) concluded that the MgO enhanced densification in alumina sintering cannot be explained by the second phase theory. Furthermore, Auger spectroscopy did not detect any significant amount of magnesia in the fractured boundaries of sintered alumina; and thus the role of MgO in the sintering of alumina remains unresolved.

Discontinuous grain growth due to the presence of a liquid
phase has been observed in UO$_2$, Lay (1968), and in ferrites, Stuijts (1973), and Paulus (1973). The rapid growth is probably due to the curvature enhanced solubility of the shrinking grain in the liquid phase and the fast diffusion path in the liquid, Lay (1968).
II-5. THERMODYNAMIC AND KINETIC PARAMETERS IN KCl

There has been a significant amount of work on diffusion and electrical conductivity in KCl. Recently, Barr and Lidiard (1970) and Fredericks (1975) made extensive reviews on the subject, and it seems not necessary to repeat here. However, it is useful to list the range of enthalpies in the thermodynamic and kinetic quantities reported in the literature, Table II-3. The data of Fuller et al (1968) and Fuller (1966) are chosen, Table II-1, for Schottky formation energy and \((V_{K}^{+}S_{\text{e}})^{*}\) binding energy because they present a set of self consistent data from the same authors.

Divalent cation impurity diffusion in KCl is due to the association of the dopant ions with the cation vacancies, Lidiard (1970). It can be shown that in the extrinsic temperature range, the probability, \(p\), of association between the divalent cations, of total concentration, \(C\), and the cation vacancy, is given as

\[
p = 1 + \frac{1}{2CK} - \sqrt{(1 + \frac{1}{2CK})^2 - 1}
\]

where the reaction constant, \(K = 12\exp(-\Delta G/kT)\), and \(\Delta G\) is the impurity-vacancy binding energy.

The impurity flux, \(J_{\text{impurity}}\), can be expressed as

\[
J_{\text{impurity}} = D_0 \frac{\lambda(C)}{\partial x} = D_0 \frac{\lambda(C)}{\partial C} \frac{\partial C}{\partial x} = D_{\text{impurity}} \frac{\partial C}{\partial x}
\]

(II-39)
<table>
<thead>
<tr>
<th>Process</th>
<th>Enthalpy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky pair formation</td>
<td>2.3 to 2.6</td>
</tr>
<tr>
<td>K vacancy migration</td>
<td>0.7 to 0.8</td>
</tr>
<tr>
<td>Cl vacancy migration</td>
<td>0.7 to 1.1</td>
</tr>
<tr>
<td>Association of K vacancies and divalent cation dopant</td>
<td>-0.3 to -0.7</td>
</tr>
<tr>
<td>Vacancy pair formation</td>
<td>-1.2 to -1.4</td>
</tr>
</tbody>
</table>
where \( D_0 \) is the diffusivity of the impurity-vacancy complexes. For \( CK \ll 1 \), \( D_{\text{impurity}} \approx 2 D_0 CK \).

Based on the experimental diffusion data of Sr in KCl, de Souza (1969), and the \((\text{Sr}K^V_x \text{K}^V_y)^*\) binding energy, Fuller et al (1968), one can calculate that

\[
\begin{align*}
D_0 K &= 2.5 \times 10^{-2} \exp (-0.77 \text{ev.}/kT) \text{ cm}^2/\text{sec} \quad \text{(II-40a)} \\
K &= 1.836 \exp (+0.57 \text{ev.}/kT) \quad \text{(II-40b)} \\
D_0 &= 0.0138 \exp (-1.34 \text{ev.}/kT) \text{ cm}^2/\text{sec} \quad \text{(II-40c)}
\end{align*}
\]

Rogalla and Schmalzried (1969) also reported the Sr diffusivity in KCl for different dopant levels; the magnitudes of their diffusion data are comparable to those in de Souza (1969). In addition, the Sr solubility in KCl is reportedly high; the solubility limit is \( 5.95 \times 10^5 \exp (-1.26 \text{ ev.}/kT) \) at temperatures between 400 and 600°C, Rogalla and Schmalzried (1969). However, Sr and Cd precipitation in NaCl were reported in Abaev (1972) and Spengler and Kaiser (1974) respectively.

Furthermore, the impurity diffusion coefficients of inert gases, \( \text{H}_2\text{O} \), \( \text{OH}^- \), monovalent and aliovalent ions in KCl, as reported in the literature, are shown in Fig. (II-3).
Fig. II-3: Impurity diffusion data in KCl.
References to the impurity diffusion data in KCl, Fig. (II-3).

<table>
<thead>
<tr>
<th>Diffusant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Schmeling (1965)</td>
</tr>
<tr>
<td>Kr</td>
<td>Pronko and Kelly (1972)</td>
</tr>
<tr>
<td>H₂</td>
<td>Grundig and Ruhenbeck (1972)</td>
</tr>
<tr>
<td>H₂O</td>
<td>Ruhenbeck (1967)</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Hanson (1970)</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Arai and Mullen (1966)</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Arnikar and Chemla (1956)</td>
</tr>
<tr>
<td>Tl⁺</td>
<td>Tierman and Wuensch (1971)</td>
</tr>
<tr>
<td>Tl⁺</td>
<td>Dobrovinskaya and Podorshanskaya (1966)</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>Haneda et al (1968)</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Allen and Fredericks (1970)</td>
</tr>
<tr>
<td>I⁻</td>
<td>Beaumont and Cabane (1961)</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Allen and Fredericks (1973)</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>de Souza (1969)</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Keneshea and Fredericks (1965a)</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Keneshea and Fredericks (1963, 64)</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>de Souza (1969)</td>
</tr>
<tr>
<td>Eu²⁺</td>
<td>Reisfeld and Honigbaum (1968a)</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Geguzin et al (1966)</td>
</tr>
<tr>
<td>Bi²⁺</td>
<td>Reisfeld and Honigbaum (1968b)</td>
</tr>
<tr>
<td>Diffusant</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>Reisfeld and Honigbaum (1968b)</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>Keneshea and Fredericks (1965b)</td>
</tr>
</tbody>
</table>
CHAPTER III RESEARCH OBJECTIVES

The original stimulus for this investigation was the problem of secondary grain growth in the hot deformed alkali halides for laser window applications. Superior mechanical properties in halide materials, without a compromise in the optical properties, were achieved by the microstructure development and grain size refinement during the hot deformation. However, a rapid secondary grain growth leads to the deterioration of the mechanical properties and the eventual material failure.

A detailed characterization of KCl grain boundary mobility over a wide temperature range is not available in the literature. Thus, experimental work, characterizing the grain growth and measuring the grain boundary mobility are required. Experimental results are to be compared with the impurity drag theories for grain boundary migration. Features pertinent to the grain boundary migration in ionic solids are incorporated in the impurity drag models. The impurity drag mechanisms are identified as the space charge potential and the strain field interaction.

For experimental samples, KCl single crystals with the desired dopant and the dopant level, which are not commercially available, are to be grown by the Czochralski method. Furthermore, the deformation structures of halides are to be
characterized to elucidate the relationship between the grain size and the deformation stress, the deformation temperature, the impurity or dopant concentration, and the crystal orientations.
CHAPTER IV  EXPERIMENTS AND RESULTS

EXPERIMENTS

IV - 1. HOT DEFORMATION OF ALKALI HALIDES

Polycrystalline KCl and KBr with low angle subgrain boundaries were prepared by the hot deformation of single crystals. The deformation temperatures ranged from 21 - 740°C and the resultant subgrain sizes ranged from 3 to 60μm.

Potassium chloride crystals of various dopant levels and impurity levels were used. High purity single crystals of KCl and KBr were purchased from Optovac\(^1\). Strontium-doped and bromine-doped crystals were obtained from Raytheon\(^2\) and AFCRL\(^3\), respectively. Calcium and strontium-doped KCl crystals were also grown in our laboratory from Fisher reagent grade powders by the Czochralski method while under a nitrogen atmosphere. The Sr-doped crystal from Raytheon was grown from a melt concentration of 200 molar ppm; while the Sr- and Ca-doped crystals grown in our laboratory had melt concentrations of 470 and 670 molar ppm, respectively. The crystal-melt distribution coefficients for Sr in KCl were reported by Chin et al (1973), Miles et al (1973) and Ikeya and Itoh (1968) and vary from 0.14 to 0.25. We have assumed

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\(^{1}\) Brookfield, Mass.

\(^{2}\) D. Readey, Waltham, Mass.

\(^{3}\) H. Posen, Bedford, Mass.
0.20 as the distribution coefficient to calculate the impurity concentration in crystals. Electrical conductivity measurements on the Raytheon crystal gave an approximate agreement with this calculation. Harrison et al (1973) reported the impurity levels in KCl crystals from Optovac\textsuperscript{4}, Table IV-1. Furthermore, Neutron activation analysis\textsuperscript{4} indicated that oxygen contents in all our Samples are less than 1 ppm.

The deformation was carried out in a cylindrical steel die in vacuum. Grafoil\textsuperscript{5} gaskets were placed between the sample surfaces and the die pistons to eliminate chemical and physical adhesion. The die was heated by a rf generator; the temperature was monitored by Chromel-Alumel thermocouples and controlled to within ±3°C of the desired temperature during the deformation. The strain rate was manually controlled to $10^{-3} \pm 5 \times 10^{-4}$ sec\textsuperscript{-1}. Crystals were deformed in the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions to a final true strain of 70 - 120%. Samples were hot-ejected from the die and quenched in the ambient atmosphere.

Polishing and controlled etching by alcohol diluted water revealed grain boundaries and substructures. Grain sizes were reported as the average linear intercepts.

\textsuperscript{4} H. Priest, AMMRC, Watertown, Mass.

\textsuperscript{5} Union Carbide pyrolytic graphite paper 0.01 inch thick.
Table IV-1

Impurity Levels, in Atomic ppm, in KCl Crystals from Optovac\textsuperscript{1}, Harrison et al (1973).

<table>
<thead>
<tr>
<th>Species</th>
<th>ppm(atomic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba</td>
<td>2</td>
</tr>
<tr>
<td>Ca</td>
<td>2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.5</td>
</tr>
<tr>
<td>Cs</td>
<td>5</td>
</tr>
<tr>
<td>Rb</td>
<td>90</td>
</tr>
<tr>
<td>Na</td>
<td>25</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
</tr>
<tr>
<td>Sr</td>
<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>1</td>
</tr>
</tbody>
</table>

Total aliovalent cations: 11

\textsuperscript{1} Brookfield, Mass.
The starting crystals typically had diameter to height ratios, $D/H$, of 1 to 2, so that by the end of the forging $D/H$ was typically 10 or more. This causes a significant hydrostatic constraint to develop because of the friction between the punch faces and sample. Flow stresses were corrected for this effect using the approximate relation from Hill (1950)

$$\sigma_y = \frac{P}{(1 + \frac{\mu D}{3H})} \quad (IV-1)$$

where $\sigma_y$ is the flow stress, and $P$ is the average forging pressure. The coefficient of friction, $\mu$, was taken as 0.12 for the Grafoil5 liners. A typical stress-strain curve during forging, Fig. (IV-1), shows that after about 40% strain the flow stress approached a constant value.
Fig. IV-1: Stress-strain relation during the hot deformation of undoped KCl. The increase in stress after the steady state region results from die wall constraint.
IV - 2. SECONDARY GRAIN GROWTH EXPERIMENTS

Grain boundary migration rates of undoped and Ca-, Sr- and Br-doped KCl were measured by the secondary grain growth of the hot deformed samples. Only the samples deformed in the $<100>$ direction were used for grain growth. The samples were cut to $3\times8\times12\text{(mm)}^3$ size. Only the samples with uniform subgrains and no detected large grains were used in the experiment. At the beginning of the anneal, the sample was placed in the furnace hot zone of the desired temperature; and the sample was hot ejected from furnace and quenched in the ambient atmosphere at the completion of the anneal. The furnace temperature was controlled to within $0.5^\circ\text{C}$ of the desired temperature by a silicon controlled rectifier. From the sample size and other appropriate heat transfer parameters, it can be shown that it takes less than 20 seconds for the sample to reach the furnace temperature. This transient time is small as compared to the anneal time, which ranged from one hour to three days. The annealed samples showed several big (mostly isolated) grains grown among the small grain matrix as shown in Fig (IV-2).
Fig. IV-2: Microstructures of hot-forged KCl, doped with about 95 ppm Sr, (a) before anneal and (b) after 1 hr. anneal at 448°C.
Fig. IV-1: Microstructure of un-doped Si, showing:
(a) before annealing at 1200°C for 1 hr. exposure at 645°C.
(b) after 1 hr. exposure at 645°C.
RESULTS

IV - 3. MICROSTRUCTURES OF HOT WORKED ALKALI HALIDES

The subgrain development during the hot deformation of KCl and KBr have been reported in Cannon et al (1975) and Yan et al (1974). The essential features of these reports are summarized here:

(a) **Deformation Texture**: There is a strong crystallographic texture retained in the deformed samples. The textures were all consistent with deformation textures expected from the theoretical work of Chin (1973). Crystals forged in the \( \langle 100 \rangle \) direction retained that texture after forging. Crystals initially oriented in either the \( \langle 110 \rangle \) or the \( \langle 111 \rangle \) direction tended to rotate to give a final orientation of \( \langle 110 \rangle \), Bowen et al (1973).

(b) **Grain Shape**: As shown in Fig. (IV-3), all the crystals exhibited a relatively equiaxed subgrain structure after forging. This is believed to be related to the fact that the severe geometrical constraint from the very small height to diameter ratio requires slip on several systems, including the secondary systems. In contrast, in single crystals with larger height to diameter ratios, slip can be restricted to one or two slip systems leading to blocky subgrains with a bimodal size distribution.
Fig. IV-3: Microstructures of uniform grain size and equiaxial grain shapes. Ca-doped KCl, deformed at 242°C and 3642 psi.
(c) **Subgrain Boundary Misorientation**: Although the subgrain structures tend to be equiaxed, there appear to be two different ranges of subgrain boundary misorientation angle. In Fig. (IV-4) it can be seen that some of the boundaries have a lower misorientation angle than others. This can be appreciated by examination of the triple junctions. When a low angle sub-boundary intersects a higher angle one the dihedral angle between the two high angle boundaries is very much greater than 120°, this indicates that the surface energy of the lower angle boundaries is very much smaller than that of higher angle sub-boundaries. However, both of these boundaries are low angle sub-boundaries resulting from deformation and are not high angle or recrystallized grain boundaries. There is a tendency for patches of these lower angle boundaries to fall within a larger subgrain which are surrounded by the higher angle types of boundary. This is indicated in Fig. (IV-5), which is from an undoped sample forged at high temperature and low stress so that the mean subgrain size is of the order of 40 µm.

(d) **In-grain Dislocation and Grain Size Distribution**: Under the proper circumstances the lower angle subgrain boundaries can be resolved into individual etch pits,
Fig. IV-4: Microstructures showing high and low angle subgrain boundaries. Ca-doped KCl, deformed at 242°C and 3640 psi.
Fig. IV-5: Microstructures showing a patch of subgrains, with lower angle boundaries, surrounded by a higher angle boundary. Undoped KCl deformed at 635°C, 390 psi.
as in Fig. (IV-6). Counting the etch pits in this micrograph gives a misorientation angle of the lower angle sub-boundaries of the order of $0.01^\circ$. In addition, the free dislocation density within the subgrains was found to be about $10^6$ cm$^{-2}$ from this figure. It must be emphasized that resolving any of the boundaries into etch pits proved to be very difficult; usually etching only revealed the light, but continuous subgrain boundaries shown in previous micrographs. Some of the scatter in the subgrain size data undoubtedly relates to the difficulty in resolving all of the lower angle sub-boundaries; the result is that the mean grain size reported tends to be an average between the finer cell size delineated by the low angle sub-boundaries and a larger size which might be obtained by counting only those grains surrounded by higher angle sub-boundaries. Measuring either of these extremes is difficult because there is not always a clear distinction between these two types of grains. However, it is generally found that the size of the low angle subgrains or cells is particularly uniform. This can be seen in Fig. (IV-7), which was taken out of focus to accentuate the small angle boundaries; this gives a visual picture of a much greater uniformity of the subgrain or
Fig. IV-6: Photomicrograph resolving the dislocation etch pits and subgrain boundaries. Undoped KCl deformed at 670°C, 575 psi and in the \langle111\rangle direction.
Fig. IV-7: Uniform fine grain microstructures in samples deformed at low temperatures. Photomicrographs were taken slightly out of focus to emphasize small subgrains. (a) Ca-doped KCl forged at 246°C and 3640 psi; (b) Undoped KBr forged at 21°C (room temperature) and 4660 psi. Both samples were forged at the 100 direction.
cell size than is indicated in some of the other figures where the low angle boundaries are less clearly resolved.

(e) **Temperature Dependence of the Flow Stress:** The range of steady state flow stresses can be seen in Fig. (IV-8) in which the normalized flow stress, $\sigma/E$, is plotted against the homologous temperature at which the experiments were done. It can be seen that the data for the undoped KBr and KCl are essentially identical on this plot. Even at the high stresses it appeared to still be in the range where steady state creep was obtained; however, at the lowest temperatures and highest stresses the behavior is closely approaching non-steady state yielding behavior. Nevertheless, the controlling creep or deformation mechanism was different over the range tested. Although most of the stress range is in the exponential creep region, however at the low stress, high temperature end the deformation is expected to satisfy a power law creep relation. In NaCl Blum (1973) and Burke (1968) estimated the transition stress between the power law and exponential creep regimes to be about 300 and 1000 psi respectively which would be $\sigma/E$ of about $0.7 \times 10^{-4}$ and $2.3 \times 10^{-4}$. The flow stresses for the KCl samples doped with divalent impurities were higher as expected from solute hardening.
Fig. IV-8: Deformation stress vs deformation temperature of KCl and KBr. Note that the data for the undoped KCl and KBr are identical, and that KCl is strengthened by the dopants.
Stress Dependence of the Subgrain Size: As has been found in many other materials, the steady state subgrain size is primarily a function of the applied stress. The results of the tests on KCl from our laboratory as well as samples from Kulin et al (1974), from Klausutis et al (1974) and from Koepke et al (1974) are shown in Fig. (IV-9), which shows the subgrain size vs. the steady state flow stress. This graph includes samples of undoped KCl as well as samples doped with Sr or Ca in the 100 - 5000 ppm range, and also a datum from the sample of KBr\textsubscript{0.68}Cl\textsubscript{0.32}. The results plotted from other laboratories include data on undoped KCl as well as for materials doped with a few percent monovalent impurities of either bromine or rubidium or with small levels of divalent europium. As can be seen a single curve satisfactorily fits the stress-subgrain size data for all of the various materials. The mode of hardening, whether from divalent impurities which induce electrostatic effects, or monovalent impurities, or simply from the development of dislocation networks appears not to significantly affect the stress-subgrain size relation.

The simple inverse relation between subgrain size and stress exists over the whole temperature range
Fig. IV-9: Subgrain size, $d$, vs deformation stress, $\sigma$, in undoped and doped KCl, showing a relation of $d \propto \sigma^{-1}$. 
tested. This is surprising since it includes materials tested at low stresses in the power law creep region and at high stresses in the exponential region.

Finally, it can be seen that the crystal orientation has no discernable effect on the subgrain size; results for \(\langle 100 \rangle\), \(\langle 111 \rangle\), and \(\langle 110 \rangle\) tests are shown and these have been done at both relatively high and low temperatures. Particularly at the higher temperatures virtually no difference in the actual flow stress for a given temperature and strain rate could be found for the \(\langle 100 \rangle\), \(\langle 111 \rangle\), or the \(\langle 110 \rangle\) oriented crystals. This further suggests that because of the strong geometrical constraints on the samples that both primary and secondary slip were required in all of the forgings.

A similar curve is shown for the KBr samples in Fig. (IV-10) in which the behavior is essentially identical to that in KCl. These results are compared with those of other halides reported in the literature, particularly for NaCl, in Fig. (IV-11). The present results are shown to agree particularly well with the results of Burke (1968) on NaCl polycrystals. The subgrain sizes measured in other single crystal experiments appear to be slightly higher than those found in the present study. This is likely due to the tendency
Fig. IV-10: Subgrain size vs deformation stress in undoped KBr.
Fig. IV-11: Subgrain size vs deformation stress in alkali halides.
to get simpler, blockier subgrains when only duplex slip occurs for \langle 100 \rangle crystals with a larger height to diameter ratio; the behavior for highly constrained single crystals is apparently more like that of poly-crystals.

An attempt to normalize the stress subgrain curves for the various materials by using \( \sigma/E \) produced two unexpected results. Unlike the \( \sigma/E \) vs. \( T/T_m \) plot, the normalization using \( \sigma/E \) did not bring the curves for KCl and KBr together. Perhaps more surprisingly, because of the strong temperature dependence of Young's modulus, \( E \), for the alkali halides, Slagle and McKinstry (1967), the plots of grain size, \( d \), vs \( \sigma/E \) more nearly fit a relation of \( d \propto (\sigma/E)^{-2} \).

(g) Dynamic recrystallization during hot deformation: At about 80% of the melting point or above occasional secondary grains form and grow into the subgrain matrix. When this happens during deformation, new subgrain structures may develop within the secondary grains. However, at higher temperatures approaching the melting point, the rate of recrystallization becomes sufficiently fast that mixed microstructures are seen and there are always significant regions in which the steady state subgrain structure is never achieved.
IV - 4. GRAIN BOUNDARY MOBILITY MEASUREMENTS

The annealed samples showed several big (mostly isolated) grains grown among a matrix of small grains. The low angle boundaries of the small grains are immobile; and the surface energy of these subgrain boundaries provides a constant driving force for the motion of high angle boundaries.

The grain boundary energy and misorientation angle of the subgrains was evaluated indirectly. Measurements of Class and Machlin (1966) showed that the grain boundary energy for $10^\circ$ twist boundaries was about 110 erg/cm$^2$. The growing grains must have high angle boundaries as suggested by the etching patterns; and thus we assumed that the grain boundary energy of the growing grain was 110 erg/cm$^2$. The dihedral angle between the growing grain boundary and the surrounding subgrain boundary was about $160^\circ$. Therefore, the grain boundary energy of the subgrains is about 1/3 that of the growing grain, i.e. about 37 erg/cm$^2$. This value of the grain boundary energy corresponds to 1-3$^\circ$ misoriented boundaries, as extrapolated from the data of Class and Machlin (1966). The grain to grain misorientation predicted here is also consistent with that determined from texture studies, Bowen et al (1973).

Based on the cleavage propagation data at $20^\circ$C and $-196^\circ$C, Class and Machlin (1966) estimated the temperature coefficient
of the grain boundary energies, $d\gamma_{g.b.}/dT$, as $-0.091$ erg/cm$^2$ $^0K$. If this value of $d\gamma_{g.b.}/dT$ is included in the boundary mobility calculations, the activation energies of the boundary mobility will be increased by less than 0.2 kcal/mole. However, the $d\gamma_{g.b.}/dT$ data are not available at high temperatures. Furthermore the scatter in the cleavage propagation data made the precise estimation of the temperature coefficient more difficult. Consequently, the temperature dependence of the grain boundary energy is not included in the mobility calculations.

The qualitative result from bicrystals of KCl doped with 0.17 at. $\%$ CaCl$_2$ showed that the grain boundary energy is reduced to 54% of that in undoped samples, Class and Machlin (1966). Impurity segregation to the grain boundary during the bicrystal growth probably occurred, and the dopant level may well exceed the solubility limit in low temperatures. Since there is no quantitative measure of the impurity effects in the grain boundary energy, the boundary energy of the undoped sample is used for mobility calculations.

In computing the grain growth velocity, the area of the largest grain was chosen because of geometrical and grain growth incubation time considerations. The grain growth velocity, $V$, is given by
\[
V = \frac{(A/n)^{1/2} - r}{t}
\]  \hspace{1cm} (IV-3)

where \( A \) is the area of the largest grain found; \( r \), the neighboring small grain radius; and \( t \), the annealing time.

The driving force, \( \Delta F \), for the motion of high angle boundaries is due to the surface energy of the neighboring subgrain boundaries,

\[
\Delta F = SV \frac{\gamma_{GB}}{L} = \frac{2 \gamma_{GB}}{L}
\]  \hspace{1cm} (IV-4)

where \( SV \), the surface area per unit volume is related to \( L \), the average length of grain intercepts, Underwood (1970), and where \( \gamma_{GB} \) was estimated above as 37 erg/cm\(^2\).

Each value of grain boundary mobility data plotted in Fig. (IV-12) is computed from

\[
M \equiv \frac{V}{\Delta F} = \left( \frac{(A/n)^{1/2} - r}{t} \right) \frac{2 \gamma_{GB}}{L}^{-1}
\]  \hspace{1cm} (IV-5)

Several features of the grain boundary mobility data are noted:

1. The apparent activation energy for boundary migration in undoped KCl at the temperature range investigated is about 35.4 kcal/mole. The boundaries in Ca- and Sr-doped KCl also have the same mobility activation energy above some transition temperature, Table IV-2.
Fig. IV-12: Grain boundary mobility of hot deformed KCl. Sources of single crystals before forging are in parantheses. Data of Gibbon (1968) and Kitazawa (1974) are for KCl bicrystals; Koepke et al (1974) for hot forged KCl; Sun and Bauer (1970a) and Schwensfeir and Elbaum (1967) for NaCl bicrystals.
2. The 45 molar ppm Sr-doped and 95 molar Sr-doped KCl have the same boundary mobility at low temperatures. The 135 molar ppm Ca-doped samples have a lower mobility. However, all doped samples have the same mobility activation energy of 18.6 kcal/mole.

3. The grain boundary mobility in KCl with 5 molar % KBr is at least an order of magnitude higher than that in samples with divalent impurities of a much lower dopant level. However, the boundary mobility in Br-doped KCl is much lower than that of the undoped samples. This shows that the Br dopant can limit the boundary mobility to a certain extent. The activation energy in the mobility data of Br-doped KCl is about 9.4 kcal/mole.

4. The present mobility data and their extrapolations in undoped KCl are higher than those observed by Gibbon (1968) and Kitazawa (1974) for KCl and Sun and Bauer (1970 a) for NaCl.

5. However, mobilities extrapolated from our data for doped and undoped samples are well below the room temperature mobility reported by Koepke et al (1974).

6. At high temperatures, the growth rate is so fast that the growing grains quickly impinge upon each other. The shapes of these secondary grains are irregular and non-equiaxial.

7. At low temperatures, the growth rate becomes nucleation limited.
### Table IV-2

Experimental Data of KCl Grain Boundary Mobility, 
\[ M = M_0 \exp\left(-\frac{Q}{RT}\right) \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature Range °C</th>
<th>Q kcal/mole</th>
<th>( M_0 (\text{cm} \cdot \text{sec}) (\text{dynes})^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl undoped</td>
<td>200-350</td>
<td>35.4</td>
<td>( \text{2.8} \times 10^4 )</td>
</tr>
<tr>
<td>Sr-doped (95 ppm)</td>
<td>250-500</td>
<td>18.6</td>
<td>( \text{1.7} \times 10^{-5} )</td>
</tr>
<tr>
<td>Sr-doped (95 ppm)</td>
<td>500-700</td>
<td>35.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Sr-doped (40 ppm)</td>
<td>250-350</td>
<td>18.6</td>
<td>( \text{1.7} \times 10^{-5} )</td>
</tr>
<tr>
<td>Sr-doped (40 ppm)</td>
<td>350-500</td>
<td>35.4</td>
<td>18</td>
</tr>
<tr>
<td>Ca-doped (135 ppm)</td>
<td>300-430</td>
<td>18.6</td>
<td>( \text{6.8} \times 10^{-6} )</td>
</tr>
<tr>
<td>Ca-doped (135 ppm)</td>
<td>430-600</td>
<td>35.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Br-doped (5%)</td>
<td>350-550</td>
<td>9.7</td>
<td>( \text{4.3} \times 10^{-7} )</td>
</tr>
</tbody>
</table>
CHAPTER V  ANALYSIS

In this chapter, we analyse the grain boundary mobility data in terms of the impurity drag theories reviewed in Chapter II. For impurity limited boundary motion, the impurity-grain boundary interaction energy as well as the impurity diffusivity, rather than the boundary core structures and properties, primarily controls the grain boundary mobility.

In contrast to a metal, an ionic solid presents a unique feature, a charged grain boundary and a space charge double layer in the region adjacent to the grain boundary, as was reviewed in Chapter II. Consequently, the interaction potential between aliovalent dopants and the grain boundary can be electrostatic as well as mechanical (strain) in nature. Furthermore, the electrostatic and the strain field interaction potential are implicitly coupled by Poisson's equation.

The transport mechanism of the charged aliovalent dopant ions and the vacancies in the space charge region is another challenging problem in ionic solids. This leads to the discussion of the dipole interaction between the space charge electric field and the impurity - vacancy complexes. In addition, we have to address ourselves to the problem of the velocity dependence of the interaction potentials. These are new features and pertinent to grain boundary mobility in ionic solids.
V - 1. NATURE OF IMPURITY - GRAIN BOUNDARY INTERACTION

In the impurity drag theories of Cahn (1962), Lucke and Stuwe (1962), the interactions between the impurity atoms and the grain boundary are important assumptions. For grain boundary migration in metals, the interaction energy has generally been assumed to be a mechanical or strain field interaction. However, it is shown in the experimental results that divalent cation impurities have a much stronger effect than monovalent impurities in retarding the grain boundary migration. Furthermore, the space charge theories predict that crystal interfaces at thermal equilibrium with the bulk crystal are electrostatically charged. Consequently, we propose that the impurity-boundary interaction energy is mainly due to the electrostatic interactions between the space charge cloud and the moving grain boundary.

In the case of a monovalent dopant, the strain field interaction, rather than the space charge potential, is more likely to be the dominant interaction potential between the dopant and the grain boundary. It is generally agreed that the strain field interaction potential originates from the size mismatch between the dopant and the matrix ions, Lucke and Stuwe (1962). However, for an aliovalent dopant with a significant ionic size mismatch with the matrix ion in the same sublattice, both the strain field and the
electrostatic interactions are significant. The strain field interaction potential affects the distribution of the charged impurity ions and therefore, the electrostatic potential in the grain boundary region. In section (V-7), we analyse the coupled effects of strain and electrostatic interactions on grain boundary mobility. But until then we assume that the space charge potential is the only interaction potential between the grain boundary and the dopant.
V - 2. VELOCITY DEPENDENCE OF THE IMPURITY - GRAIN BOUNDARY INTERACTION ENERGY

The origin of the space charge cloud is essentially due to the difference in the distributions of the charged species, namely the unassociated Sr ions, and K and Cl vacancies. The space charge potential, $\phi$, must satisfy Poisson's equation,

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\epsilon}.$$  

However, $\rho(x)$ is composed of two major components, namely free Sr ions, $\text{Sr}^+_k$, and free K vacancies, $\text{V}_k^-$. The contribution of free Cl vacancies, $\text{V}_{\text{Cl}}^-$, is not significant in Sr-doped KCl in the extrinsic temperature region. Furthermore, the relative proportion of $\text{Sr}^+_k$ and $\text{V}_k^-$ in the total charge density, $\rho(x)$, also varies with temperature. At temperatures above the isoelectric temperature, the $\text{V}_k^-$ constitutes the bulk of the charge density whereas at temperatures below the isoelectric temperature, the charge density is mainly due to the $\text{Sr}^+_k$ impurity cloud.

When the grain boundary migrates, the space charge potential will be affected by the variation of the impurity distribution which is a function of the boundary velocity. This will introduce a velocity dependence to the interaction energy, $U$, between the dopant and a moving boundary. We can estimate the scope of the velocity dependence in the interaction energy by considering the extreme case of
a high boundary velocity that the total Sr impurity profile breaks down to a uniform distribution. However, the vacancies, because of their relatively high diffusivities, can adjust themselves to the distribution profiles of the minimum energy.

With the additional assumption of uniform Sr distribution,
\[ n_1(x) = n_f(x) + n_b(x) = \text{constant} \]
where \( n_f \) and \( n_b \) are the density of unassociated \((\text{Sr}^*_K)\) and associated \((\text{Sr}^*_K V^*_K)^*\) respectively, the free energy in the grain boundary region is minimized as shown in Appendix A.

An interesting result of the free energy minimization is that the equilibrium constant of the impurity-vacancy association reaction is invariant in the grain boundary region
\[
\frac{[\text{Sr}^*_K V^*_K]^* (x)}{[V^*_K(x)]^* \text{Sr}^*_K(x)} = 12 \exp \left(-\frac{B_+}{kT}\right) = \text{constant}
\]
where \( B_+ \) is the impurity-vacancy binding energy.

The Poisson's equation in the break-away grain boundary region was solved to give the space charge potential distribution, Appendix A.

At temperatures above the isoelectric temperature, the calculated potential distributions are very similar to those given in Kliewer and Koehler (1965) for a stationary boundary, Fig. (V -1). This is because the K vacancies, which constitute the majority of the charge density, are free to adjust
Fig. V-1: Velocity dependence of the space charge potential distribution at 700°C ($> T_0$).
themselves to the minimum free energy configuration. However, the unassociated Sr concentration profile is restricted by the condition of uniform total Sr\textsubscript{K} concentration. The impurity and vacancy profiles in the region of a break-away grain boundary are compared with those in the region of a stationary grain boundary, Fig. (V -2).

However, at temperatures below the isoelectric temperature, the impurity cloud has a larger proportion of the total charge density, and the potential distribution for a break-away boundary is different by about 30\% of that for a stationary boundary, Fig. (V -3). The distribution profiles of the charged species for the break-away boundary are compared with those in the stationary boundary in Fig. (V -4). Due to the condition of uniform total impurity concentration, the \([\text{Sr}_K]\) in the break-away grain boundary approaches the total impurity concentration as \(x/\delta \to 0\). However, the \([\text{Sr}_K]\) in a stationary grain boundary is free to exceed the bulk impurity concentration.

Since the space charge potential distributions for this high velocity boundary, do not deviate significantly from the potential distributions for a stationary boundary, the interaction energy between the impurity cloud and a moving boundary can be approximated by the space charge potential associated with a static grain boundary.
Fig. V-2: Redistributions of the unassociated Sr ions and K vacancies at 700°C as the grain boundary migrates very rapidly.
Fig. V-3: Velocity dependence of the space charge potential distribution at 200°C ($< T_0$).
Fig. V-4: Redistribution of the unassociated Sr ions and K vacancies at 200°C as the grain boundary migrates very rapidly.
V - 3. TRANSPORT MECHANISMS OF SR IONS IN THE SPACE CHARGE POTENTIAL

In Appendix B, it is shown that the space charge contributions to the diffusivity and conductance parallel to the grain boundary are modest in magnitude (<10^3 D_1) and limited in range (10 - 200 Å). However in the case of the solute drag theory of grain boundary migration, we are concerned with the impurity diffusion normal to the grain boundary.

There are several mechanisms which can influence the transport of Sr ions in the space charge potential field. Each mechanism is discussed separately to elucidate its contribution to the Sr flux. Furthermore, we attempt to relate the Sr ionic mobility to the diffusion coefficient relevant to the particular transport mechanism being examined.

(a) The Electric Field Effects: In a space charge potential, the unassociated Sr impurities, Sr*, which are positively charged, experience an electrostatic force in the field direction. One is tempted to relate the diffusivity of Sr ions, D_{Sr}, and the mobility of Sr ions, M_{Sr}, by the Einstein relation,

\[ \frac{M_{Sr}}{D_{Sr}} = \frac{e}{kT} \]  

However, based on the Sr diffusion data in a cleaved NaCl crystal under a uniform electric field,
Chemla (1956) reported that $\frac{M_{Sr}}{D_{Sr}}$ is much less than $e/kT$. Howard and Lidiard (1964) studied the kinetics of Sr transport in a field and concluded that

$$\frac{M_{Sr}}{D_{Sr}} = \frac{e}{kT} \frac{10W_3}{W_1 + 3.5W_3}$$

where $W_3$ is the dissociation frequency of the vacancy-impurity complex and $W_1$ is the jumping frequency of the associated vacancy from one nearest neighbor position of Sr to another. Consequently, the Sr flux due to the space charge electric field is

$$J_E = \frac{D_{Sr}C}{kT} \frac{10W_3}{W_1 + 3.5W_3} \frac{d\phi}{dx}$$

(b) The Electric Field Gradient Effects: In the space charge region, the electric field is highly non-uniform, varying from about $10^6$ volt/cm at the surface to $10^2$ volt/cm or less at about 10 - 20 Å in the bulk. The field gradient exerts an attractive force on the dipole in the $(Sr_{KV}^*)$ complexes. The interaction between the electric field and the dipoles was neglected in the space charge theory of Kliewer and Koehler (1965). The dipole interaction has been treated in Appendix C and the derivations are summarized here. It was assumed that the impurity-vacancy complexes can be classified
according to their dipole orientation with respect to the electric field. The interactions between the dipoles and the electric field gradient are included in the free energy calculation. The free energy of the system, which includes the formation energies of the charged species and dipoles, and their interactions with the field, is minimized following the procedures used in Kliewer and Koehler (1965). Poisson's equation is solved numerically and the electric field is evaluated to illustrate the effects of the field - dipole interactions. However, further refinement of the space charge theory with the consideration of dipole-field interaction, results in no significant modifications in the space potential nor the electric field profiles in the grain boundary region even at temperatures as low as 200°C, Fig. (V -5). As temperature increases the probability of impurity-vacancy association decreases and the contribution of the dipole-field interactions to the potential and the electric field becomes even more negligible.

However, the interaction between the electric field and the dipole complexes has a significant effect on the distribution profiles of dipoles with different orientations. In Appendix C, it is shown that for a planar
Fig. V-5: Effect of dipole interactions on the space charge electric field distribution in a grain boundary region. Dotted line shows the distribution without dipole interactions.
grain boundary normal to the $\langle 100 \rangle$ direction, with $m_1$, $m_2$ and $m_3$ denoting the number of dipole complexes with a resolved dipole moment parallel, perpendicular and anti-parallel to the electric field respectively, the quantities $m_1$, $m_2$ and $m_3$ are given as

$$m_1 = \frac{1}{3} C_\infty \rho_\infty N \exp\left(\frac{e\alpha}{2kT} \frac{d\varphi}{dx}\right) \quad (V - 5a)$$

$$m_2 = \frac{1}{2} C_\infty \rho_\infty N \quad (V - 5b)$$

$$m_3 = \frac{1}{3} C_\infty \rho_\infty N \exp\left(-\frac{e\alpha}{2kT} \frac{d\varphi}{dx}\right) \quad (V - 5c)$$

where $N$ is the site density for cation or anion in the crystal. These distributions profiles in the grain boundary region are shown in Fig. (V - 6).

Since the dipole-field interactions only lead to a negligible modification in the space charge potential, Appendix C, the expression for the space charge potential given in Kliwer and Koehler (1965) can be used for the estimation of the dipole flux, $J_{\text{dipole}}$.

$$J_{\text{dipole}} = -M_0 (m_1 - m_3) \frac{e\alpha}{4} \frac{d^2\varphi}{d\chi^2}$$

$$= -M_0 C_\infty \rho_\infty N \frac{e\alpha}{2} \sinh\left(\frac{e\alpha}{2kTdx}\right) \frac{d^2\varphi}{d\chi^2} \quad (V - 6)$$
Fig. V-6: Polarization of vacancy-impurity dipole complexes in the grain boundary region. $m_1$, $m_2$ and $m_3$ denote the normalized concentration of dipoles with the resolved dipole moment anti-parallel, perpendicular and parallel to the electric field respectively.
where $M_0$ is the mobility of the dipoles.

(c) **The Effects of a Vacancy Wind:** When a grain boundary migrates, the vacancies, because of their relatively high diffusivities, maintain the distribution profiles by the vacancy fluxes near the moving boundary. The Sr transport, which depends on the association with cation vacancies, is facilitated by the vacancy flux. In the reference frame of the moving boundary, the vacancy flux is \( \left[ V_K^v(x) - V_K^v(\infty) \right] v \), where \( v \) is the boundary velocity; \( V_K^v(x) \) is the K vacancy concentration at the location, \( x \), away from the boundary; and \( V_K^v(\infty) \) is the K vacancy concentration in the bulk. A Sr flux of the same magnitude as the vacancy flux is then required to maintain the charge density, $\rho$, and the space potential distribution, $\varphi(x)$, in the grain boundary region. Moreover, a quantitative measure of the vacancy wind contribution to Sr transport requires a simultaneous solution of the flux equations for vacancies and impurities, as well as the Poisson's equation which couples the defect concentrations. This approach will involve complex mathematics and it is beyond the scope of the present treatment.

The above discussions identify the electric field, the field gradient and the cation vacancy wind as the driving
force for the Sr transport. However, these discussions also fail to suggest a useable expression for the Sr mobility in a space charge electric field. In view of these difficulties, we relate the atomic mobility to the diffusivity by the Einstein relation, Eq. (V -2), and the net force field for Sr transport is assumed to be the space charge electric field. Consequently, the total Sr flux, $J_{Sr}$ due to the diffusion down a concentration gradient and the drift in a space charge electric field is taken as

$$J_{Sr} = -D \frac{dC}{dx} - \frac{DC}{kT} \frac{d\phi}{dx}$$  \hspace{1cm} (V-7)

where D is the Sr diffusivity and $D=Do\rho$, Lidiard (1955), as discussed in the next section.
V - 4. **Sr DIFFUSION IN Sr DOPED KCl**

Since Sr$^{2+}$ can only diffuse by associating with potassium vacancies, Lidiard (1955), the probability of association, $p$, must be considered. It is defined as

$$p = \frac{[\left(V'_K \ Sr'_K\right)^*]}{\left(V'_K \ Sr'_K\right)^* + [Sr'_K]}$$

(V -8)

and is a function of location in the crystal.$^+$

We define $P_\infty$ as the degree of association in the bulk. Since we neglect the interactions between the dipole complexes and the space charge electric field, Appendix C, the distribution of the associated complexes, which are neutral, is uniform throughout the grain boundary region. The concentration of the complexes, $\left(V'_K \ Sr'_K\right)^*$, is

$$\left(V'_K \ Sr'_K\right)^* = C_\infty P_\infty$$

(V -9)

where $C_\infty$ is the total Sr concentration in the bulk. However, the space charge potential will strongly affect the equilibrium distribution of the charged, unassociated strontium. Since the grain size (>10 $\mu$m) is much larger than the Debye length ($10^{-3}$ to $10^{-2}$ $\mu$m), it is reasonable to neglect effects of

$^+$ Kroger-Vink notation where $'$, $'$, $^*$ indicate effective negative, positive and neutral charge respectively.
specimen size; and the unassociated Sr concentration, 
\[ [\text{Sr}_K^*(x)] \], Kliewer and Koehler (1965), is 
\[ [\text{Sr}_K^*(x)] = (1-p_\infty) C_\infty \exp \left( - \frac{e\varphi(x) - e\varphi_\infty}{kT} \right) \]  
(V -10)

Combining Eqs. (V -8) to (V -10), we have the probability of association near the boundary

\[ p(x) = \frac{p_\infty}{p_\infty + (1-p_\infty) \exp \left( - \frac{e\varphi(x) - e\varphi_\infty}{kT} \right)} \]  
(V -11)

The Sr diffusion coefficient is then given as

\[ D^r(x) = D_0 p(x) = \frac{D_0 p_\infty}{p_\infty + (1-p_\infty) \exp \left( - \frac{e\varphi(x) - e\varphi_\infty}{kT} \right)} \]  
(V-12)

where \( D_0 \) is the diffusion coefficient of the associated vacancy-impurity complexes, section (II-5).

In Appendix B, we discuss the effect of the space charge potential on the diffusion and conductance in the grain boundary region. The space charge potential may lead to either an enhancement and a reduction in diffusion or conductance parallel to a grain boundary.
V - 5. **NUMERICAL CALCULATIONS OF Sr DISTRIBUTION**

The impurity distribution, \( C(x) \), about a moving grain boundary can be evaluated from the steady state flux equation of the impurities, based on the model of Cahn (1962) as reviewed in Chaper II. The impurity flux equation, Eq. (II-16),

\[
D \frac{dC}{dx} + \frac{DC}{kT} \frac{dU}{dx} + V (C - C_\infty) = 0 \tag{V -13}
\]

in which the term, \( D \frac{dC}{dx} \), is the diffusive flux due to the concentration gradient; \( \frac{DC}{kT} \frac{dU}{dx} \) is the drift flux due to the interactions between the impurity ions and the grain boundary and \( V (C - C_\infty) \) is the convective flux due to the boundary motion.

As discussed in sections (V -3) and (V -4) of this chapter the Sr diffusivity, \( D^{Sr} \), and the impurity - grain boundary interaction energy, \( U \), are assumed to have the following forms,

\[
D^{Sr}(x) = \frac{D_0 p_\infty}{p_\infty + (1-p_\infty) \exp (-\frac{e - e_\infty}{kT})} \tag{V -14a}
\]

\[
U = e - e_\infty \tag{V -14b}
\]

When \( U(x) \) and \( D(x) \) are independent of \( V \), the flux equation, Eq. (V-13), has a solution, as given in Cahn (1962),

\[
C(x, V) = C_\infty V \int_{-\infty}^{x} \exp \left( \frac{U(\eta) - U(x)}{kT} \right) \cdot \exp \left( \int_{x}^{\eta} \frac{d\gamma}{D(\eta)} \right) \frac{d\eta}{D(\eta)} \tag{V-15}
\]
With further algebraic manipulations, it can be shown that

For $x < 0$
\[
C(x, v)/C_\infty = \frac{2m}{\ell^2} \left( \frac{\ell + 1}{\ell - 1} \right)^m \exp \left( -\frac{2m(1-p_\omega)}{\ell} \right) \cdot \int_1^{\eta} \left( \frac{\eta - 1}{\eta + 1} \right)^m \frac{\exp \left( \frac{2m(1-p_\omega)}{\eta} \right)}{(\eta+1)(\eta-1)} d\eta
\]

For $x > 0$
\[
C(x, v)/C_\infty = \frac{2m}{\ell} \left( \frac{\ell - 1}{\ell + 1} \right)^m \exp \left( \frac{2m(1-p_\omega)}{\ell} \right) \cdot \left\{ \left( \frac{\eta + 1}{\eta - 1} \right)^m \exp \left( -\frac{4m(1-p_\omega)}{\eta} \right) \int_1^{\eta} \left( \frac{\eta - 1}{\eta + 1} \right)^m \frac{\exp \left( \frac{2m(1-p_\omega)}{\eta} \right)}{(\eta+1)(\eta-1)} d\eta \right\}
\]

where
\[
\ell = \exp \left\{ \left( e\Phi(x) - e\Phi_\infty \right)/2kT \right\} = \ell(x) \quad (V-17a)
\]
\[
\eta = \exp \left\{ \left( e\Phi(0) - e\Phi_\infty \right)/2kT \right\} = \text{a constant} \quad (V-17b)
\]
\[
m = V/(D_0p/5) \quad (V-17c)
\]

$V$ = actual boundary velocity

$D_0p$ = the bulk Sr diffusivity
Physically, $D_0 p/\delta$ is the velocity with which the Sr ions move across the space charge layer; and $m$ is the normalized boundary migration velocity with respect to the diffusion velocity.

The singularity, at $y = 1$, in the integrands of Eqs. (V -16) and (V -17), can be removed by proper partial integrations. Furthermore, it can be shown that the integrals are convergent.

Numerical integrations of Eqs. (V -16a,b), using Simpson's method, were performed in a PDP-11 computer of Digital Corporation. For a 50 ppm Sr doped KCl sample, typical Sr distribution profiles in the neighborhood of a moving grain boundary, at a reduced velocity of $0.01 < m < 2$, are shown in Fig. (V -7) and (V -8). The coordinate system in the reference frame of the moving grain boundary is adopted for these curves. Several features are noted:

(a) The profile is assymmetrical; and the degree of assymetry increases with velocity.

(b) At temperatures below the isoelectric point, $T < T_o$, the interaction energy between the negatively charged boundary and the Sr ions is attractive and Sr segregation to the moving boundary occurs. As velocity increases, the segregation decreases. Furthermore, the maximum peak in the concentration profile trails slightly behind
Fig. V-7: Normalized distributions of Sr ions in a moving grain boundary, showing segregation at low temperature. The arrow sign denotes the motion direction; $m$, defined in Eq. (V-17c), is proportional to boundary velocity, $V$. 

$T = 200^\circ C$

$[Sr_k(\infty)]_{TOT} = 50 \text{ ppm}$

$\delta = 24.5 \text{ Å}$
the moving boundary core, Fig. (V-7).

(c) At temperature above the isoelectric point, \( T > T_0 \), the Sr ions are repelled from the positively charged grain boundary. As the velocity increases, Sr ions pile up ahead of the boundary. The maximum of the Sr pile-up can be twice the bulk concentration and occurs at about 20 Å (\( \delta \) to 2\( \delta \)) from the boundary, Fig. (V-8).
Fig. V-8: Normalized distributions of Sr ions in a moving grain boundary, showing desorption at high temperatures. The arrow sign denotes the motion direction; \( m \), defined in Eq. (V-17c), is proportional to boundary velocity, \( V \).

\[
\frac{[\text{Sr}_k(x)]_{\text{TOT}}}{[\text{Sr}_k(\infty)]_{\text{TOT}}} = 50 \text{ ppm}
\]

\[ T = 700^\circ \text{C} \]

\[ \delta = 11.2 \text{ Å} \]
V - 6. NUMERICAL CALCULATIONS OF IMPURITY DRAG

The impurity drag force can be calculated either from the impurity profiles directly, or from an approximate expression, which is constructed from Taylor's expansions of the integral form of the drag force at the high and low velocity limits, Cahn (1962). These two approaches are discussed in the following sections.

(a) Impurity Drag Calculations Based on the Impurity Concentration Profiles: The impurity drag on a moving grain boundary can be calculated from the impurity distribution profiles, Cahn (1962).

The drag force due to the interactions between the unassociated Sr ions, \((\text{Sr}^+)\), and the space charge electric field is

\[
\Delta F_{[\text{Sr}^+]} = -\int_{-\infty}^{\infty} N \left[ C(x) \left[ 1 - p(x) \right] - C(\infty) \left[ 1 - p(\infty) \right] \right] \frac{d\phi}{dx} \, dx
\]

\[
= - \int_{-\infty}^{\infty} \frac{d\alpha}{dx} N \left[ C(x) - C(\infty) \right] \frac{d\phi}{dx} \, dx + \int_{-\infty}^{\infty} \frac{d\alpha}{dx} N \left[ C(x) p(x) - C(\infty) p(\infty) \right] \frac{d\phi}{dx} \, dx
\]

\[
\approx - \int_{-\infty}^{\infty} \frac{d\alpha}{dx} N \left[ C(x) - C(\infty) \right] \frac{d\phi}{dx} \, dx
\]

\[\text{(V-18)}\]
We assume that $C(x)p(x) = C(\infty)p(\infty)$ and we neglect the interactions between the dipole complexes and the space charge electric field; the dipole-field interactions are treated in Appendix C.

The drag force due to the associated impurity-vacancy dipole complexes, $(Sr^+ V^-)_K^*$, can be given as

$$\Delta F[Sr^+ V^-]_K^* = -\int_{-\infty}^{\infty} dx \left[ m_1(x,V) - m_2(x,V) \right] \frac{d^2 \phi}{dx^2} \frac{ea}{2}$$

(V -19)

where $m_1(x,V)$ and $m_2(x,V)$ are the numbers of the dipole complexes, with their respective dipole moments parallel and anti-parallel to the space charge electric field in a moving grain boundary of velocity, $V$, Appendix C. However, in the discussion of the impurity flux equation, we made no explicit estimation of the velocity dependence of the dipole distribution profiles. The dipole distributions calculated were for the minimum free energy at zero velocity and since they are symmetrical on both sides of a grain boundary, there is no net drag force on the grain boundary.

Consequently, the drag force, $F(V)$, due to the Sr ion distribution profiles in the grain boundary region of a moving boundary with velocity, $V$, is given as

$$\Delta F(V) = -\int_{-\infty}^{\infty} dx \ N \left[ C(x,V) - C(\infty,V) \right] \frac{d \phi}{dx}$$

(V -20)
Numerical integrations of Eq. (V-20) were performed to calculate the impurity drag on a slowly moving grain boundary with the dimensionless velocity, \( m \ll 2 \). In the impurity limited, low velocity regime, the intrinsic drag can be neglected, and the external driving force is balanced by the impurity drag force alone. The mobility of a grain boundary, defined as velocity per unit driving force, was plotted as a function of temperature and compared with the experimental data in Fig. (V-9). However, the comparison is not rigorous because the experimental boundary velocity or the dimensionless velocity, \( m \), is not constant throughout the temperature range. The predicted boundary mobilities are based on the calculated impurity drag for a boundary moving at a fixed dimensionless velocity, \( m \); whereas in secondary grain growth experiments, the driving force, which is essentially constant, controls the boundary velocity.

(b) Impurity Drag Calculation Based on Approximations in the High and Low Velocity Limits: According to Cahn (1962), the total drag force, \( F \), experienced by a moving grain boundary with velocity, \( V \), can be approximated as

\[
F = \lambda V + \frac{\alpha C_m V}{1 + \beta^2 V^2} \tag{V-21}
\]
Fig. V-9: Grain grain mobility calculated from the impurity distribution profiles. At the isoelectric temperatures, the high mobility is only limited by the intrinsic drag.
where $\lambda^{-1}$ is the intrinsic boundary mobility, $\alpha^{-1}$ is the mobility per unit impurity concentration in the impurity controlled low velocity region; and $\beta^{-1}$ is the drift velocity of the impurity atoms across the grain boundary and it is also the boundary velocity at which the impurity drag reaches the maximum. Furthermore, as shown in Cahn (1962), the quantities $\alpha$ and $\beta$ are related to the impurity-boundary interaction energy, $U(x)$, and the impurity diffusivity, $D(x)$,

$$\alpha = 4NkT \int_{-\infty}^{\infty} \frac{\sinh^2 U(x)/2kT}{D(x)} \, dx$$  \hspace{1cm} (V -22)

$$\frac{\alpha}{\beta^2} = \frac{N}{kT} \int_{-\infty}^{\infty} (\frac{dU}{dx})^2 \cdot D(x) \, dx$$  \hspace{1cm} (V -23)

where $N$ is the number of atoms per unit volume.

In the context of space charge interaction between the impurity cloud and the grain boundary, the interaction energy, $U(x)$, and the Sr impurity diffusivity, $D(x)$, are given in Eqs. (V -14b) and (V -14a) respectively. The quantities, $\alpha$ and $\beta$ are evaluated from Eqs. (V -22) and (V -23), Appendix D. An estimation of the intrinsic grain boundary mobility, $\lambda^{-1}$, is made from the
experimental data, Appendix G, as

\[ \lambda^{-1} = 4.64 \times 10^{-6} \exp(-7.73 \text{kcal/RT}) \text{(cm/sec)} \cdot (\text{dyne/cm}^2)^{-1} \]

(\text{V -24})

With the drag and drift parameters \( \alpha, \beta \) and \( \lambda \), we can calculate the mobilities in the low velocity limit, the breakaway velocities and the grain boundary velocities under an external driving force.

In the low velocity limit, the grain boundary mobilities, \((\lambda + \alpha C_w)^{-1}\), are shown in Fig. (V -10) as a function of temperature and dopant concentration. The high mobilities at the isoelectric temperatures are due to the vanishing space potential. When the role of the space charge potential diminishes, other impurity-boundary interactions, e.g. the strain field interaction, becomes relatively important, Section (V -7).

The calculated values of \( \beta^{-1} \), the boundary velocities at which the impurity cloud exerts the maximum drag, are compared with the experimental velocity data, as shown in Fig. (V -11). Since \( \beta^{-1} \) also corresponds to the break-away velocity of a moving grain boundary from the associated impurity cloud, the comparison suggests that the experimental migration velocities are in the neighborhood of the breakaway velocities. However, it is contrary to the expectation that the velocity data in
Fig. V-10: Grain boundary mobility in the low velocity limit.
Fig. V-11: The break-away velocity, $\beta^{-1}$, as compared with the experimental boundary velocity. Data are for 50 ppm Sr doped KCl.
the high temperature range are above the break-away velocity and those in the low temperature range are below the break-away.

A more rigorous test of the theory can be made by comparing the experimental velocity data with those predicted in the theory. Since the drag forces must be balanced by the driving force in order to maintain a steady state boundary motion, Eq. (V -21), presents a cubic equation of the boundary velocity for a given driving force. The solutions of boundary velocities under a driving force of $10^5$ dynes/cm$^2$, which corresponds to an average of $7.3 \mu m$ for the linear grain size intercepts, are shown in Figs. (V -12) to (V -14).

The drag force has a local maximum of $P_{\text{max}} \simeq \frac{C_w\alpha}{2}\beta^{-1}$ at the boundary velocity, $V_{\text{max}} \simeq \beta^{-1}(1+\frac{4\lambda}{C_0\alpha})^{1/2}$ and also a local minimum of $P_{\text{min}} \simeq 2(\lambda\alpha C_0)^{1/2}\beta^{-1}$ at $V_{\text{min}} \simeq (\frac{C_w\alpha}{\lambda})^{1/2}\beta^{-1}$, as reviewed in chapter II. When the experimental driving force, $\Delta F$, is $P_{\text{min}} < \Delta F < P_{\text{max}}$, there exist three possible velocity solutions for Eq. (V -21), as shown in Figs. (V -12) to (V -14) in some temperature range.

When the experimental data are compared with the predicted velocities we observe that:
Fig. V-12: Grain boundary velocity as predicted from the electrostatic space charge drag mechanism for 1 ppm Sr doped KCl. Experimental data are of undoped KCl.
Fig. V-13: Grain boundary velocity as predicted from the electrostatic space charge drag mechanism for 50 ppm Sr doped KCl.
Fig. V-14: Grain boundary velocity as predicted from the electrostatic space charge drag mechanism for 100 ppm Sr doped KCl.
1. For KCl with a dopant level of 50 or 100 ppm Sr, the experimental boundary velocities at low temperatures are within an order of magnitude of the predicted low velocity region.

2. In the high temperature range, when the experimental driving force, $\Delta F$, exceeds the local maximum drag force, $P_{\text{max}}$, only a high velocity solution is predicted from Eq. (V - 21). However, the experimental velocities, in this temperature range, are closer to those extrapolated from the low velocities predicted at low temperatures than the predicted high velocities. This suggests that the experimental velocity data at high temperatures are in the stage of break-away.

3. For undoped samples with an estimated Sr concentration of 1 ppm, the experimental data are in the break-away stage; but with little agreement with the theory. The anomalously high boundary velocities of Koepke et al (1974) are in the predicted high velocity region; however the particularly good agreement is fortuitous, and is in part a result of our estimation of the intrinsic mobility.
V - 7. STRAIN FIELD INTERACTION WITH THE SPACE CHARGE POTENTIAL

In the previous sections we considered the space charge potential as the only interaction energy between the grain boundary and the impurity cloud. This assumption may be justified by the relatively modest effects of the monovalent dopant, Br\(^-\), as compared to the divalent dopant, Sr\(^{2+}\), in inhibiting the grain boundary mobility. However the strain field interactions between impurity atoms and the grain boundary become important at the isoelectric temperature where the space charge potential vanishes. Furthermore, Kitazawa (1975) reported that both the ionic radius and the ionic charge of an impurity dopant have important effects in limiting the grain boundary mobility measured for KCl.

Auger Electron Spectroscopy studies of Johnson et al (1974) on the intergranularly fractured surface of alumina, sintered to 100% theoretical density with 0.1-0.2 atomic % Mg dopant and 40-50 atomic ppm Ca in the bulk showed a strong segregation of 3 atomic % Ca but only a modest enhancement of 0.2-0.4 atomic % Mg at the grain boundary along the fractured surfaces. Whereas both the Mg and Ca ions have the same ionic charge, the ionic radii of Mg\(^{2+}\) and Ca\(^{2+}\) are 144% and 209% respectively of the Al\(^{3+}\) radius. Based on the elastic strain energy induced in a lattice by
a solute ion of different radius, and the equilibrium segregation theory of McLean (1951), Johnson and Stein (1975) calculated the dopant concentrations segregated to the grain boundary and found a reasonable fit to the experimental data.

Given the individual importance of the mechanical strain field interaction as well as the electrostatic space charge interaction between an aliovalent dopant and a grain boundary, the strain field and the space charge potential also couple with each other in enhancing the impurity segregation and in limiting the grain boundary mobility.

The strain field interaction affects the distribution of impurity ions and vacancies. Thus, the charge density and the space potential are also modified by the strain field. Consequently, it is necessary to analyse the free energy of the system. In order to have a general applicability, we assume strain interaction terms, $U^i_s$, between the defects (vacancies, vacancy complexes, vacancy-impurity complexes, unassociated and associated impurity ions) and the grain boundary. Furthermore, we assume that certain binding energies are required for an excess quantity of Sr, K and Cl ions to accumulate in the grain boundary core.

The free energy, $F$, in a system of $N_+(x)$ cation vacancies, $N_-(x)$ anion vacancies, $N_B(x)$ vacancy complexes, $N_f(x)$ unassociated impurities and $N_{ib}(x)$ associated vacancy-impurity
complexes, can be expressed as

\[
\mathcal{F} = \int_0^L \left[ n^+_c(F^+ + U_c^+) + n^-_c(F^- + U_c^-) + n^+_a(F^+ - B + U_a^+) + n^-_a(U_a^-) + n^+_k(F^- - B_k + U_k^+) + \frac{1}{2} \rho \phi \right] \\
- T S_c + \frac{1}{2} \sigma \phi + N^+_s F^+_s + N^-_s F^-_s + N^+_n F^+_n
\]  
(V-25)

where \( F^+ \) and \( F^- \) are the formation energies of cation and anion vacancies respectively; \( B \) and \( B^+ \) are the binding energies of vacancy complexes, \((V^+_K V^-_{Cl})^*\), and vacancy-impurity complexes, \((V^+_K Sr^-_{K})^*\), respectively; \( \frac{1}{2} \rho \phi \) is the electrostatic energy term for a charge density, \( \rho \), and space charge potential, \( \phi \); \( S_c \) is the configurational entropy of the system but excluding that in the boundary core; \( \frac{1}{2} \sigma \phi \) is the electrostatic energy term for the core with a "surface" charge, \( \sigma \), and "surface" potential, \( \phi_1 \); \( N^+_s, N^+_n \) and \( N^-_s \) are the number of the unassociated \( Sr, K \) and \( Cl \) ions respectively in the boundary core with their respective binding energies \( F^+_s, F^+_n \) and \( F^-_s \).

The charged species in the crystal are related by the Poisson's equation,

\[
\frac{d^2 \phi}{dx^2} = - \frac{4 \pi e}{\epsilon} (n^+_f + n^- - n^+_f)
\]  
(V-26)
We further assume that the surface charge, $\mathcal{C}$, is due to
the excess ions in the boundary core,

$$\mathcal{C} = e(N_f^+ + N_{f}^+ - N_{f}^-) \quad (V-27)$$

and that the unassociated Sr ions in the core and in the
boundary region are conserved,

$$N_{S} f^+ + \int_0^L n_f \, dx = \text{constant} \quad (V-28)$$

and that the excess matrix ions in the core are compensated
by the vacancies in the same sublattice of the crystal,

$$N_s^+ = \int_0^L n_+(x) \, dx \text{ and } N_s^- = \int_0^L n_-(x) \, dx \quad (V-29)$$

After the minimization of the free energy, $F$, with these
assumptions, Appendix (E), we obtain,

$$\frac{n_+}{N} = \exp -\left( \frac{F^+ + U^+ + F^+ - e\varphi}{kT} \right) \quad (V-30)$$

$$\frac{n_-}{N} = \exp -\left( \frac{F^- + U^- + F^- + e\varphi}{kT} \right) \quad (V-31)$$

$$\frac{n_f}{N} = \exp -\left( \frac{U_f - F_f + e\varphi + \alpha_H}{kT} \right) \quad (V-32)$$

$$\frac{n_{ib}}{N} = 12 \exp -\left( \frac{F^+ - B^+ + U^f + \alpha_H}{kT} \right) \quad (V-33)$$
where $\alpha_H$ is the Lagrange multiplier for the condition that the total number of impurities must be conserved.

The bulk potential, $\phi_\infty$, can be defined from the electrical neutrality condition in the bulk, $n_+(\infty) = n_-(\infty) + n_f(\infty)$,

$$\exp\left(-\frac{F+U^+_s(\infty)+F^-}{kT}\right) = \exp\left(-\frac{F+U^+_s(\infty)+F^-}{kT}\right) + \exp\left(-\frac{U^f_s(\infty)-F^+_s + e\phi_0 + \alpha_H}{kT}\right)$$  \hspace{1cm} (V-34)

In the extrinsic temperature range, the anion vacancies are negligible. We further assume that $U^+_s$ has no spatial dependence. In Appendix E, the Poisson's equation is reduced to

$$\frac{dZ}{dS^z} = \frac{1}{2} \left[ e^{-Z} - e^{-(U^f_s(x) - U^f_s(\infty))/kT} \right].$$ \hspace{1cm} (V-35)

$$Z \equiv (\phi - \phi_0)/kT$$ \hspace{1cm} (V-36)

$$S \equiv \chi/\delta$$ \hspace{1cm} (V-37a)

$$\delta \equiv \left[ \frac{8\pi N e^2}{e k T} \exp\left(\frac{e\phi_0 - (F^+_s + F^- + U^+_s)}{kT}\right) \right]^{-1/2}$$ \hspace{1cm} (V-37b)
We assume a truncated ramp shaped strain field interaction energy,

\[ U_{f}^{\alpha}(x) - U_{f}^{\alpha}(\infty) = \begin{cases} 
U_{0}(1-x/2a) \text{ ev} & x \leq 2a \\
0 \text{ ev} & x > 2a 
\end{cases} \tag{V-35}\]

where \( a \) is the lattice constant.

The range of the strain field interaction energy is chosen as two lattice spacings; and the magnitudes of \( U_{0} \) are chosen as \( \pm 0.2 \text{ ev.} \) and \( \pm 0.05 \text{ ev.} \) for the numerical integration of Eq. (V-35). The calculated potential distributions are shown in Figs. (V-15) to (V-18).

At temperatures above the isoelectric point, the Sr ions are repelled from the negatively charged grain boundary. An attractive strain field, \( U_{0} < 0 \), counter-balances the electrostatic space charge effect and increases the space charge potential. However, a repulsive strain field, \( U_{0} > 0 \), decreases the space charge potential to a more negative value, Figs. (V-15) and (V-16).

At temperatures below the isoelectric point, the attractive space charge potential is complemented by an attractive strain field to such a level that even the bulk potential is exceeded, Figs. (V-17) and (V-18).

The distribution profiles of the K vacancies and the Sr ions in the grain boundary region, for an attractive impurity strain field, \( U_{0} = -0.2 \text{ ev.} \), are shown in Fig. (V-19).
Fig. V-15: Potential distributions in the grain boundary region due to the coupled effects of the electrostatic space charge and the mechanical strain field interactions at 500°C ($>T_0$).
Fig. V-16: Potential distributions in the grain boundary region due to the coupled effects of the electrostatic space charge and the mechanical strain field interactions at 450°C (≥ T₀).
KCl
$[Sr_K]_{tot} = 50$ ppm
$T = 440°C$
$e\phi_\infty = 6.2 \times 10^{-3}$ ev
$\delta = 11.6 \text{ Å}$
$U_{\text{strain}} = \begin{cases} U_0 (1 - x/2a) \text{ ev} & x \leq 2a \\ 0 \text{ ev} & x \geq 2a \end{cases}$

Fig. V-17: Potential distributions in the grain boundary region due to the coupled effects of the electrostatic space charge and the mechanical strain field interactions at $440°C \quad (\leq T_0)$
Fig. V-18: Potential distributions in the grain boundary region due to the coupled effects of the electrostatic space charge and the mechanical strain field interactions at 400°C (< T₀).
Fig. V-19: \([\text{Sr}_K^*]\) and \([\text{V}_K^*]\) distribution profiles, under the coupled effects of the electrostatic and the mechanical strain interactions in the grain boundary region of 50 ppm Sr doped KCl.
At the location where the concentrations of K vacancies and Sr ions are equal, there is no net charge density (with Cl vacancies neglected); and this location corresponds to the inflection point, $\frac{\partial^2 \phi}{\partial x^2} = 0$, in the potential distributions shown in Figs. (V-15) to (V-18). The segregation of Sr ions within two lattice spacings of the grain boundary is due to the attractive strain field. Beyond the range of strain field interaction, the space charge potential is repulsive to Sr ions even at $400^\circ$C, Fig. (V-19).

Based on the calculated potential distributions and the assumed strain field interaction energies, we can calculate the drag parameters $\alpha$ and $\beta$, following the general framework discussed in section (V-6b), and by the numerical integration of Eqs. (V-22) and (V-23).

At temperatures below the isoelectric point, $\alpha$, the drag force per unit velocity, per unit dopant concentration is increased by an attractive strain field, which further enhances the Sr segregation. However, a repulsive strain field counteracts the attractive space charge and reduces the net drag force, Fig. (V-20).

At temperatures above the isoelectric point, the space charge potential is repulsive to Sr ions, and the drag force is increased by a repulsive strain field but is decreased by an attractive strain field, Fig. (V-20).
Fig. V-20: Calculated values of $\alpha$, the drag force per unit velocity, per unit dopant concentration, on a moving grain boundary, by the coupled interactions of the electrostatic and mechanical strain fields.
Fig. (V-20) also shows that at temperatures near the isoelectric point the drag parameter, $\alpha$, does not vanish for a finite strain field of either sign.

The break-away velocities, $\beta^{-1}$, are similarly calculated and shown in Fig. (V-21). The strain field interaction tends to decrease the break-away velocities over most of the temperature range.

Following the general framework discussed in section (V-6b), and using the calculated drag parameters $\alpha$ and $\beta$, we can solve for the boundary velocities under an external driving force, Eq. (V-21). The predicted grain boundary velocities due to the coupled effects of a space charge potential and a strain field interaction are shown in Figs. (V-22) and (V-23).

For a significant strain field interaction term, $U_0 = \pm 0.2$ ev., the predicted velocities are remarkably different from those predicted in the case with an electrostatic space charge interaction alone. Furthermore, the temperature range, in which the driving force exceeds the maximum drag force and keeps a moving grain boundary in the high velocity limit, is much smaller than the like temperature range in the case without any strain field, Fig. (V-22).
Fig. V-21: Calculated values of $\beta^{-1}$, the break-away velocity of a grain boundary from the associated impurity cloud. Both the electrostatic and mechanical strain interactions are included.
For a smaller strain field interaction term, $U_0 = \pm 0.05$ ev. the strain field effects are less pronounced. This is probably due to the relatively large bulk potential, ranging from -0.27 ev. at 700°C and 0.21 ev. at 200°C for KCl with 50 ppm Sr. More importantly, it is also due to the small strain force term, $\frac{dU_s^f}{dx} = \frac{U_0}{2a}$, as compared with the space charge electric field term.
Fig. V-22: Grain boundary velocities calculated from the impurity drag model, which includes the electrostatic space charge and a large ($\pm 0.2$ ev.) mechanical strain field.
Fig. V-23: Grain boundary velocities calculated from the impurity drag model, which includes the electrostatic space charge and a small ($\pm 0.05$ ev.) mechanical strain field.
CHAPTER VI  DISCUSSION

The reported grain boundary mobility data are fairly consistent and reproducible; and it is rather unlikely that the boundary motion is nucleation limited, except possibly at low temperatures. The nucleation limited grain growth imposes the minimum temperature to which the experimental technique can be extended. At high temperatures, the growth rate is so rapid that the growing grains impinge upon each other; and the reported mobility data, based on the assumption of a constant driving force for grain growth, become erroneous. The occurrence of a significant grain impingement defines the maximum temperature for the experimental technique.

The driving force for the secondary grain growth is derived from the statistically averaged subgrain size in the neighborhood of the growing high angle boundary. Some of the subgrain boundaries may not be fully revealed during the chemical etching, and this leads to some error in the estimation of the driving force. In addition, the subgrain boundary energy is a function of misorientation angles, Class and Machlin (1966). However, despite some evidences of the relative misorientation angle among the subgrain boundaries, we are uncertain about the absolute value of the misorientation angle. Besides, the driving forces due to in-grain dislocations and the residual strain energy resulted from the hot deformation are not considered explicitly; and it can be shown that these
driving forces are relatively smaller than the driving force due to grain boundary curvature.

Although there has been no adjustable parameter in the analysis of the electrostatic space charge drag mechanism, the choice of the intrinsic grain boundary mobility, \( \lambda^{-1} \), is rather arbitrary, Appendix G.

The reported experimental results on isoelectric temperatures or the bulk potentials in the literature are not consistent with each other, Whitworth (1975); and there has been few experimental justification for the calculated values of the formation energies of cation and anion vacancies, Dreyfus and Norwick (1962).

It can be shown from Eq. (II-9b) that if the dopant level is mistaken by a factor of two, the bulk potential is erred by about \( RT \ln 2 \), i.e. about 0.029 ev. and 0.058 ev. at 200°C and 700°C respectively, where the impurity-vacancy association is neglected. Furthermore, a 10% uncertainty in the estimation of the cation vacancy formation energy, \( \Delta F^+ \simeq \pm 0.05 \) ev., may lead to a variation in the isoelectric temperature of \( \pm 63^0K \), for KCl with 100 ppm Sr dopant.

The change in the activation energy of the grain boundary mobility of doped KCl from 18.6 kcal/mole at low temperatures to 35.4 kcal/mole at high temperatures may indicate that the boundary motion is impurity limited at low temperatures and the boundaries are breaking away from the impurity cloud at
high temperatures. However, a comparison between the experimental data and the calculated break-away velocity, $\beta^{-1}$, is not conclusive. Furthermore, the calculated boundary velocities at high temperatures show a "gap" in which the boundary is only limited by the intrinsic drag. However, the predicted high velocities in the "gap" are not substantiated by the experimental observation.

In the case of the strain field interaction, the assumption of a ramp shaped strain field potential is more a matter of convenience rather than having a strong physical justification. However, the chosen values of $U_0$ are in the same order of magnitude of those predicted from the ionic size misfit by the elastic theory, which gives a strain energy of 0.11 ev. for $\text{Sr}^{2+}$, 0.31 ev. for $\text{Ca}^{2+}$; $3.3 \times 10^{-3}$ ev. for $\text{Ba}^{2+}$; and $6.1 \times 10^{-2}$ ev. for $\text{Br}^{-}$ in KCl, Gordon and Vandermeer (1966).

In the analysis, we do not explicitly treat the mechanisms of impurity transport across the grain boundary; and the boundary core structures and properties are not considered in detail. Although the core diffusion is not relevant in the study of an impurity limited grain boundary motion at low velocity, it undoubtedly plays an important role in the grain boundary stability and in the initiation of the grain boundary break-away phenomenon.
In addition, the space charge potential may well have a certain orientation dependence, Blakely and Danyluk (1973). Along the circumference of a secondary grain, there is a distribution of misorientation angles between the growing high angle boundaries and the matrix subgrains. Consequently, the non-uniform impurity drag forces originate from a distribution of bulk potentials on the grain boundary surface and a non-equaxed grain shape may result. However, during low temperature anneals, the preferred growth direction of an intrinsic grain boundary may lead to secondary grains with straight boundaries and sharp corners as observed in our laboratory and reported in Koepke et al (1974).
CHAPTER VII  SUMMARY AND CONCLUSIONS

(1) Grain boundary mobilities of undoped and Sr-, Ca-, and Br- doped KCl were measured by secondary grain growth experiments with hot deformed samples. The measured mobilities varied between $10^{-13}$ and $10^{-7}$ (cm/sec)(dyne/cm$^2$)$^{-1}$, over a wide temperature range, $0.45 < T/T_m < 0.95$.

(2) During secondary grain growth, only the high angle boundaries are mobile, whereas the low angle subgrain boundaries remain immobile.

(3) The KCl grain boundary mobility is lowered by both monovalent or divalent dopants; however the grain boundaries in samples with 5 molar % Br are at least 10 times more mobile than those in samples with 50-100 molar ppm of aliovalent Sr or Ca, dopant.

(4) A grain boundary impurity drag model due to the electrostatic space charge interactions between grain boundary and impurity was formulated for ionic solids. The redistributions of the impurity and vacancy charge density associated with a moving grain boundary affect the space charge. However, numerical solutions show that the velocity dependence of the space charge potential is rather modest in the case of impurity limited grain boundary motion.

(5) The three mechanisms, which can influence the transport of divalent cation impurities in a space charge potential
field, are the electric field effects, the electric field gradient effects and the effects of a vacancy wind. The interactions between the impurity-vacancy dipole complexes and the space charge electric field are included in the analysis of the defect distributions in the grain boundary region. Numerical calculations show that the dipole-field interactions have a negligible effect on the space charge potential distribution. However, the dipole field interactions tend to polarize the distribution of impurity-vacancy associated complexes and cause a modest attraction of dipoles to the boundary.

(6) Impurity distributions in a grain boundary with a steady velocity were calculated by numerical integration of the flux equation. The distributions are asymmetrical about the grain boundary. In the grain boundary region, Sr segregation at low temperatures and desorption at high temperatures are predicted. Furthermore, the magnitude of segregation and desorption decreases as the boundary velocity increases.

(7) The impurity drag is calculated and the boundary velocity is predicted for a given driving force. Near the isoelectric temperature, the theoretical calculations, based on the space charge interaction alone, show a very high boundary velocity, limited only by the intrinsic mobility.
In addition to the space charge interaction potential, the strain field interaction between the impurity ions and the grain boundary also contributes to the impurity drag. Furthermore, the distribution of the charged impurity and the space charge potential are modified by the strain field interaction with aliovalent ions. The impurity drag was calculated for the coupled effects of the electrostatic space charge and a ramp shaped strain field with an assumed magnitude and range. The predicted grain boundary velocities are within an order of magnitude of the experimental data in the low temperature range. However, the predicted high velocities for the breakaway grain boundaries are not in agreement with the experimental data in the high temperature range.

For sample preparation, single crystals of Sr-, Ca-, Ba- and Al- doped KCl were grown by the Czochralski method. The doped KCl as well as the undoped KCl and KBr single crystals, with the diameter to height ratio of 1 or 2, were deformed at a strain rate of about $10^{-3}$ sec$^{-1}$, at a homologous temperature ranging from 0.28 to 0.98, and with a normalized true stress, $\sigma/E$, varying between $2 \times 10^{-3}$ and $2 \times 10^{-4}$. The stress direction was in either $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ orientation of the single crystal. The deformation microstructures showed a uniform subgrain size and equiaxed grain shapes, but with a distribution of subgrain misorientation.
angles. An inverse relation between stress and subgrain size was found in which effects of temperature, dopants and crystal orientations were indirect through the effect on the flow stress.

(10) The contributions of the space charge cloud to impurity and self diffusion in the grain boundary region of doped KCl are calculated and shown to be modest in magnitude \( <10^3 \) and limited in range \( (10 - 200 \) Å). Both enhancement and reduction in the charge cloud contribution to boundary diffusivities are predicted. Only for the ion on the sub-lattice opposite that of the principal impurity is appreciable diffusivity enhancement in the charge cloud ever indicated. Large boundary diffusion enhancements and wide boundary widths in "pure" and doped samples, often assumed in the literature cannot be explained by the space charge contribution.
CHAPTER VIII  SUGGESTIONS FOR FUTURE WORK

Several suggestions for future work in both experimental and theoretical aspects are outlined here:

(1) Texture determination of a sample after secondary recrystallization can provide useful information for the preferred orientations of the nucleation and growth of the high angle boundaries, Krongberg and Wilson (1949). The success of this experiment can give a substantial support to the coincidence model or other special orientation relation in ceramic grain boundaries. Some work on texture determination of hot deformed samples has been reported, Bowen et al (1973).

(2) The strain field interaction potential between a grain boundary and an impurity dopant can be studied by characterizing the effect of ionic sizes of monovalent dopants on the grain boundary migration rate. Li\(^+\) and Cs\(^+\) cation dopants and F\(^-\) and I\(^-\) anion dopants represent the extremes of the ionic radii of dopants on both sublattices of KCl.

(3) The strain field interactions between Ba\(^{2+}\) dopant and KCl grain boundaries are negligible due to the small difference in the radii of Ba\(^{2+}\) and K\(^+\) ions. Grain boundary mobility measurement in Ba\(^{2+}\) doped KCl can elucidate the electrostatic interactions, but without the complication of mechanical strain interactions, between the dopant and the charged grain boundaries. Further, an allovalent anion, e.g. oxygen, dopant could be more potent in limiting the grain
boundary mobility of KCl, especially at low temperatures. The magnitude of the space charge potential in 0-doped KCl is larger than that in Sr-doped samples. More importantly, there exists no isoelectric point in KCl with an aliovalent anion dopant.

(4) The driving force dependence of the grain boundary mobility is one of the more important aspects in the impurity drag models. The hot deformed KCl samples, with the as-deformed average grain sizes ranging from 3 to 62 µm, give a wide range of driving forces for grain growth. Furthermore, a more careful measurement of the subgrain size and the dislocation density also would help to better characterize the driving force for grain growth.

(5) A change in the ionization state of a cation dopant, by controlling the vapor pressure of the anion, has a significant effect in the space charge potential as well as in the dopant diffusivity. During a grain growth experiment, a conversion of Bi$^{2+}$ to Bi$^{3+}$ and Hg$^+$ to Hg$^{2+}$ in KCl or Fe$^{2+}$ to Fe$^{3+}$ in MgO can thus affect the growth rate. However, the equilibration time of the specimen to the ambient atmosphere may be a limiting factor for this suggested experiment. The change of impurity diffusivity with the ambient atmosphere adds further complication to the analysis.

(6) Microstructure development during the hot deformation can be characterized from samples, deformed at different strain levels, by chemical etching and texture determination.
Furthermore, dislocation etching and TEM studies of hot deformed samples are suggested. In fact, Hesse and Hobbs (1972) have measured a relation between the flow stress and the screw dislocation density in a deformed NaCl single crystal by TEM.

(7) Since the functional form of the strain field potential is not known in detail, it is of interest to know how the predicted boundary velocity may vary with the different expressions of the strain potential of a given magnitude and a given range. In contrast to the case of a monovalent dopant, the strain field interaction between a divalent dopant and the grain boundary is coupled to the electrostatic space charge; thus the velocity calculations in the latter case are probably less sensitive to the detail functional form of the strain field.

(8) It was shown that the space charge potential distribution is a function of boundary velocity and that the Sr transport is due to the electric field effect, the electric field gradient effect and the effect of vacancy. The formulation of the individual flux equation for each charged species and the Poisson's equation in the grain boundary region represents a more rigorous approach for the impurity drag model of an ionic solid. However, the solution of these coupled differential equations may be formidable.
Appendix A: Space Charge Potential Distribution in a Moving Grain Boundary

In this Appendix, we discuss the effects of the grain boundary motion on the space charge potential. While the distribution profile of a given impurity species or vacancy is governed by the individual flux equation, of the type similar to Eq. (V-13), all these distribution profiles are coupled and related to the space charge field by Poisson's equation. The solutions of the potential as a function of the boundary velocity involve four coupled differential equations, Brown (1960). Instead of solving the complicated mathematics, we consider the extreme case where boundary velocity was high such that the total Sr impurity profile breaks down to a uniform distribution. However, the vacancies, because of their relatively high diffusivity, can adjust to a profile of the minimum free energy. The assumed uniform Sr distribution requires that

\[ n_i(x) = n_{if}(x) + n_{ib}(x) = \bar{c} \]  

(A-1)

\[ \delta n_{if}(x) = -\delta n_{ib}(x) \]  

(A-2)

where \( n_{if} \) and \( n_{ib} \) are the densities of unassociated \((\text{Sr}\gamma^*)\) and associated \((\text{Sr}\gamma\gamma^*)\) strontium, respectively.

With the condition, Eq. (A-2), and after the minimization of the free energy, as discussed in Kliewer and Koehler
and reviewed in Chapter II, we obtain

\[ S \rho_i \left\{ -\frac{F^+ - B^+}{kT} \ln \left( \frac{N_i}{\rho_i} \right) \right\} = 0 \]

\[ \therefore \frac{\rho_{ih}}{\rho_i} = 12 \cdot \exp \left( -\frac{F^+ - B^+ - e\phi}{kT} \right) \]  \hspace{1cm} (A-3)

where \( F^+ \) is the cation vacancy formation energy and \( B^+ \) is the binding energy of the \( (\text{Sr}_{K_i}^+ \text{V}_{K_K}^+) \) complexes.

Combining Eqs. (A-1) and (A-3), we get

\[ \rho_i = \frac{\bar{C}}{1 + 12 \cdot \exp \left( -\frac{F^+ - B^+ - e\phi}{kT} \right)} \]  \hspace{1cm} (A-4)

With the expressions for cation and anion vacancies, as derived in Kliewer and Koehler (1965), Poisson's equation becomes

\[ \frac{d^2 \phi}{dx^2} = -\frac{4\pi NE}{\varepsilon} \left\{ \frac{\bar{C}}{1 + 12 \exp \left( -\frac{F^+ - B^+ - e\phi}{kT} \right)} + \exp \left( -\frac{F^+ + e\phi}{kT} \right) - \exp \left( -\frac{F^+ - e\phi}{kT} \right) \right\} \]  \hspace{1cm} (A-5)

It can be shown that the bulk potential, \( \varepsilon \phi_\infty \), in this case of a migrating grain boundary, is identical to that in the case of a stationary boundary. Further algebraic manipulations reduce Poisson's equation to

\[ 2\bar{C}(1-p_a) \frac{d^2 \phi}{ds^2} = -\left\{ \frac{\bar{C}}{1 + 12 \exp \left( -\frac{F^+ - B^+ - e\phi}{kT} \right)} + \exp \left( -\frac{F^+ + e\phi}{kT} \right) - \exp \left( -\frac{F^+ - e\phi}{kT} \right) \right\} \]  \hspace{1cm} (A-6)
with \[ S = \frac{\chi}{\delta} \] (A-7)

and \[ S = \left[ \frac{\epsilon kT}{8\pi Ne^2\bar{\epsilon}(1-p_0)} \right]^{1/2} \] (A-8)

where the Debye length, \( \delta \), is identical to that in the case of stationary grain boundary in the extrinsic temperature range.

Upon the integration of Eq. (A-6), and with the boundary conditions that \( d\phi/ds = 0, \phi = \phi_\infty \) at \( S \to \infty \), we get

\[
\frac{1}{C} \left[ \frac{d(e\phi-e\phi_\infty)/kT}{dx} \right]^2 = \frac{1}{1 + 12 \exp(-F^2B_e-e\phi)/kT} \left\{ C(e\phi-e\phi_\infty)/kT - C \ln \left[ 1 + 12 \exp(-F^2B_e-e\phi)/kT \right] \right. \\
+ \exp(-F/kT) \left[ \exp(e\phi/kT) - \exp(-e\phi_\infty/kT) \right] \\
+ \exp(-F/kT) \left[ \exp(e\phi/kT) - \exp(e\phi_\infty/kT) \right] \}
\] (A-9)

Numerical integration of Eq. (A-9) give the space potential distribution for a crystal in the temperature range of 200-700°C. At temperatures above the isoelectric temperature, the calculated potential distributions are very similar to those given in Kliewer and Koehler (1965) for a stationary boundary, as shown in Fig. This is expected
because the vacancies, which constitute the majority of the charge density, are free to adjust themselves to the minimum free energy distribution. The perturbation in the space charge potential due to the boundary motion is therefore minimal. The defect distributions in the neighborhood of a break-away grain boundary are shown in Fig. (V-2).

However, at temperatures below the isoelectric temperature, the impurity cloud has a larger contribution to the charge density, and the potential distribution for a mobile boundary deviates from that for a stationary boundary as shown in Fig. (V-3); and the defect distributions are shown in Fig. (V-4).
Appendix B: Space Charge Contribution to Grain Boundary Diffusion*

The purpose of this appendix is to elucidate quantitatively the effects of the space charge cloud on diffusion in ionic materials. For illustrative purposes, Sr and O impurity diffusion as well as K and Cl self diffusion in Sr and O doped KCl are studied in detail. The distributions of impurities and vacancies about grain boundaries as formulated by Kliewer and Koehler (1965), are used in the calculations of the diffusivities in the space charge cloud. In the section of Formal Theory, we consider the case of a gas exchange type of diffusion experiment; however, the pertinent results derived there have a universal applicability for ionic conductance parallel to a grain boundary.

* This appendix is taken from a paper co-authored by M. F. Yan, R. M. Cannon, H. K. Bowen and R. L. Coble. The paper was accepted for publication in the Journal of American Ceramic Society.
B - I. Theory

(1) Formal Theory:

In ionic materials with predominantly Schottky type defects, e.g. KCl, both the impurity ions and the matrix ions diffuse only by associating with vacancies on the same sublattice. The diffusive flux of the ions, \( J \), is the same as the flux of the associated vacancy-ion complexes, \( J_{\text{complex}} \).

For a gas exchange tracer diffusion experiment in a semi-infinite bicrystal, as shown in Fig. (B-1), a uniform chemical potential is maintained in the bicrystal sample by keeping the same vapor pressure of the chemical species of the diffusing ions on both sides of the sample, \( y = 0 \) and \( y = L \). However, if the vapor phase at \( y < 0 \) consists of the tracer isotope and the vapor phase at \( y > L \) consists of the major isotope, there exist concentration gradients of both isotopes parallel to the grain boundary in the bicrystal sample.

For simplicity, we treat the space charge effects only in the grain boundary region and neglect those at the surfaces. Since there is a strong electric field in the space charge regions of grain boundaries, a drift term due to the electric field as well as the usual diffusive term due to the concentration gradient is included in the flux equation of the vacancy-ion complexes,
Fig. B-1: Schematic diagram of a grain boundary diffusion experiment, with the path of conductance parallel to the boundary.
\[ J^{(i)} = J_{\text{complex}}^{(i)} \quad i = 1, 2 \]

\[ = [-D_v \nabla (\rho C^{(i)}) - \beta B \rho C^{(i)} \nabla (\phi(x) - e \phi_\infty)]_{i = 1, 2} \]

\[ = \{ -D_v \rho \frac{\partial C^{(i)}}{\partial x} + D_v C^{(i)} \frac{\partial \rho}{\partial x} + \beta B C^{(i)} \rho \frac{\partial}{\partial x} (\phi(x) - e \phi_\infty) \} \hat{x} \]

\[ - D_v \rho \frac{\partial C^{(i)}}{\partial y} \hat{y} - D_v \rho \frac{\partial C^{(i)}}{\partial z} \hat{z} \quad i = 1, 2 \]  

(B-1)

where the quantity with a superscript, \( i = 1 \), denotes that of the tracer isotope and \( i = 2 \), for that of the major isotope; \( C \) is the local concentration of the ions; \( D_v \) is the diffusion coefficient of the vacancy-ion complexes; \( B \) is the effective mobility of these complexes in the space charge electric field; \( q \) is the effective charge number of the complexes; \( e \) is the absolute value of the electronic charge; \( p \) is the probability of association to form the complexes; \( \phi(x) - \phi_\infty \) is the potential difference between the bulk potential, \( \phi_\infty \), and the potential at a distance \( x \) from a planar boundary or free surface, which is normal to the \( x \)-axis. In general, \( D_v \) is not affected by the space charge potential and therefore is not a function of location in the crystal.

It was shown in section (B-IV) that the total concentration of both isotopes, \( C(x, y) \) is independent of \( y \),

\[ C^{(1)}(x, y) + C^{(2)}(x, y) = C(x) \]  

(B-2)
and that the tracer isotope concentration, $C^{(1)}(x,y)$, can be expressed in terms of the total concentration, $C(x)$, as

$$C^{(1)}(x,y) = C(x) \frac{f(y)}{C(\infty)}$$  \hspace{1cm} (B-3)

where $f(y)$ is the tracer concentration at distance far from the grain boundary and $C(\infty)$ is the total concentration of both isotopes in the bulk.

For diffusion parallel to the grain boundary, we only consider the $y$- component of the flux vector in Eq. (B-1); and the tracer diffusivity, $D$, is given as

$$D = D_o p$$  \hspace{1cm} (B-4)

The space charge enhancement to the tracer diffusion and conductance parallel to the boundary can be evaluated by integrating the $y$ component flux, $J_y$, over both sides of the boundary,

$$\Delta J = 2 \int_{\infty}^{\infty} [J_y(x) - J_y(\infty)] dx$$

$$= 2 \int_{\infty}^{\infty} [D_o p(x) \frac{dC^{(1)}(x,y)}{dy} - D \rho(\infty) \frac{dC^{(1)}(\infty,y)}{dy}] dx$$

$$= 2 \int_{\infty}^{\infty} [D_o p(x) C(x) - D \rho(\infty) C(\infty)] \frac{df(y)}{dy} dx$$  \hspace{1cm} (B-5)

This quantity is a measure of the conductance parallel to the boundary, but gives no information regarding the "effective" width or diffusivity for transport across the
boundary or the space charge cloud.

However, for diffusion normal to the grain boundary, the ionic flux is the \( x \)-component of the flux vector in Eq. (B-1). Although the last two terms in this component, \( D_0 C(i) \frac{\partial p}{\partial x} \) and \(-qBC(i)p\frac{\partial}{\partial x}(e\phi(x) - e\phi_0)\), will be of opposite signs, numerical calculations show that they can be of a magnitude larger than the first term in the flux component, \( D_0 p \frac{\partial C}{\partial x} \). The term \( D_0 C(i) \frac{\partial p}{\partial x} \) can be derived from \( p \), the association probability of the diffusing ions with vacancies, discussed in the subsequent sections; and is proportional to the space charge electric field. Since this electric field is an odd function with respect to the grain boundary, Kliwer and Koehler (1965),

\[
-\frac{\partial(e\phi - e\phi_0)}{\partial x} = \pm 2kT \sinh \left( \frac{e\phi(x) - e\phi_0}{2kT} \right); \quad x > 0
\]
\[
= \pm 2kT \sinh \left( \frac{e\phi_0 - e\phi(x)}{2kT} \right); \quad x < 0
\]

(B-6)

the net flux due to the \( D_0 C(i) \frac{\partial p}{\partial x} - qBC(i)p\frac{\partial}{\partial x}(e\phi(x) - e\phi_0) \) terms reverses direction on the opposite sides of the boundary. Therefore it is likely that these fluxes have no net contribution to diffusion across the boundary. Consequently, Eq. (B-5) may also be approximately correct for some problems involving diffusion across the grain boundary.

Furthermore, for Eq. (B-4) to be applicable, the diffusion of impurity ions, either parallel or normal to the boundary,
is restricted to tracer diffusion or sufficiently small concentration gradients that the space charge is adequately characterized by the average impurity concentration near the boundary. A significant quantity of impurity introduced into the matrix by impurity diffusion will change the space charge potential and require a more complicated analysis. For the present purposes, the case of tracer diffusion may well illustrate the essential features of the problem. Besides, results for the self diffusion coefficients are also applicable to mass transport for ionic conduction, creep or sintering.

(2) Sr Diffusion in Sr Doped KCl:

Since Sr$^{2+}$ can only diffuse by associating with potassium vacancies, Lidiard (1962), the probability of association, $p$, is defined as

$$p = \frac{[V'_k S'_k]^*}{[(V'_k S'_k)^*] + [S'_k]}$$

and is a function of location in the crystal.$^+$

$^+$ Kroger-Vink notation where $'$, $\cdot$, $^*$ indicate the effectively negative, positive and neutral charged species respectively.
We define \( p_\infty \) as the degree of association in the bulk. Since the space charge potential does not affect the associated complexes, which are neutral; the concentration of the complexes, \( (V^*_K \text{Sr}_K^*)^* \), is

\[
[(V^*_K \text{Sr}_K^*)^*] = C_\infty p_\infty \quad \text{(B-8)}
\]

where \( C_\infty \) is the total Sr concentration in the bulk.

The space charge potential will strongly affect the equilibrium distribution of the charged, unassociated strontium. Since the grain size \( (\gtrsim 10 \mu m) \) is much larger than the Debye length \( (10^{-3} \text{ to } 10^{-1} \mu m) \), it is reasonable to neglect effects of specimen size. The unassociated Sr concentration, \( [\text{Sr}_K^*] \), as given in Kliewer and Koehler (1965) is

\[
\text{Sr}_K^* = (1-p_\infty) C_\infty \exp \left(-\frac{e\phi(x) - e\phi_\infty}{kT}\right) \quad \text{(B-9)}
\]

Combining Eqs. (B-7) - (B-9), we have the probability of association near the boundary

\[
p(x) = \frac{p_\infty}{p_\infty + (1-p_\infty) \exp \left(-\frac{e\phi(x) - e\phi_\infty}{kT}\right)} \quad \text{(B-10)}
\]
Fig. B-2: Normalized Sr diffusivities near the grain boundary of Sr doped KCl.
Combining Eqs. (B-2) and (B-7), we can express the ratio of the Sr diffusivity in the boundary region, $D^{Sr}(x)$, to that in the bulk, $D^{Sr}(\infty)$,

$$\frac{D^{Sr}(x)}{D^{Sr}(\infty)} = \frac{D^{Sr}_p(x)}{D^{Sr}_p(\infty)} = \frac{1}{p_\infty + (1-p_\infty) \exp \left(-\frac{e\phi(x) - e\phi_\infty}{kT}\right)}$$  \hspace{1cm} \text{(B-11)}

The $D^{Sr}(x)/D^{Sr}(\infty)$ ratio, plotted in Fig. (B-2), as a function of distance normalized with respect to the Debye length, $\delta$, shows a moderate enhancement of Sr diffusivity in the region near the boundary at temperatures above the isoelectric point, which is 440°C for 50 ppm Sr doped KCl. However, at temperatures below the isoelectric point, there is a significant reduction of Sr diffusivity near the boundary.

The Debye length, $\delta$, for extrinsic temperatures as given in Kliuever and Koehler (1965), is

$$\delta = \left[\frac{\epsilon kT}{8\pi N e^2} \frac{I}{C_\infty (1-p_\infty)}\right]^{1/2}$$  \hspace{1cm} \text{(B-12)}

where $\epsilon$ is the static dielectric constant and $N$ is the density of anion or cation sites in the crystal. The diffusion and impurity-vacancy association data of Fuller et al (1968) and the defect formation energies of Dreyfus and Norwich (1962), are given in Table (II-1) of Chapter II.
The calculated values of bulk potentials, Debye lengths and impurity-vacancy association probabilities are given in Table (II-2) of Chapter II. This and subsequent calculations neglect SrCl$_2$ precipitation in the matrix which may occur in heavily doped samples, Abaev (1972), Splengler and Kaiser (1974), Rogella and Schmalzried (1968).

In the space charge theory of Kliewer and Koehler (1965) the impurity-vacancy complexes are assumed to be electrically neutral and to have no interaction with the space charge potential or the potential gradient; thus the concentration of the complexes, $p(x)C(x)$, is uniform across the boundary region, and $p(x)C(x) = p(\infty)C(\infty)$. Consequently, the presence of the space charge layers has no integrated enhancement of Sr diffusion flux parallel to the grain boundary, as given in Eq. (B-5), $\Delta J_{Sr} = 0$.

However, the impurity-vacancy complexes are electric dipoles; the interaction between the dipole moments and the space charge electric field has a significant effect on the distribution of dipole complexes with different moment orientations, Appendix C. Furthermore, because of the high value of the electric field gradient, the distribution of dipole complexes is not uniform, i.e. $C(x)p(x) \neq C(\infty)p(\infty)$; and it can be shown that the integrated enhancement to diffusion parallel to the grain boundary, $\Delta J$, as given
in Eq. (B-5), is

$$\Delta J = 2D_c c_p \rho_o \int_0^\infty \left[ \exp \left( \frac{-a \phi}{2x} / \kappa T \right) - 1 \right] \left[ \exp \left( -\frac{-a \phi}{2x} / \kappa T \right) - 1 \right] dx \frac{df}{dy}$$

where the space charge potential, $\phi$, differs by only a negligibly amount from the potential distribution in Kliewer and Koehler (1965), in which the complex dipole-electric field interaction is neglected. Numerical integration shows that $\Delta J$, in Eq. (B-13), are $0.133\Delta D^{Sr}(\infty) \frac{df}{dy}$ and $0.157\Delta D^{Sr}(\infty) \frac{df}{dy}$ for 200°C and 700°C respectively. These values are at least an order of magnitude smaller than the integrated enhancement for the self diffusion of K and Cl ions as shown in the following sections, Table (B-1).

(3) K Self Diffusion in Sr Doped KCl:

Since potassium ions diffuse by a vacancy mechanism, the $p$, as used in Section (1) for vacancy-ion association, is simply $z [V_{K}]$ where $z$ is the coordination number i.e. 12 for KCl and $[V_{K}]$ is the concentration of potassium vacancies free from Sr association. The K diffusivity, $D^K$, is then given as

$$D^K = [V_{K}] D^K_V$$

where $D^K_V$ is the potassium vacancy diffusion coefficient.

Although the space charge potential has little effect on the vacancy diffusivity, it does determine the distribution of
potassium vacancies in the vicinity of the grain boundary. The potassium vacancy concentration near the boundary is,

\[ \frac{V^*_K(x)}{V^*_K(\infty)} = \exp \left( \frac{e\phi(x) - e\phi_\infty}{kT} \right) \quad (B-15) \]

From Eqs. (B-13) and (B-14), the enhancement or reduction in K diffusion in the space charge region at temperatures above or below the isoelectric point have a similar trend as in the case of Sr diffusion and are shown in Fig. (B-3).

For the integrated enhancement of K flux, the \( c^K(x) \), as in Eq. (B-5), is simply \( \{1 - [V^*_K(x)]\} \), and

\[ \Delta J = 2 \int_0^\infty \left\{ D_v [V^*_K(x)] \{1 - [V^*_K(x)]\} - D_v [V'_K(\infty)] \{1 - [V'_K(\infty)]\} \right\} \frac{df}{dy} d\chi \]

\[ = 4D^K(\infty) \delta \left\{ \frac{\exp(-e\phi_\infty)}{2kT} - 1 \right\} + [V'_K(\infty)] \left( \frac{4}{3} - \frac{1}{3} \exp(-\frac{3e\phi_\infty}{2kT}) - \exp(-\frac{e\phi_\infty}{2kT}) \right) \frac{df}{dy} \]

(B-16)

which gives values of \(-3.69\delta D^K(\infty)\frac{df}{dy}\) at 200°C and \(+15.93\delta D(\infty)\frac{df}{dy}\) at 700°C for 50 ppm Sr doped KCl.

4) Cl Self Diffusion in Sr Doped KCl:

Due to the suppression of chlorine vacancies by Sr dopant, the Cl diffusivity is decreased in the extrinsic temperature region. However, the contribution due to potassium-chlorine
Fig. B-3: Normalized K diffusivities near the grain boundary of Sr doped KCl.
vacancy pairs, \( (V_i^+ V_j^-) \), is then significant. The ratio of vacancy pair diffusion, \( D_p^{Cl} \), to single anion vacancy diffusion in the bulk, \( D_s^{Cl}(\infty) \), can be calculated from equations by Fuller (1966) and with an assumption about the Sr impurity to K vacancy binding energy, Fuller et al (1968). The \( D_p^{Cl}(\infty)/D_s^{Cl}(\infty) \) ratios for various Sr contents are shown in Fig. (B-4).

Since the vacancy pairs are neutral and with the effects of dipole moment-electric field interaction neglected, their contribution to diffusion is not affected by the space charge potential. At high temperatures, when the contribution of single vacancies, \( V_i^+ \), to diffusion is significant, the space charge potential will affect the Cl diffusivity in a similar manner as to the K diffusivity. However, in this case, the ratio \( D_s^{Cl}(x)/D_s^{Cl}(\infty) \) is the reciprocal of that given in Eq. (B-14) for \( D_K(x)/D_K(\infty) \).

When both the single anion vacancy and vacancy pair contributions are included \( D_{tot}^{Cl} \), the Cl diffusivity in the region near the boundary can be expressed as

\[
\frac{D_{tot}^{Cl}(x)}{D_{tot}^{Cl}(\infty)} = \frac{D_s^{\alpha}(x)/D_s^{\alpha}(\infty) + D_p^{\alpha}(\infty)/D_s^{\alpha}(\infty)}{1 + D_p^{\alpha}(\infty)/D_s^{\alpha}(\infty)}
\]

(B-17)
Fig. B-4: The ratio of the vacancy pair, \((V_{K}\text{Cl})^*\), contribution to the single anion vacancy \((V_{\text{Cl}})^*\), contribution to Cl diffusion in Sr doped KCl.
This ratio is plotted for different temperatures in Fig. (B-5). Because of a significant contribution of vacancy pairs to diffusion at low temperatures both the magnitude and the effective range of the space charge enhancement are significantly reduced.

The integrated enhancement for the Cl diffusion flux,

\[
\Delta J = 2 D_{\text{tot}}^{c} \int_{0}^{\infty} \left( \frac{D_{\text{tot}}^{c}(x)}{D_{\text{ref}}^{c}(\infty)} \right) \left( 1 - [V_{c}^{*}(x)] - (1 - [V_{c}^{*}(\infty)]) \right) \frac{dx}{y} - 0
\]

\[
= \frac{4 D_{\text{tot}}^{c}(\infty)}{1 + D_{s}^{c}(\infty)/D_{s}^{c}(\infty)} \frac{dy}{y} \left[ \left( 1 - [V_{c}^{*}(\infty)] \frac{D_{s}^{c}(\infty)}{D_{s}^{c}(\infty)} \right) \left( \exp \left( \frac{e_{f}^{c}}{2kT} \right) - 1 \right) \right.
\]

\[
+ \left. \left[ V_{c}^{*}(\infty) \left( \frac{4}{3} - \frac{1}{3} \exp \left( \frac{3e_{f}^{c}}{2kT} \right) - \exp \left( \frac{e_{f}^{c}}{2kT} \right) \right) \right] \right]
\]

(B-18)

is \(-2.08 \delta D_{\text{tot}}^{c}(\infty) \frac{dy}{y}\) at 700°C and \(+0.71 \delta D_{\text{tot}}^{c}(\infty) \frac{dy}{y}\) at 200°C, for 50 ppm Sr doped KCl.

(5) K Self Diffusion in O Doped KCl:

For KCl doped with divalent anion impurity, e.g., K₂O, a negative bulk potential is always required. Physically it is due to the fact that the formation energy of anion vacancies is larger than that of cation vacancies. At intrinsic temperatures, the bulk potential approaches that of the pure KCl,
Fig. B-5: Normalized Cl diffusivities near the grain boundary as contributed by both single anion vacancies, \( (V_{Cl}^-) \), and vacancy pairs, \( (V_{Cl}^- V_{K}^-) \).
-0.27 eV. At extrinsic temperatures, the anion vacancy concentration at the surface, is always less than the impurity concentration. As temperature decreases, the surface concentration of anion vacancies is free to decrease; but because of the neutrality condition in the bulk, the anion vacancy concentration in the bulk is constrained by the impurity concentration. Consequently, as temperature decreases, an increasingly negative bulk potential is required to maintain the increasingly larger concentration differential between the surface and the bulk.

With an analysis similar to that by Kliewer and Koehler (1965) but for anion divalent dopants, it can be shown that the bulk potential for the 0-dopant KCl, \( \phi_\infty(0) \), and that for the Sr-doped KCl, \( \phi_\infty(Sr) \) are related by

\[
\phi_\infty(Sr) + \phi_\infty(0) = F^+ - F^-
\]  

(B-19)

provided that the binding energy between \( O^\ast_{Cl} \) and \( V^\ast_{Cl} \) is the same as that between \( Sr^\ast_K \) and \( V^\ast_K \), as shown in Fig. (II-1). Furthermore, the Debye length, \( \delta \), for extrinsic temperatures is the same as that given in Eq. (B-12).

Based on the calculated values of the bulk potentials and the solutions of Poisson's equation, vacancy and impurity distributions were calculated; and from these, K diffusion due to single vacancies were evaluated by Eq. (B-15) and are shown in Fig. (B-6). Because of the large bulk potential,
Fig. B-6: Normalized K diffusivities near the grain boundary of O doped KCl.
there is a strong enhancement of K diffusion in the space charge layer. In contrast to the case of K diffusion in Sr doped KCl, the enhancement in K₂O doped samples increases as the temperature decreases.

The integrated enhancement of K diffusion flux is also given by Eq. (B-16) and is

$$+55.2 \delta^{K(\infty)} \frac{\partial \mathcal{F}}{\partial Y} \text{ at } 500^\circ C \quad \text{and} \quad +1543 \delta^{K(\infty)} \frac{\partial \mathcal{F}}{\partial Y} \text{ at } 300^\circ C,$$

for 5 ppm K₂O doped KCl. Since the K diffusion in K₂O doped KCl is suppressed by this dopant, the bulk K diffusivity is much less than that in Sr doped samples.

Similar to the case of Cl diffusion in Sr doped KCl, the vacancy pair contribution to K diffusion in K₂O doped KCl will be significant, and the effective enhancement due to the space charge will be reduced. But since the enhancement factor ($10^2 - 10^5$) is much larger than the $\frac{D_p^{K}}{D_S^{K(\infty)}}$ ratio ($1 - 10^2$), the effective enhancement remains rather significant; in contrast to the case of the Sr dopant.

(6) Cl and O Diffusion in O Doped KCl:

The Cl and O diffusivities in the boundary region of K₂O doped KCl will be reduced by the space charge effects analogous to the previous cases. The integrated reduction in Cl diffusion flux is
\[ \Delta J = 2D^{(\infty)} \int_0^\infty \frac{D(x)}{D^{(\infty)}} \left\{ (1 - [\nu_0(x)]) \cdot D(\infty) - (1 - [\nu_0(\infty)]) \right\} dx \]

\[ = 4D^{(\infty)} \delta \left\{ \exp\left(\frac{e\varphi_0}{2kT}\right) - 1 + [\nu_0(\infty)] \left( \frac{4}{3} - \frac{1}{3} \exp\left(\frac{e\varphi_0}{2kT}\right) - \exp\left(\frac{e\varphi_0}{2kT}\right) \right) \right\} \frac{df}{dy} \]

(B-20)

giving \(-3.73\delta D^{\text{Cl}}(\infty) \frac{df}{dy}\) at 500°C and \(-3.99\delta D^{\text{Cl}}(\infty) \frac{df}{dy}\) at 300°C for 5 ppm K2O doped KCl.

Similar to the case of Sr diffusion in Sr doped KCl, there is no integrated enhancement of 0 diffusion flux in 0-doped KCl when the dipole attraction terms are neglected.
There have been several reports of boundary enhanced cation, anion and impurity diffusion in alkali halides. Anion diffusion has been typically found to be more enhanced than cation diffusion. Most of these experiments involved sintered samples e.g. Laurent and Benard (1957), Cabane (1962), and some involved bicrystals e.g. Geguzin et al (1967) and Sabharwal et al (1975). The grain boundaries in the samples may have been preferentially contaminated during the processing. Grain boundary diffusion for O and Br ions was observed in KBr; and O ions diffuse 100 times faster than Br, Barr and Dawson (1968). However, enhanced grain boundary diffusion was not observed for either cation or anions in hot deformed and recrystallized CsI polycrystals, Klotsman et al (1968). Boundary enhanced Tl diffusion in KCl bicrystals was not observed except in bicrystals intentionally synthesized in the presence of water vapor, Tiernan (1971). Water-enhanced grain boundary electrical conduction in KCl was reported, Geschwind and Machlin (1967); and cation grain boundary diffusion in NaCl was observed only if the Na-isotopes were accompanied by water contamination, Riggs and Wuttig (1969). As a result, there appear to be no good experimental estimates of $wD_b$ (the boundary width times the boundary diffusivity) for clean alkali halide boundaries, due in part to the relative

* Harris and Quang (1975) reported Ca segregation to the grain boundary region during KBr bicrystal growth.
insensitivity of diffusion measurement techniques in bicrystals.

There are conflicting reports about the grain boundary width in ionic materials. Boundary widths of 2-10 lattice spacings were estimated for MgO, Holt and Condit (1966), ZrO₂, Lightstone and Pamsler (1968), Al₂O₃, Johnson and Berrin (1967). However, a boundary width ~1μm was suggested for alkali halides, Barr and Hoodless (1960). When grain growth and diffusion data were compared, the boundary widths were estimated to be ~1μm for NaCl, 2μm for MgO, 150 Å for BeO and 100 Å for Al₂O₃, Mistler and Coble (1974). Boundary widths of 2 and 75μm were estimated for MgO by Wang (1965) and Minkes and Wuttig (1971) respectively based on the diffusion data of Wuensch and Vasilos (1964). Microhardness measurements of doped Al₂O₃, Jorgensen and Westbrook (1964) and doped Y₂O₃, Jorgensen and Anderson (1967) showed an effective boundary width of 10 - 20μm; but these are likely due to nonequilibrium solute segregation which occurred during cooling.

When the reported magnitude and extent of boundary-enhanced diffusion data are compared with those predicted by the space charge theory, several discrepancies, both qualitative and quantitative, are noted.
Boundary enhanced K and Sr diffusivities are predicted at temperatures above the isoelectric point; whereas reduced K and Sr diffusivities are predicted at temperatures below the isoelectric point. The inversion from enhancement to reduction is also predicted for Cl diffusion. An exception to the predicted inversion is the diffusivity in K₂O doped KCl, which has no isoelectric point. However, no data on reduced boundary diffusivities have been reported, nor would they be easily measurable by direct diffusion experiments.

The predicted magnitude of enhancement is much less than the reported value of $10^3 - 10^6$ in the cases of observed boundary diffusion.

The predicted boundary widths are in the range of 10 - 200 Å, depending on temperatures and impurities, much less than some reported values (≈ 1 µm). Only a few results of temperature dependent widths have been inferred from sintering studies in Al₂O₃, Johnson and Berrin (1967) and diffusion studies in ZnO bicrystals, Kim (1971) and ZrO₂ polycrystals, Lightstone and Pamsler (1968).

The present calculations give much lower values of Debye lengths and of the integrated diffusivity enhancements than for pure crystals. Inferred from the calculations of Lehovec (1953), the integrated Na diffusivity enhancements are $20.2D_{Na}^{∞}$ at 900 K and $55.6D_{Na}^{∞}$ at 600 K for pure
NaCl. More importantly, the Debye lengths, $\delta$, for pure NaCl are $\approx 80$ Å at $900^\circ$K and 2000 Å at $600^\circ$K, Lehovec (1953). The nearly micron size value of the Debye length at $600^\circ$K is valid only if the divalent impurity concentration is less than 0.01 ppm so that the bulk cation vacancies are predominantly Schottky defects. Consequently, the present calculations give a more realistic estimate of the space charge effects for presently obtainable crystals.

The diffusivity calculations are based on the space charge theories formulated by Frenkel (1946), Lehovec (1953), Eshelby et al (1958) and Kliewer and Koehler (1965). In these theories, the effects of adsorbates and the energies of excess vacancies at the surfaces were neglected; Lifshitz and co-workers (1965, 67) observed that these surface properties will introduce a crystallographic orientation dependency in the potential and charge distributions in the space charge layer. Poeppel and Blakely (1969) and Blakely and Danyluk (1973) made certain simplifying assumptions about the surface structures and were able to obtain a solution for the surface potential with the surface site density and binding energy as parameters. They suggested that the isoelectric temperatures in AgCl are independent of the surface site density, Blakely and Danyluk (1973). Given further refinement in the theory, it is not likely to change certain essential features,
e.g. the existence of the isoelectric point in divalent-cation doped KCl. But it is precisely these essential features of the theory that give the most interesting and unobserved predictions.

Furthermore, these space charge theories are formulated for ionic materials only. However, since many oxides, e.g. NiO, MgO, ZnO₂, ZrO₂, UO₂, Y₂O₃, at high temperatures, are at least partially electronic conductors, Kofstad (1972), the present forms of space charge theory are not strictly applicable; and the difference in formation energies of electrons and holes should also be included in the evaluation of the bulk potential, eφ, in these oxides.

In terms of the conceptual separation of at boundary, near boundary, and boundary associated phenomena, Kingery (1974), the reported micron size boundary widths and many observed enhanced diffusivities in contaminated boundaries may be classified as the boundary associated phenomenon, and usually resulted from second phase films at the boundary. As calculated, the space charge enhanced diffusivity, a near boundary phenomenon, is usually rather modest.

For clean boundaries, without impurity films, enhanced diffusion can be expected in the "core" of the boundary as well as in the charge cloud. A significant openness or disorder exists in the core to accommodate the lattice mismatch.
In addition, there will be excess ions of one sign at the boundary to balance the space charge cloud. The concentration of these excess ions per unit area, $\Delta Q$, will be:

$$
\Delta Q = 4C_V \delta \left( \exp \left( \pm \frac{e\phi_s}{kT} \right) - 1 \right)
$$

where $C_V$ is the vacancy concentration in the bulk, and the negative sign is for K ions and the positive sign is for Cl ions. The ratio of $\Delta Q/C_V$ is proportional to the integrated enhancements of the self diffusivities in the charge cloud and is usually rather small. This total excess ion or defect concentration in the core is probably very small compared to the effective defect concentration caused by the structural misfit. The mobilities of vacancies or interstitials in the core are different, and possibly significantly higher, than in the lattice. Therefore, no theoretical estimate of the core contribution to $wD_b$ can be made based solely on space charge effects. Finally, because of the small contribution from the charge cloud, if significant enhancement of the grain boundary diffusivity is observed, it is likely due to enhanced diffusivity in the core, even for clean boundaries.
B - III. Summary

The contribution from the space charge cloud to enhanced K, Cl, Sr and O diffusivities in alkali halides were calculated based on the present form of the space charge theory for ionic materials. The calculated diffusivities show only modest enhancements near the boundaries; and the range of enhancement is limited to $10 - 200$ Å. Only for the ion on the opposite sublattice from the principle impurity is appreciable diffusivity enhancement in the space charge cloud ever indicated. Therefore, the space charge enhanced diffusion cannot explain the large enhancement and wide boundary widths reported in some boundary diffusion data in ionic materials.
IV. Appendix

For the gas exchange diffusion experiment described in the text, whereas a uniform chemical potential is maintained throughout the bicrystal sample, a concentration gradient of the tracer isotope exists parallel to the grain boundary.

Since there is no potential gradient in the sample, both the \(x\) and \(y\) components of the net flux of the tracer and major isotopes vanish,

\[
J_x = J_x^{(i)} + J_x^{(a)} = 0 \quad \text{(B-22)}
\]

where

\[
J_x^{(i)} = -D_0 p \frac{\partial C^{(i)}}{\partial x} - C^{(i)} \left(D_0 \frac{\partial p}{\partial x} - q \frac{\partial p}{\partial x} (e\phi - e\phi_x) \right) \quad \text{(B-23)}
\]

\[
J_x^{(a)} = -D_0 p \frac{\partial C^{(a)}}{\partial x} - C^{(a)} \left(D_0 \frac{\partial p}{\partial x} - q \frac{\partial p}{\partial x} (e\phi - e\phi_a) \right) \quad \text{(B-24)}
\]

\[
J_y = J_y^{(i)} + J_y^{(a)}
\]

\[
= -D_0 p \left( \frac{\partial C^{(i)}}{\partial y} + \frac{\partial C^{(a)}}{\partial y} \right) = 0 \quad \text{(B-25)}
\]

\[
\therefore C(x, y) + C^{(2)}(x, y) = C(x) \quad \text{(B-26)}
\]

where \(C(x)\) is the integration constant and the total concentration of the two isotopes are independent of \(y\).
With the usual assumption that \( J_x \) and \( J_y \) are independent of each other and that the steady state is achieved, the equation of continuity requires that

\[
\frac{\partial J_x^{(1)}}{\partial x} = \frac{\partial J_x^{(2)}}{\partial x} = \frac{\partial J_y^{(1)}}{\partial y} = \frac{\partial J_y^{(2)}}{\partial y} = 0
\]

(B-27)

i.e. \( J_x^{(1)} \) and \( J_x^{(2)} \) are independent of \( x \), and \( J_y^{(1)} \) and \( J_y^{(2)} \) are independent of \( y \).

By symmetry of the diffusion sample, the quantities \( C^{(1)}(x,y) \), \( C^{(2)}(x,y) \), \( p(x) \), \( \varnothing(x) \) are even functions of \( x \). Therefore the fluxes, \( J_x^{(1)} \) and \( J_x^{(2)} \) are odd functions of \( x \), and these fluxes vanish at \( x = 0 \),

\[
J_x^{(1)}(0,y) = J_x^{(2)}(0,y) = 0
\]

(B-28)

It is obvious from Eqs. (B-27) and (B-28) that

\[
J_x^{(1)}(x,y) = J_x^{(2)}(x,y) = 0
\]

(B-29)

With Eqs. (B-23), (B-24), we observe that both \( C^{(1)} \) and \( C^{(2)} \) satisfy the same differential equation,

\[
-D \varrho \frac{\partial \psi^{(i)}}{\partial x} - C^{(i)} \left( D \frac{\partial \psi}{\partial x} - q \beta p \frac{\partial}{\partial x} (\varnothing - e \varphi) \right) = 0 ; \quad i = 1, 2
\]

(B-30)
therefore $C^{(1)}(x,y)$ and $C^{(2)}(x,y)$ must have the same $x$ dependence; in addition to the requirement stated in Eq. (B-26). Consequently, it can be shown that

$$C^{(1)}(x,y) = C(x) \frac{f(y)}{C(\infty)} \quad \text{(B-31)}$$

$$C^{(2)}(x,y) = C(x) \left[ 1 - \frac{f(y)}{C(\infty)} \right] \quad \text{(B-32)}$$

where $f(y)$ is the tracer concentration at distance far from the grain boundary, $x = \infty$. 
Table B-1

$\Delta J$, Integrated Enhancement in the Diffusion Flux of Impurity and Matrix Ions.

<table>
<thead>
<tr>
<th>Diffusant</th>
<th>Temperature</th>
<th>$\Delta J/\delta V$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample: KCl with 50 ppm Sr.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr 200°C</td>
<td>0, (0.133$\delta^{Sr}(\infty)$)** 0, (0.52$\delta^{Sr}(\infty)$)*</td>
<td></td>
</tr>
<tr>
<td>Sr 700°C</td>
<td>0, (0.157$\delta^{Sr}(\infty)$)** 0, (0.28$\delta^{Sr}(\infty)$)</td>
<td></td>
</tr>
<tr>
<td>K 200°C</td>
<td>-3.69$\delta^{K}(\infty)$ -14.4$\delta^{K}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>K 700°C</td>
<td>+15.93$\delta^{K}(\infty)$ +28.3$\delta^{K}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>Cl 200°C</td>
<td>+0.718$\delta^{Cl}<em>{tot}(\infty)$ +2.77$\delta^{Cl}</em>{tot}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>Cl 700°C</td>
<td>-2.088$\delta^{Cl}<em>{tot}(\infty)$ -3.70$\delta^{Cl}</em>{tot}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>Sample: KCl with 5 ppm O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K 300°C</td>
<td>+154.3$\delta^{K}(\infty)$ +7180$\delta^{K}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>K 500°C</td>
<td>+55.2$\delta^{K}(\infty)$ +228$\delta^{K}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>Cl 300°C</td>
<td>-3.99$\delta^{Cl}(\infty)$ -18.5$\delta^{Cl}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>Cl 500°C</td>
<td>-3.73$\delta^{Cl}(\infty)$ -15.4$\delta^{Cl}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>O 300°C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O 500°C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sample: KCl without any aliovalent dopant.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K 300°C</td>
<td>57.1$\delta^{K}(\infty)$ 18253$\delta^{K}(\infty)$</td>
<td></td>
</tr>
<tr>
<td>K 500°C</td>
<td>26.19$\delta^{K}(\infty)$ 444$\delta^{K}(\infty)$</td>
<td></td>
</tr>
</tbody>
</table>

* $a$ - lattice constant; ** Dipole attraction included.
Appendix C: Effects of Dipole Interactions in the Space Charge Potential Theory

The space charge theory, as formulated in Kliewer and Koehler (1965), neglected the interactions between the bound charges, e.g. the \((\text{Sr}^+_K \text{V}^-_K)^*\) dipoles, and the space charge electric field. As shown in Jackson (1962), the interaction energy, \(U_{dipole}\), of the polarizable dipoles of dipole moments, \(\vec{p}\), in an electric field, \(\vec{E}\), is given as

\[
U_{dipole} = -\frac{1}{2} \vec{E} \cdot \vec{p}
\]  

(C-1)

For the rocksalt crystal structure, the dipole moment of the \((\text{Sr}^+_K \text{V}^-_K)^*\) complexes can be of any of the 12 vectors, \(\vec{p}_i\), of the type, \(\frac{e}{a}/2\) (110); and each vector has a magnitude of \(\frac{e}{a}\sqrt{2}\), where \(e\) is the electronic charge, \(1.6 \times 10^{-19}\) coulomb; and \(a\) is the lattice constant, \(6.293\) Å for KCl. We further assume that there are \(m_i(x)\) vacancy-impurity dipoles, \((\text{Sr}^+_K \text{V}^-_K)^*\), with a dipole moment, \(\vec{p}_i\), at the location \(x\).

However, the dipole moment of \((\text{V}^+_K \text{V}^-_{\text{Cl}})^*\) complexes can only be one of the 6 vectors, \(\vec{q}_j\), of the type, \(\frac{e}{a}/2\) (100); and each has a magnitude of \(\frac{e}{a}/2\). Similarly, we assume that there are \(n_j(x)\) vacancy-vacancy dipoles, \((\text{V}^+_K \text{V}^-_{\text{Cl}})^*\), with dipole moment, \(\vec{q}_j\), at the location \(x\).

The net dipole moment, \(\vec{p}\), of the \(m_i(x)\) and \(n_j(x)\) dipoles with moments, \(\vec{p}_i\) and \(\vec{q}_j\), respectfully, when resolved in the direction of the electric field, which is normal to the planar **Tallon (1975) treated dipole interactions in ionic conductivity three months before this work was completed.**
grain boundary, is
\[ \vec{P} = (\sum_{i=1}^{12} \vec{p}_i \cdot m_i + \sum_{j=1}^{6} \vec{q}_j \cdot n_j) \cdot \vec{E} / |\vec{E}| \]
\[ = \sum_{i=1}^{12} p_{ix} m_i + \sum_{j=1}^{6} q_{jx} n_j \]  
(C-2)

where \( p_{ix} \) and \( q_{jx} \) are the components of \( \vec{p}_i \) and \( \vec{q}_j \) in the field direction, \( \vec{x} \).

The interaction energy, \( U_{\text{dipole}} \), between all these dipoles and the electric field, \( \vec{E} \), is
\[ U_{\text{dipole}} = -\frac{1}{2} \vec{E} \cdot (\sum_{i=1}^{12} \vec{p}_i m_i + \sum_{j=1}^{6} \vec{q}_j n_j) \]
\[ = \frac{1}{2} \left( \sum_{i=1}^{12} p_{ix} m_i + \sum_{j=1}^{6} q_{jx} n_j \right) \phi' / d\vec{x} \]  
(C-3)

where \( \phi' \) is the potential associated with the field.

When the interaction energy term, \( U \), is included, the free energy, \( F \), of a crystal, of length \( 2L \), is
\[ F = 2 \int_{0}^{L} dx \left\{ n_+(x) F^+ + n_-(x) F^- + \sum_{i=1}^{12} m_i(x) [F^+ - B_+ - \vec{p}_i \cdot \vec{E}/2] + \sum_{j=1}^{6} n_j(x) [F^- + F^+ - \vec{q}_j \cdot \vec{E}/2] \right. \]
\[ + \left. \frac{1}{2} \rho(x) \phi(x) \right\} - TS_c \]  
(C-4)

where \( n_+(x) \) is the number of cation vacancies with formation energy, \( F^+ \); \( n_-(x) \) is the number of anion vacancies with formation energy, \( F^- \); \( B_+ \) and \( B \) are the binding energies of
the \((\text{Sr}_{K}^{V_{K}})^*\) complexes and of the \((\text{V}_{K}^{V_{C}^*})^*\) complexes respectively; and \(\rho_f\) is the free charge density in the crystal.

The free energy of the crystal can be minimized by varying the 21 independent quantities of defect and impurity concentrations, and with the following two constraints:

1. **Poisson's Equation:**
   \[
   \frac{d}{dx}(-\varepsilon \frac{df}{dx} + 4\pi P) = 4\pi \varepsilon (n_f + n_- - n_+) \tag{C-5}
   \]
   where \(n_f\) is the number of free Sr atoms.

2. **Impurity conservation:**
   \[
   \int_{0}^{L} dx \left\{ n_f(x) + \sum_{i=1}^{12} m_i(x) \right\} = \bar{C}N \tag{C-6}
   \]
   where \(\bar{C}\) is the average concentration of Sr impurities and \(N\) is the density of anion or cation sites in the crystal.

A variation of the free energy, \(F\), as defined in Eq. \(\text{(C-4)}\), gives,

\[
\delta (F/2) = \int_{0}^{L} \left[ \varepsilon \frac{df}{dx} + \frac{1}{2} \sum_{i=1}^{12} m_i(x) \frac{d^2}{dx^2} + \frac{1}{2} \sum_{j=1}^{6} n_j(x) \right] \frac{d\varepsilon}{dP} + \frac{1}{2} \rho_f(x) \delta (x) dx - \delta (\bar{C}N) \tag{C-7}
\]
In the following sections, we discuss the variations of the last four terms of Eq. (C-7):

(C1) For the dipole interaction of \((\text{Sr}_K^* \text{V}_K^*)^*\) complexes with the electric field:

we define \(F_{d1} \equiv -\delta \int_0^L d\chi \sum_{i=1}^{L_2} m_i(\chi) \vec{p}_i \cdot \vec{E}/2\)

\[= \delta \int_0^L \sum_{i=1}^{L_2} m_i(\chi) \frac{\partial \phi}{\partial \chi} \frac{d\phi}{d\chi} d\chi\]

\[= \int_0^L \frac{d\phi}{d\chi} \sum_{i=1}^{L_2} \frac{\partial \phi}{\partial \chi} m_i(\chi) d\chi\]

\[+ \int_0^L \sum_{i=1}^{L_2} \frac{\partial \phi}{\partial \chi} m_i(\chi) S \frac{d\phi}{d\chi} d\chi\]

\[\equiv I_1 + I_2 \quad \text{(C-8)}\]

(C2) Similarly, for the dipole interaction of \((\text{V}_K^* \text{V}_C^*)^*\) complexes with the electric field:

\[-\delta \int_0^L \sum_{j=1}^{L_3} n_j(\chi) \vec{g}_j \cdot \vec{E}/2 d\chi = \int_0^L \frac{d\phi}{d\chi} \sum_{j=1}^{L_3} \frac{\partial \phi}{\partial \chi} n_j(\chi) d\chi\]

\[+ \int_0^L \sum_{j=1}^{L_3} \frac{\partial \phi}{\partial \chi} n_j(\chi) S \frac{d\phi}{d\chi} d\chi\]

\[\equiv J_1 + J_2 \quad \text{(C-9)}\]
(C-3) For the electrostatic energy of the free charge density:

we define

\[ \delta F_e = \delta \int_0^L \frac{1}{2} \rho_s(x) \phi(x) \, dx \]

\[ = \int_0^L \frac{1}{2} \rho_s(x) \delta \phi(x) \, dx + \int_0^L \phi(x) \delta \rho_s(x) \, dx \]

\[ = M + N \quad \text{(C-10)} \]

\[ M = \int_0^L \frac{1}{2} \rho_s(x) \delta \phi \, dx \]

\[ = -\frac{\varepsilon}{\varepsilon_0} \int_0^L \frac{d^2 \phi}{dx^2} \delta \phi \, dx + \frac{1}{2} \int_0^L \left( \sum_{k=1}^n m_k \delta p_k + \sum_{j=1}^m \delta q_j \right) \delta \phi \, dx \]

\[ = M_1 + M_2 \quad \text{(C-11)} \]

\[ M_1 = -\frac{\varepsilon}{\varepsilon_0} \int_0^L \frac{d^2 \phi}{dx^2} \delta \phi \, dx \]

\[ = -\frac{\varepsilon}{\varepsilon_0} \frac{d \phi}{dx} \bigg|_0^L + \frac{\varepsilon}{\varepsilon_0} \int_0^L \delta \left( \frac{d \phi}{dx} \right) \frac{d \phi}{dx} \, dx \quad \text{(C-12a)} \]

after integration by parts.

For fixed potentials at the surface and in the bulk,

\[ \delta \phi(0) = \delta \phi(L) = 0 \]

\[ \therefore M_1 = \frac{\varepsilon}{\varepsilon_0} \int_0^L \frac{d \phi}{dx} \delta \left( \frac{d \phi}{dx} \right) \, dx \]

\[ = \frac{\varepsilon}{\varepsilon_0} \delta \phi(x) \left. \frac{d \phi}{dx} \right|_0^L - \frac{\varepsilon}{\varepsilon_0} \int_0^L \phi(x) \delta \left( \frac{d \phi}{dx} \right) \, dx \quad \text{(C-12b)} \]

again after integration by parts.
We define \( \frac{d\phi}{dx} = 0 \) in the bulk, \( L \), due to the symmetry of the crystal.

\[
\therefore M_L = -\frac{\varepsilon}{8\pi} \phi(0) \frac{d}{dx} \left( \frac{d\phi}{dx} \right) \bigg|_0^L - \frac{\varepsilon}{8\pi} \int_0^L \phi(x) \delta \left( \frac{d^2\phi}{dx^2} \right) \, dx
\]

\[
= -\frac{\varepsilon}{8\pi} \phi(0) \frac{d}{dx} \left( \frac{d\phi}{dx} \right) \bigg|_0^L - \frac{1}{8\pi} \int_0^L \phi(x) \left[ 4\pi \left( \sum_{i=1}^{12} q_{ix} \delta n_i + \sum_{j=1}^{6} q_{jx} \delta n_j \right) \right] \, dx
\]

\[
= -\frac{\varepsilon}{8\pi} \phi(0) \frac{d}{dx} \bigg|_0^L + 4\pi \left( \sum_{i=1}^{12} q_{ix} m_i + \sum_{j=1}^{6} q_{jx} n_j \right) \bigg|_0^L = 4\pi \int_0^L \Theta(x) \, dx
\]  

(C-12c)

\[
\therefore \frac{d\phi}{dx} \bigg|_{x=0} = \int_0^L 4\pi \Theta(x) \, dx - 4\pi \left( \sum_{i=1}^{12} q_{ix} m_i + \sum_{j=1}^{6} q_{jx} n_j \right) \bigg|_0^L
\]

\[
= \int_0^L 4\pi \Theta(x) \, dx + 4\pi \left( \sum_{i=1}^{12} q_{ix} m_i(0) + \sum_{j=1}^{6} q_{jx} n_j(0) \right)
\]  

(C-13)

and we assumed that there is no net polarization term in the bulk, \( \sum_{i=1}^{12} q_{ix} m_i(L) = \sum_{j=1}^{6} q_{jx} n_j(L) = 0 \)

\[
\therefore M_1 = -\frac{1}{4\pi} \int_0^L \delta \phi(0) \, dx - \frac{1}{4\pi} \phi(0) \delta \left( \sum_{i=1}^{12} q_{ix} m_i + \sum_{j=1}^{6} q_{jx} n_j \right) \, dx + \frac{1}{4\pi} \int_0^L \phi(x) \frac{d}{dx} \left( \sum_{i=1}^{12} q_{ix} \delta m_i + \sum_{j=1}^{6} q_{jx} \delta n_j \right) \, dx
\]  

(C-14a)
Since
\[ \int_0^L \frac{\partial}{\partial x} \left[ \sum_{i=1}^{2^L} p_{ix} \delta m_i(x) + \sum_{j=1}^6 \varphi_j(x) \delta n_j(x) \right] \, dx \]
\[ = \phi(x) \left( \sum_{i=1}^{2^L} p_{ix} \delta m_i(x) + \sum_{j=1}^6 \varphi_j(x) \delta n_j(x) \right) \bigg|_0^L - \int_0^L \left( \sum_{i=1}^{2^L} p_{ix} \delta m_i(x) + \sum_{j=1}^6 \varphi_j(x) \delta n_j(x) \right) \frac{d\phi}{dx} \, dx \]
\[ . \quad M_1 = \frac{1}{L} \int_0^L \left[ \phi(x) - \phi(x) \right] \delta \varphi \omega(x) \, dx + \frac{1}{L} \int_0^L \left( \sum_{i=1}^{2^L} p_{ix} \delta m_i(x) + \sum_{j=1}^6 \varphi_j(x) \delta n_j(x) \right) \frac{d\phi}{dx} \, dx \]
(C-14b)

From Eq. (C-11),
\[ M_2 = \frac{1}{L} \int_0^L \frac{d}{dx} \left( \sum_{i=1}^{2^L} m_i(x) p_{ix} + \sum_{j=1}^6 n_j(x) \varphi_j(x) \right) \delta \varphi \, dx \]
\[ = \frac{1}{L} \left( \sum_{i=1}^{2^L} m_i(x) p_{ix} + \sum_{j=1}^6 n_j(x) \varphi_j(x) \right) \delta \varphi \bigg|_0^L - \frac{1}{L} \int_0^L \left( \sum_{i=1}^{2^L} m_i(x) p_{ix} + \sum_{j=1}^6 n_j(x) \varphi_j(x) \right) \frac{d\delta \varphi}{dx} \, dx \]
\[ = -\frac{1}{L} \int_0^L \left( \sum_{i=1}^{2^L} m_i(x) p_{ix} + \sum_{j=1}^6 n_j(x) \varphi_j(x) \right) \delta \left( \frac{d\varphi}{dx} \right) \, dx \]
(C-15)

From Eq. (C-10),
\[ \delta F = M + N \]
\[ = M_1 + M_2 + N \]
\[ = \frac{1}{L} \int_0^L \left( \phi(x) - \phi(x) \right) \delta \varphi \omega(x) \, dx - \frac{1}{L} \int_0^L \left( \sum_{i=1}^{2^L} p_{ix} \delta m_i(x) + \sum_{j=1}^6 \varphi_j(x) \delta n_j(x) \right) \frac{d\phi}{dx} \, dx \]
\[ - \frac{1}{L} \int_0^L \left( \sum_{i=1}^{2^L} m_i(x) p_{ix} + \sum_{j=1}^6 n_j(x) \varphi_j(x) \right) \delta \left( \frac{d\varphi}{dx} \right) \, dx + \int_0^L \frac{1}{2} \phi(x) \delta \varphi_\omega(x) \, dx \]
(C-16)
Since we assign an arbitrary potential, $\phi(0)$, at the crystal surfaces, we have to include an electrostatic energy term, $F_s$, due to this surface potential and on the surface free charge, $\sigma_s$,

$$
\delta F_s = \frac{1}{2} \phi(0) \sigma_s = -\frac{1}{2} \frac{1}{\varepsilon} \phi(0) \int_0^L \rho_i(x) \, dx \tag{C-17}
$$

Consequently, the total electrostatic energy, $F_{e,\text{tot}}$, due to the free charges, $\delta F_{e,\text{tot}} = \delta F_e + \delta F_s$

$$
= \int_0^L (\phi(x) - \phi(0)) \delta \rho_i \, dx - \frac{1}{2} \int_0^L \sum_{j=1}^b m_i \delta p_i \, dx + \sum_{j=1}^b \gamma_j \delta \varphi_j \frac{d\phi}{dx} \, dx
+ \frac{1}{2} \int_0^L \left( \sum_{i=1}^a p_i \delta m_i + \sum_{j=1}^b \delta \gamma_j \delta \varphi_j \frac{d\phi}{dx} \right) \, dx \tag{C-18}
$$

We also note that only the potential difference with respect to the crystal surfaces appears in the expression of the crystal free energy, therefore a choice of zero surface potential, $\phi(0) = 0$, results in no loss of generality.

\textbf{(G4)} The variation of the entropy term, $S_c$, is similar to the case discussed in Kliewer and Koehler (1965). However, since the dipoles with different orientations, $\vec{p}_i$ or $\vec{q}_i$, are considered as separate entities, the potassium vacancy must
be in the unique nearest neighbor position of the Sr ion in order to form a \((\text{Sr}_K^+ \cdot \text{V}_K^-)^*\) dipole of a specific moment. Similarly, a potassium vacancy must also be in the unique nearest neighbor position of a chlorine vacancy to form a \((\text{V}_K^+ \cdot \text{V}_{Cl}^-)^*\) dipole of a specific moment. With this consideration and based on the work of Kliewer and Koehler (1965), we obtain

\[
\delta S_c = k \int_0^L dx \left[ \delta n_i \ln \left( \frac{N}{n_i} \right) + \sum_{i=1}^{21} \delta n_i \ln \left( \frac{N}{n_i} \right) + \sum_{j=1}^{21} \delta n_j \ln \left( \frac{N}{n_j} \right) \right] \tag{C-19}
\]

with the usual assumption of low impurity and defect concentrations, \((n_f^i, m_1^i, n_1^i, n_+^i, n_-^i) \ll N\), where \(N\) is the density of anion or cation sites in the crystal.

Consequently, the variation of the crystal free energy can be expressed in terms of the variations of the 21 independent variables, \(n_f, m_1, m_2, \ldots, m_{12}, n_1, n_2, \ldots, n_6, n_+\) and \(n_-\).

\[
\delta F = \int_0^L \sum_{i=1}^{21} \left( F^i - B + m_i \frac{d \phi}{d x} - kT \ln \left( \frac{N}{m_i} \right) + \alpha \right) \delta m_i(x) \, dx \\
+ \int_0^L \sum_{j=1}^{21} \left( F^+ - B + q_j \frac{d \phi}{d x} - kT \ln \left( \frac{N}{n_j} \right) \right) \delta n_j(x) \, dx \\
+ \int_0^L \left( e\phi + \alpha - kT \ln \left( \frac{N}{n_f} \right) \right) \delta n_f(x) \, dx \\
+ \int_0^L \left( e\phi - kT \ln \left( \frac{N}{n_+} \right) \right) \delta n_+(x) \, dx \\
+ \int_0^L \left( F^- - e\phi - kT \ln \left( \frac{N}{n_-} \right) \right) \delta n_-(x) \, dx \tag{C-20}
\]
where $\alpha$, the Lagrange multiplier, is introduced for the conservation of impurity atoms, Eq. (C-6).

The minimization of the free energy will require $\delta F$ to be zero and we obtain the corresponding relations for the independent variables of the defect and impurity concentrations:

$$m_i^N = \exp\left[-(F^+ - B + \rho_i \frac{d\phi}{d\chi} + \alpha) / kT\right]$$
$$= \frac{C_i}{2} \rho_i \exp\left(-\rho_i \frac{d\phi}{d\chi} / kT\right)$$

$$n_i^N = \exp\left[-(F^+ - B + q_j \frac{d\phi}{d\chi}) / kT\right]$$

$$n_e^N = \exp\left[-(e\phi + \alpha) / kT\right]$$
$$= (1 - \rho_i) C_e \exp\left[-(e\phi - e\phi_i) / kT\right]$$

$$n_p^N = \exp(-(F^+ - e\phi) / kT)$$

$$n_\text{N}^- = \exp(-(F^- + e\phi) / kT)$$

With these expressions for the impurity and defect concentrations, Eq. (C-21) - Eq. (C-25), Poisson's equation, Eq. (C-5), becomes

$$\frac{d}{d\chi}\left[-\varepsilon \frac{d\phi}{d\chi} + 4 \pi \sum_{i} \rho_i m_i(x) + 4 \pi \sum_{j} q_j n_j(x)\right] = N 4 \pi e \left[C_e (1 - \rho_i) \exp(-(e\phi - e\phi_i) / kT)\right]$$
$$+ \exp(-(F^- - e\phi) / kT)$$
$$- \exp(-(F^+ - e\phi) / kT)$$

(C-26)
where the contribution of the vacancy - vacancy dipoles, $(V^*_K V^*_C)^*$, are neglected.

For a grain boundary normal in the (100) direction, a third of the $(Sr^*_K V^*_C)^*$ dipole vectors have $p_{ix} = ea/2$, another third have $p_{ix} = -ea/2$, and the rest have $p_{ix} = 0$. We define $m_1$ for the concentration of dipoles with $p_{ix} = ea/2$, $m_2$ for $p_{ix} = 0$, and $m_3$ for $p_{ix} = -ea/2$. Thus Poisson's equation, Eq. (C-26) is simplified to

\[
\left[ 1 + \frac{\mu N e^2}{\epsilon R T} \frac{a^2}{4} \frac{C_0 p_0}{3} 2 \cosh \left( \frac{a}{2 \delta} \frac{d z}{d s} \right) \right] \frac{d^2 z}{d s^2} = \sinh z \tag{C-27}
\]

where the reduced distance $S$ is given as

\[
S = \frac{\chi}{\delta} \tag{C-28}
\]

\[
\delta = \left[ \frac{\mu N e^2}{\epsilon R T} \exp \left( -\left( F^+ - e \Phi_\infty \right) / kT \right) \right]^{-\frac{1}{2}} \tag{C-29}
\]

and the reduced potential, $\bar{Z}$, is given as

\[
\bar{Z} = \frac{(e \Phi - e \Phi_\infty)}{kT} \tag{C-30}
\]

and the bulk potential, $e \Phi_\infty$, is defined from the condition of charge neutrality in the bulk,

\[
(1 - p_\infty) C_\infty + \exp \left( -\left( F^+ - e \Phi_\infty \right) / kT \right) - \exp \left( -\left( F^- - e \Phi_\infty \right) / kT \right) = 0 \tag{C-31}
\]
The bulk potential, $\varepsilon \phi_\infty$, and the Debye length, $\delta$, are similar to those defined in Kliewer and Koehler (1965).

The numerical solutions of Eq. (C-27) for the space charge potential and the space charge electric field were performed. It was shown in Fig. (V-5), that the space charge electric field, $E$, when corrected for the dipole interactions is not significantly different from that derived in Kliewer and Koehler (1965), in which the dipole interactions are neglected. However the distributions of $(S r^*_K V^*_K)^*$ dipoles, namely $m_1$ and $m_3$, each with a net dipole moment resolved in the electric field direction, are non-uniform in the grain boundary region, Fig. (V-6).

With the dipole-field interaction, the net concentration of vacancy-impurity dipole complexes is always enhanced. The integrated enhancement, $\Delta m$, over both sides of the grain boundary region is given as

$$\Delta m = 2 \frac{C_\infty \rho^\infty}{3} \int \left\{ \exp \left( \frac{e a}{2} \frac{d \phi}{d \chi} / kT \right) - 1 \right\} \left\{ \exp \left( -\frac{e a}{2} \frac{d \phi}{d \chi} / kT \right) - 1 \right\} d\chi$$

$$\geq 0$$  \hspace{1cm} (C-32)
Appendix D: Evaluation of the Quantities $\alpha$ and $\beta$

The quantities $\alpha$ and $\beta$ are evaluated in this Appendix. According to Cahn (1962),

$$\alpha \equiv 4kTN \int_{-\infty}^{\infty} \frac{\sinh^2(\frac{U}{2kT})}{D(x)} \, dx \quad (D-1)$$

$$\frac{\alpha}{\beta^2} \equiv \frac{N}{kT} \int_{-\infty}^{\infty} (\frac{dU}{dx})^2 D(x) \, dx \quad (D-2)$$

For $U \equiv e\phi - e\phi_\infty \quad (D-3)$

and $D \equiv \frac{D_0 \rho_\infty}{\rho_\infty + (1-\rho_\infty)e^{-\frac{e\phi-e\phi_\infty}{kT}}} \quad (D-4)$

With the definitions of $\delta = (e\phi-e\phi_\infty)/kT$; $S = X/\delta$ and

$$\delta \equiv \left[ \frac{e\phi - e\phi_\infty}{\delta \eta N e^2} \right]^{1/2} \left[ \exp \left( \frac{e\phi - e\phi_\infty}{\delta \eta N e^2} \right) \right]^{1/2} \quad \text{we get}$$

$$\alpha = 4NkT \int_{-\infty}^{\infty} \frac{\sinh^2(\frac{U}{2kT})}{D_0 \rho_\infty \left[ \rho_\infty + (1-\rho_\infty)e^{-\frac{e\phi-e\phi_\infty}{kT}} \right]} \, dx$$
SIMILARITY

(6-5)

\[
\begin{align*}
(1 - \frac{1}{\exp(\sum_{1}^{n} (1-I)^{-1} - I)} - \frac{1}{\exp(\sum_{1}^{n} (1-I)^{-1} - I)} \right)^{\frac{1}{n}} \frac{2\pi}{\sqrt{\Gamma(2n+1)\Gamma(n)}} \frac{\Gamma(n/2)}{\Gamma((n+1)/2)} N = \frac{\pi}{\gamma} \\
\end{align*}
\]

(6-5)

\[
\begin{align*}
(1 - \frac{1}{\exp(\sum_{1}^{n} (1-I)^{-1} - I)} - \frac{1}{\exp(\sum_{1}^{n} (1-I)^{-1} - I)} \right)^{\frac{1}{n}} \frac{2\pi}{\sqrt{\Gamma(2n+1)\Gamma(n)}} \frac{\Gamma(n/2)}{\Gamma((n+1)/2)} N = \frac{\pi}{\gamma} \\
\end{align*}
\]
Appendix E: Strain Field Interactions with the Space Charge Potential

From the text, the free energy of the system is given as

$$ F = \int_{0}^{L} d\chi \left[ n_{+}(F^{+}U_{s}^{+}) + n_{-}(F^{-}U_{s}^{-}) + n_{s}(F^{+}F^{-}B - U_{s}^{b}) + n_{ib}(F^{+}B_{s}^{+} + U_{s}^{ib}) \right] $$

$$ + n_{+}U_{s}^{+} + \frac{1}{2} \rho \phi \right] + \frac{1}{2} \sigma \phi + N_{s}^{+}F_{s}^{+} + N_{s}^{+}F_{s}^{+} + N_{s}^{-}F_{s}^{-} - TS $$ (E-1)

with the following assumptions:

1. $$ \sigma = e(N_{s}^{+} + N_{s}^{+} - N_{s}^{-}) $$ (E-2a)

2. $$ N_{s}^{+} + \int_{0}^{L} n_{+}(\chi) d\chi = \text{a constant} $$ (E-2b)

3. $$ N_{s}^{+} = \int_{0}^{L} n_{+}(\chi) d\chi $$ (E-2c)

4. $$ N_{s}^{-} = \int_{0}^{L} n_{-}(\chi) d\chi $$ (E-2d)

Minimization of the free energy requires

$$ \delta F = 0, $$

where $$ \delta F $$ is given as,

$$ \delta F = \int_{0}^{L} d\chi \left[ \delta n_{+}(F^{+}U_{s}^{+}) + \delta n_{-}(F^{-}U_{s}^{-}) + \delta n_{s}(F^{+}F^{-}B - U_{s}^{b}) + \delta n_{ib}(F^{+}B_{s}^{+} + U_{s}^{ib}) \right] $$

$$ + \delta n_{+}U_{s}^{+} + \frac{1}{2} \delta (\rho \phi) \right] + \frac{1}{2} \phi \delta \sigma + F_{s}^{+}S_{s}^{+} + F_{s}^{-}S_{s}^{-} + F_{s}^{+}S_{s}^{+} + S_{s}^{-}S_{s}^{-} - TS $$ (E-3)

By an analysis similar in Kliewer and Koehler (1965),

$$ \int_{0}^{L} \delta \left( \frac{1}{2} \rho \phi \right) d\chi = \int_{0}^{L} \left[ \phi(\chi) - \phi_{0}/2 \right] \delta \rho d\chi $$ (E-4)

With the above assumptions, we get

$$ \frac{1}{2} \phi \delta \sigma = - \frac{1}{2} \int_{0}^{L} \phi \delta \rho d\chi $$ (E-5)
\[ \delta F = \int \delta x \left[ (F^+ + U_s^+ + F_s^+ - e \phi') \delta n_+ + (F^- + U_s^- + F_s^- + e \phi') \delta n_- + (F^+ + F^- - B + U_s^o) \delta n_B + (F^+ B + U_s^{ib}) \delta n_{ib} + (U_s^f - F_s^f + e \phi) \delta n_f \right] - T \delta S \]  

(E-6)

where \( \phi' = \phi - \phi_1 \) and again \( \phi_1 \) can be set to zero, without loss of generality.

The entropy term, \( S \), is identical to that in the analysis of Kliewer and Koehler (1965). Consequently,

\[ \frac{n_+}{N} = \exp \left( - \frac{F^+ + U_s^+ + F_s^+ - e \phi}{kT} \right) \]  

(E-7a)

\[ \frac{n_-}{N} = \exp \left( - \frac{F^- + U_s^- + F_s^- + e \phi}{kT} \right) \]  

(E-7b)

\[ \frac{n_f}{N} = \exp \left( - \frac{U_s^f - F_s^f + e \phi + \alpha}{kT} \right) \]  

(E-7c)

\[ \frac{n_{ib}}{N} = \exp \left( - \frac{F^+ B + U_s^{ib} + \alpha}{kT} \right) \]  

(E-7b)

where \( \alpha \) is the Lagrange multiplier for the condition that the total number of impurities must be conserved.

The bulk potential, \( e \phi_\infty \), can be defined from the neutrality condition in the bulk, \( n_+(\infty) = n_-(\infty) + n_f(\infty) \),

\[ \exp \left( - \frac{F^+ U_s^+(\infty) + F_s^+ - e \phi_\infty}{kT} \right) = \exp \left( - \frac{F^- U_s^-(\infty) + F_s^- + e \phi_\infty}{kT} \right) + \exp \left( - \frac{U_s^f - F_s^f + e \phi_\infty + \alpha}{kT} \right) \]  

(E-8)
However, because of the possible spatial dependence of the strain interaction energies, $U^+_S$, $U^-_S$ and $U^f_S$, Poisson's equation can be simplified to the following form:

$$\frac{d^2 \xi}{dx^2} = \frac{4\pi N e^2 \exp(-e\phi_0/kT)}{\epsilon \kappa T} \left[ e^\xi \left\{ \exp\left( \frac{-2e\phi_0 - (F^+_S + U^+_S + F^+_f)}{\kappa T} \right) \right\} 
- e^{-\xi} \left\{ \exp\left( \frac{-(F^-_S + U^-_S + F^-_f)}{\kappa T} \right) + \exp\left( -\frac{U^f_S - F^+_f + e\phi_0}{\kappa T} \right) \right\} \right]$$

(E-9)

where $Z \equiv (e\phi - e\phi_\infty)/kT$  

(E-10)

At extrinsic temperatures, the anion vacancies are negligible and we further assume that $U^+_S$ has no spatial dependency, the Poisson's equation can be simplified to:

$$\frac{d^2 \xi}{ds^2} = \frac{1}{2} \left[ e^\xi - e^{-\xi} \cdot e^{-(U^f_S(s) - U^f_S(\infty))/\kappa T} \right]$$

(E-11)

where $s = \xi/\delta$  

(E-12a)

and $\delta = \left[ \frac{8\pi N e^2}{\epsilon \kappa T} \exp\left( \frac{e\phi_0 - (F^+_S + U^+_S + F^+_f)}{\kappa T} \right) \right]^{-1/2}$

(E-12b)

The Debye length, $\delta$, has a similar functional dependency as that defined in Kliewer and Koehler (1965).

Furthermore, at $x \to \infty$, $U^f_S(x) \to U^f_S(\infty)$, Eq. (E-11) becomes

$$\frac{d^2 \xi}{ds^2} = \sinh \xi$$

(E-13)
Numerical solution of Eq. (E-11) for different temperature are shown in the text, Fig. (V-15) to (V-18). Furthermore, the distribution of charged defects due to the coupled effects of electrostatic space charge and mechanical strain field interactions are shown in Fig. (V-19).
Appendix F: Comment on the Stability of a Moving Grain Boundary

Recently, Roy and Bauer (1975) discussed the effects of impurities on the stability of a grain boundary moving in \( \hat{x} \) direction at a velocity, \( V \). They concluded that the moving boundary is inherently unstable if \( V_1 < V < V_2 \), where \( V_2 \) is the breakaway velocity of the boundary from the impurity atmosphere, and

\[
V_1 = k^*(D/D')^{1/2} \approx \frac{2\pi(D/D')^{1/2}}{\lambda_l}
\]  

where \( k^* \) is the characteristic wave number of the initial perturbation and is related to the sample size, \( \lambda_l \); \( D \) and \( D' \) are the diffusivities parallel and normal to the boundary respectively.

Although these authors recognized that the boundary mobility is a complicated function of velocity, \( V \), they treated the mobility term as a parameter which is independent of velocity, \( V \). However, according to Cahn (1962), the impurity drag, \( F_{\text{ex}} \) can be approximated as

\[
F_{\text{ex}} = \frac{C_\infty V\alpha}{1 + \beta^2 V^2}
\]  

where \( C_\infty \) is the impurity concentration in the bulk; \( \alpha \) is
the boundary mobility per unit concentration in the low velocity limit and $\beta^{-1}$ is the impurity drift velocity to cross the grain boundary.

Before we can include the impurity drag term, Eq. (F-2), in the perturbation treatments of Roy and Bauer (1975), we should note a major difference between these theories. In the direction of boundary motion, $x$, Cahn (1962) assumed a continuous distribution profile, $C(x)$, for the impurity species. However, Roy and Bauer (1975) implicitly assumed a step function for the impurity distribution.

$$C(x) = \begin{cases} C_0 & |x| < a_1 \\ C_\infty & |x| > a_1 \end{cases} \quad (F-3)$$

where $a_1$ is some characteristic length and $C_0$ is the average impurity concentration in the boundary region. However, in the $\hat{y}$ direction, perpendicular to the boundary motion, the impurity profile, $C(y)$, is allowed to fluctuate from the average concentration, $C_0$, Roy and Bauer (1975). A fluctuation of the impurity profile in the lateral, $\hat{y}$, direction will likely lead to a corresponding fluctuation in the normal, $x$, direction. A rigorous solution for the stability of the impurity profile requires the formulation of a set of two dimensional impurity flux equations with an appropriate
impurity chemical potential in the neighborhood of a non-linear-shaped boundary. A force balance equation between the drag forces and the driving force gives additional information about the coupled relation of impurity profile and the boundary shape. The mathematical complexity of this approach is beyond the scope of this appendix; however, the impurity profiles, $C(x)$, are given in terms of the bulk concentration, $C_\infty$, Eqs (11) and (14) in Cahn (1962). These equations show that $C_\infty = k_1 C_o$, while the proportionality constant, $k_1$, is a function of boundary velocity, $V$. If we can neglect the velocity dependence in $k_1$, as a second order effect, we can readily apply the impurity drag term of Cahn (1962) to the perturbation treatment of Roy and Bauer (1975),

$$F_{ex} = \alpha k_1 C_o V \frac{V}{1 + \frac{\beta^2 V^2}{2}} \sim \alpha k_1 C_o \frac{\partial C}{\partial t} \frac{\partial x}{\partial t}$$

$$= \frac{\alpha k_1 C_o V_0}{1 + \beta^2 V_0^2} + \frac{\alpha k_1 V_0 \Delta C}{1 + \beta^2 V_0^2} + \frac{\alpha k_1 C_o (1 - \frac{\beta^2 V_0^2}{(1 + \beta^2 V_0^2)^2}) \frac{\partial \Delta x}{\partial t}}$$

where $x(y,t) = V_0 t + \Delta x(y,t)$

$$C(y,t) = C_0 + \Delta C(y,t)$$

as similarly defined in Eqs. (2.1) and (2.2) of Roy and Bauer (1975) for a boundary displacement $x(y,t)$. 
Therefore the force balance equation in Eq. (3.2) of Roy and Bauer (1975) becomes

\[
\left\{-\lambda + \frac{\alpha h e_v (1 - \beta V_o^2)}{(1 + \beta^2 V_o^2)^2}\right\} \frac{\partial \Delta x}{\partial t} - \frac{\alpha V_o h_i \Delta C}{1 + \beta^2 V_o^2} + \gamma \frac{\partial^2 \Delta C}{\partial y^2} = 0
\]

(F-6)

while the flux balance equation in Eq. (3.3) of Roy and Bauer (1975) remains unchanged,

\[
\frac{\partial \Delta C}{\partial t} = h_i D \frac{\partial^2 \Delta C}{\partial y^2} + C_o \frac{h_i V_o}{1 + \beta^2 V_o^2} \frac{\partial \Delta x}{\partial y^2}
\]

(F-7)

With the initial conditions proposed in Roy and Bauer (1975),

\[
\Delta C(y, 0) = \Delta C_0 \cos h_i y
\]

(F-8a)

and

\[
\Delta x(y, 0) = \Delta x_0 \cos h_i y
\]

(F-8b)

Eq. (5) and (6) can be solved by appropriate transformations,

\[
\Delta x(y, t) = A \exp\left(\frac{q^+ t}{2}\right) + B \exp\left(\frac{q^- t}{2}\right)
\]

(F-9a)

\[
\Delta C(y, t) = C \exp\left(\frac{q^+ t}{2}\right) + D \exp\left(\frac{q^- t}{2}\right)
\]

(F-9b)

where

\[
\frac{q^\pm}{2} = \frac{1}{2} \left\{\frac{-\lambda + \frac{\alpha h e_v (1 - \beta V_o^2)}{(1 + \beta^2 V_o^2)^2}}{\sqrt{(D + \gamma \frac{dF}{dV_o})^2 - 4 D \frac{\gamma \beta^2 V_o^2}{C \alpha h_i \frac{1}{\beta^2 (1 + \beta^2 V_o^2)}}} + \frac{4 \gamma \beta^2 V_o^2}{C \alpha h_i \frac{1}{\beta^2 (1 + \beta^2 V_o^2)}}}\right\}
\]

(F-10)

where

\[
\frac{dF}{dV_o} = \lambda + \frac{h_i \alpha C_0 (1 - \beta^2 V_o^2)}{(1 + \beta^2 V_o^2)^2}
\]

(F-11)
and the pre-exponential factors, A, B, C and D are the fluctuation amplitudes. Since the time exponent, $q^-$, is always negative, the fluctuations due to this component always decay. However if

$$\frac{D \gamma}{C_0 \alpha \kappa_i} < \frac{V_o^2}{\kappa^2 (1 + \beta V_o^2)}$$  \hspace{1cm} (F-12)

then the time exponent, $q^+$, is positive, a fluctuation grows and the impurity profile as well as the boundary shape becomes unstable. Fig. (F-1) illustrates the stability condition, Eq. (F-12), by plotting the reduced boundary velocity, $V \beta$, against a dimensionless factor which involves the diffusivity, dopant level and the wave-number of the perturbation. The limiting wave-number is related to the sample size, $\lambda_L$, Roy and Bauer (1975).

Cahn (1962) suggested the possibility of three boundary velocity solutions for a certain combination of driving force and impurity drag. It was shown that the intermediate velocity solution is unstable. In the rest of this appendix, we apply the analysis of Roy and Bauer (1975) to this velocity region and show that an initially stable perturbation becomes unstable as the velocity increases above the velocity of maximum drag and into the intermediate velocity range. The de-stabilizing fluctuations in a low velocity boundary provide
Fig. F-1: Stability condition as a function of grain boundary velocity.
a probable mechanism in nucleating a high velocity boundary.

At the local maximum in the drag-velocity curve, \( \frac{dF}{dV_o} = 0 \), and \( V_\beta \approx 1 \), Cahn (1962), the positive time component, \( q^+ \), becomes

\[
q^+_{\text{max}} = \frac{k^2}{2} \left\{ -D + \sqrt{D^2 - \frac{4D\gamma}{C_0\alpha k_i} + \frac{2}{\beta^2 k^2}} \right\}
\]

(F-13)

If we assume that for the wave-number, \( k_{\text{max}} \), the initial fluctuation remains static (neither grows nor decays), i.e.

\[
\frac{4D\gamma}{C_0\alpha k_i} = \frac{2}{\beta^2 k_{\text{max}}^2} \quad q_{\text{max}} = 0
\]

(F-14)

As the boundary velocity increases to \( V_\beta > 1 \), the increase in the time exponent, \( \Delta q^+ \), is

\[
\Delta q^+ = q^+ - q^+_{\text{max}} = q^+ = \frac{k^2}{2} \left\{ -D + \sqrt{(D+\gamma\lambda)^2 - \frac{2V_o^2(1-2V_o^2\beta^2)}{k_{\text{max}}^2}} \right\}
\]

\[
= \frac{C_0\alpha k_i}{4\beta^2 D\gamma} \left\{ -D + \sqrt{(D+\gamma\lambda)^2 - \frac{2V_o^2(1-2V_o^2\beta^2)}{k_{\text{max}}^2}} \right\}
\]

\[
\Delta q^+ (D+\gamma\lambda) = \frac{(D+\gamma\lambda)^2 C_0\alpha k_i}{V_o^2 4\beta^2 D\gamma} \left\{ 1 - \frac{1 - \frac{4D\gamma V_o^2\beta^2}{(D+\gamma\lambda)^2 C_0\alpha k_i^2} (1-2V_o^2\beta^2)}{1+\beta^2 V_o^2} \right\}
\]

(F-15)

If we define \( f \equiv \frac{\Delta q^+ (D+\gamma\lambda)}{V_o^2} \); \( g \equiv \frac{D+\gamma\lambda (C_0\alpha k_i)^{1/2}}{V_o (4\beta^2 D\gamma)^{1/2}} \)
then Eq. (F-15) becomes

\[ f = \frac{g^2(-1 + \sqrt{1 - \frac{1}{g^2}(1 - \beta^2 V^2)/(1 + \beta^2 V^2)})}{(F-16b)} \]

A plot of this curve for different values of \( V/\beta \) is shown in Fig. (F-2). Furthermore, it is obvious from Eq. (F-16) that \( \Delta q \) is positive. It implies that as velocity increases beyond the break-away velocity, an initially stable fluctuation becomes unstable in both the boundary shape and the impurity profile.
Fig. F-2: Perturbation growth exponent for a velocity increment.
Appendix G: An Estimation of Intrinsic Grain Boundary Mobility from the Experimental Data of KCl

The intrinsic grain boundary mobility can be estimated from the mobility data of the undoped samples, Fig. (IV-12); the maximum mobility data in these samples probably show the intrinsic behavior. We assume that the temperature dependence of the intrinsic mobility can be obtained by the straight line joining the maximum mobility at high temperatures, i.e.

\[ 10^{-7}(\text{cm/sec})(\text{dyne/cm}^2)^{-1} \text{ at } T/T_m = 1, \text{ from Gibbon (1968)}, \]

and the maximum mobility at intermediate temperatures, i.e.

\[ 1.2 \times 10^{-8}(\text{cm/sec})(\text{dyne/cm}^2)^{-1} \text{ at } T/T_m = 0.6 \text{ from our data}. \]

This estimation gives the intrinsic mobility, \( \lambda^{-1} \), as

\[ \lambda^{-1} = 4.64 \times 10^{-6} \exp(-7.63 \text{ kcal/RT}) \left( \frac{\text{cm}}{\text{sec}} \right) \left( \frac{\text{dyne}}{\text{cm}^2} \right)^{-1} \]  

(G-1)

The activation enthalpy of the intrinsic grain boundary mobility corresponds to the of grain boundary diffusion. The enthalpy of 7.6 kcal/mole is comparable to the 6.9 kcal/mole for the pipe diffusion in LiF edge and screw dislocations, Tucker et al (1963); and the 5.6 kcal/mole for grain boundary diffusion of Co\(^{2+}\) in KCl bicrystals; and the 5.6 kcal/mole for grain boundary diffusion of Ni\(^{2+}\) in NaCl bicrystals, with misorientation angle ranging from 12° to 14°, Geguzin et al (1967).
Furthermore, the pre-exponential term in Eq. (G-1), $\lambda_0$, 4.64 x 10^{-6} \text{ (cm/sec)(dyne/cm}^2)^{-1}$, has a fair agreement with that predicted in Turnbull's model, Eq. (II-11) of Chapter II,

$$\lambda_0 \text{ (intrinsic)} = \frac{eaV_m}{hN} \exp(S_G/k) \quad (G-2)$$

for a = 6.3 Å, $V_m$=37.3 cc/mole and $S_G/k \gg 0$. 

\[ \gg 1.6 \times 10^{-3} \text{ (cm/sec)(dyne/cm}^2)^{-1} \]
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BIOGRAPHICAL NOTE

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