ELECTRICAL CONDUCTIVITY OF POTASSIUM

IODIDE BETWEEN 200°C AND ROOM TEMPERATURE

by

MAHENDRA PRASAD

M.Sc., Ranchi University, Ranchi, (INDIA) 1964.

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department
of
Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

December, 1968
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date 21st Jan. '69
ABSTRACT

The electrical conductivity of pure KI and CdI$_2$-doped KI has been studied in the temperature range 200 to 23°C. Two regions A and B (corresponding to different activation energy of conductivity) are identified. The region A can be given a conventional interpretation in terms of migration of cation vacancies in the bulk, their concentration being determined by impurities. U (the energy for migration of cation vacancies) amounts to 0.96 ± 0.02 eV. Observed activation energies higher than this value are accounted for by association and precipitation effects. Association energy of cation vacancies with impurities (0.48 eV. for Cd$^{+2}$) and heat of solution (0.25 eV. for CdI$_2$) obtained here are comparable with known values for other alkali halides.

Region B found in this work represents unusual behaviour and has not previously been observed in any alkali halides. The activation energy of conductivity is considerably less than the energy needed for the migration of cation vacancies in the bulk. The activation energy $E_B$ (for region B) is about 0.57 eV. in a single crystal and 0.38 eV. in a pure KI pellet. Such low activation energies cannot be given a similar interpretation as for region A. It is suggested that the cation vacancies are in regions of unusually high mobility such as dislocations and grain boundaries. This effect may arise partly from a lower activation energy for motion of vacancies in these regions and partly from a vacancy concentration in these regions which increases with decreasing temperature, under the control of "space-
charge effects. The value 0.57 eV. appears to refer to isolated dislocations or low angle boundaries, while the value of 0.38 eV. refers to large angle intercrystalline boundaries in a pellet.

A strong piece of evidence for this suggestion comes from the conductivity runs on single crystals. In an untreated single crystal, just as in pure pellets, two regions A and B are identified but region B disappears in crystals annealed overnight and reappears in a mechanically strained crystal. Moreover, region A remains almost undisturbed in each case. This means that the conduction process in region B is governed by dislocations and grain boundaries whereas region A is governed by motion of cation vacancies in the bulk.
TABLE OF CONTENTS

Title Page
Abstract ii
Table of Contents iv
List of Figures vi
List of Tables viii
Acknowledgements ix

INTRODUCTION

Review of work on alkali halides 1
Ionic point defect 1
Theories of conductivity in region II 5
(a) Smekal Crack Concept 5
(b) Frozen Equilibrium Concept 6
(c) Impurity Effect Concept 7
Association and precipitation effects 11
Previous work on KI 15
Object of present work 17

EXPERIMENTAL

Apparatus 18
Conductivity Cell 18
Circuit 20
Electric Furnace 22
Preparation of pellets 22
Analysis of the pellet to check the impurity content 23
Experimental procedure 24
Polarization effects 26
Blank run 26
RESULTS

DISCUSSION
Region A 41
(a) Absolute value of $\sigma_{\text{sp}}$ and impurity content 41
(b) $E_A$ for pure samples and $U$ 42
(c) $E_A$ for impure samples; association and precipitation 42
Region B 44

APPENDIX
Tables 1 - 9 50-55

BIBLIOGRAPHY 56
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Typical Arrhenius plot of conductivity</td>
<td>2</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Ionic point defects</td>
<td>4</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Plot of conductivity versus impurity content (Wagner &amp; Hantlemann)</td>
<td>10</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Plot of conductivity versus impurity content (Etzel and Maurer)</td>
<td>10</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Typical conductivity plot for lower temperatures (NaCl, Dreyfus and Nowick)</td>
<td>12</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Baijal's conductivity plot for KI</td>
<td>16</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Conductivity cell and guard ring arrangements</td>
<td>19</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Circuit</td>
<td>21</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Polarization effect in ionic crystal</td>
<td>27</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Conductivity plot for blank run</td>
<td>29</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Conductivity plot for pure KI pellet</td>
<td>32</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Conductivity plot for doped KI</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>(0.05 mole% CdI₂)</td>
<td></td>
</tr>
<tr>
<td>Figure 13</td>
<td>Conductivity plot for doped KI</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>(0.10 mole% CdI₂)</td>
<td></td>
</tr>
<tr>
<td>Figure 14</td>
<td>Conductivity plot for doped KI</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>(0.25 mole% CdI₂)</td>
<td></td>
</tr>
<tr>
<td>Figure 15</td>
<td>Summary of conductivity plots</td>
<td>36</td>
</tr>
<tr>
<td>Figure 16</td>
<td>Plot of conductivity versus impurity content (this work)</td>
<td>37</td>
</tr>
</tbody>
</table>
Figure 17. Conductivity plot of single crystal (untreated)

Figure 18. Conductivity plot of single crystal (heated overnight)

Figure 19. Conductivity plot of single crystal (strained)
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.</td>
<td>Energy of Association for divalent impurity ion and cation vacancy</td>
<td>14</td>
</tr>
<tr>
<td>Table 2.</td>
<td>Analysis of impurity content</td>
<td>24</td>
</tr>
<tr>
<td>Table 3.</td>
<td>Summary of experimental results</td>
<td>31</td>
</tr>
<tr>
<td>Table 4.</td>
<td>Comparison with previous results</td>
<td>31</td>
</tr>
</tbody>
</table>

APPENDIX

| Table 1. | Electrical conductivity of KI pellet (23°C - 203°C)                                               | 50   |
| Table 2. | Electrical conductivity of doped KI pellet (0.05 mole% CdI₂) (23°C - 215°C)                       | 50   |
| Table 3. | Electrical conductivity of doped KI pellet (0.1 mole% CdI₂) (23°C - 212°C)                       | 51   |
| Table 4. | Electrical conductivity of doped KI pellet (0.25 mole% CdI₂) (23°C - 200°C)                       | 51   |
| Table 5. | Electrical conductivity of untreated KI single crystal (23°C - 200°C)                            | 52   |
| Table 6. | Electrical conductivity of annealed overnight KI single crystal (23°C - 205°C)                   | 52   |
| Table 7. | Electrical conductivity of strained KI single crystal (23°C - 201°C)                             | 53   |
| Table 8. | Specification from Fisher Scientific Company of KI used in this work.                            | 54   |
| Table 9. | Specification from Mallinckrodt Chemical Works of KI used in Baijal's work.                     | 55   |
ACKNOWLEDGEMENTS

I wish to express my sincere gratitude and thanks to Professor L.G. Harrison for his guidance and supervision throughout the work. Thanks are also due to Professor C.A. McDowell for Departmental facilities.

I am also grateful to Mr. A.K. Rantamaa, who made the conductivity measurement apparatus.
INTRODUCTION
Review of work on alkali halides

The electrical conductivity of alkali halides has been studied\textsuperscript{1-3,4} mainly in the region from melting point down to about 300°C and usually shows two regions of different activation energy. A typical Arrhenius plot of conductivity, indicating different slopes corresponding to different regions, is shown in Figure (1). Region I is usually called the intrinsic region. The conductivity in this range is reproducible from sample to sample and does not depend on the previous thermal history. On the other hand, in the low temperature region, usually referred to as Region II, the behaviour is different. Conductivity in this region is not the same from sample to sample and purity and thermal history of the sample play an important role. Various explanations have been given by different workers in order to account for this anomalous behaviour.

Ionic Point Defects

The ionic conductivity of alkali halides is due mainly to the presence of ionic point defects, in particular cation vacancies. For the electrical conductivity of ionic crystals, three kinds of lattice defects may be distinguished.

1) Atoms or ions of the crystals may be displaced from normal lattice sites to the interstices. They are then known as interstitials.

2) Lattice sites may be unoccupied; these sites are called vacancies.

3) Lattice positions may be occupied by impurity or misplaced atoms or ions.
Fig. (1)

Typical Arrhenius plot of conductivity

$\log_{10} \sigma T$

$10^3/T \ (°K)$

$\sim 300°C$

I region

II region
The formation of the first two types of defect may be visualised with reference to the ideal crystal. A cation or an anion may be displaced from its normal lattice site to an interstitial position. The resulting defect is known as a Frenkel defect and consists of an interstitial ion together with a cation or anion vacancy. This sort of defect is common in silver halides and is shown in Figure (2.a). From thermodynamic considerations, the concentration of the defects in a crystal containing only Frenkel defects is given by the equation (1)

$$n_i = (N N_i) \frac{1}{2} \exp(-W_i/2kT)$$

where $n_i$ is the concentration of ions in interstitial positions at equilibrium, $N$ is the total number of lattice sites and $N_i$ is the total number of possible interstitial sites. $W_i$ is the energy required to form a Frenkel defect.

Schottky defects are formed when, in an ideal crystal, cations and anions are removed from their normal lattice sites to external or internal surfaces of the crystal with the result of expansion of the lattice, Figure (2.b). In order to maintain the electrical neutrality of the crystal as a whole, cation and anion vacancies must be equal in number in a pure crystal. In any crystal containing Schottky defects, the defect concentrations are related by the equation (2)

$$n_+ n_- = N^2 \exp(-W/kT)$$

and in a pure crystal containing Schottky defects only

$$n_- = n_+ = N \exp(-W/2kT)$$
Fig. 2

Ionic point defects

Fig. (2.a)

Frenkel Defects

\[
\begin{align*}
+ & - + - + - + - + \\
- & + - + - + - + \\
+ & + \square - + - + - \\
- & + - + - + - + \\
+ & + - - + \square + - \\
- & + - + - + - + \\
\end{align*}
\]

Fig. (2.b)

Formation of a Schottky pair

\[
\begin{align*}
- & + - + - + - + + + - + - + - + + - + \\
+ & - + - + - + - + - + - + - + - + - + \\
- & + - + - + - + - + - + - + - + - + - + \\
+ & + - - + \square - + - + - + - + - + - + \\
- & + - + - + - + - + - + - + - + - + - + \\
+ & + - - + - + - + - + - + - + - + - + \\
\end{align*}
\]

Fig. (2.c)

Divalent impurity in a 1:1 crystal

\[
\begin{align*}
+ & - + - + - + - + \\
- & + - \square - + - + \\
+ & + - ++ - + - + \\
- & + - + - + - + + \\
\end{align*}
\]
where $n_+$ and $n_-$ are the concentrations of cation and anion vacancies respectively. $W$ is the energy required to form a Schottky pair.

Vacancies or interstitials can also be produced by the incorporation of another type of imperfection, such as chemical impurities. For instance, the substitution of a divalent cation for a monovalent one introduces an extra positive charge in the crystal. In order to preserve the electrical neutrality of the crystal as a whole, either an extra negative ion should be incorporated interstitially or a positive ion vacancy must be formed at a lattice site, Figure (2.c). Since the latter process requires less energy, a cation vacancy is formed by each divalent impurity ion.

In alkali halides the Schottky defects predominate and in this account, all discussions are made with reference to these defects.

Theories of Conductivity in Region II

On the basis of lattice defects mentioned above, the appearance of different regions in conductivity plot of alkali halides has been explained by several authors\(^2\).

(a) Smekal Crack Concept: The first suggestion was made by Smekal\(^3\), who suggested that, in the conduction process for the impurity region, the low activation energy and low pre-exponential factor result from diffusion of a small number of ions through grain boundaries and cracks known as "Smekal Cracks". Different crystals would be expected to have different concentrations of cracks and consequently the conductivity would be structure sensitive. It seems likely that the activation energy for diffusion via cracks will be considerably less than that through the lattice via vacancies or interstitial positions,
and that this type of movement would be favoured at low temperature.

(b) Frozen Equilibrium Concept: Another suggestion based on the concept of frozen equilibrium at lower temperature was made by Jost. According to this suggestion, in Region I, there is an equilibrium between the defect concentrations and a small change in temperature is followed by a rapid adjustment of the cation defect concentration to a new equilibrium value according to the equation (3). At lower temperature, under these conditions a region of low activation energy of conductivity is expected, because the equilibrium distribution of the defects predicted by this equation cannot be achieved within appropriate time, and changes in temperature have no effect on the defect concentration. In this situation the variation of conductivity with temperature would be due to the effect of temperature on the mobility of the defects at constant concentration of defects. Thus at higher temperature, the conductivity \( \sigma \) is given by the general equation (4)

\[
\sigma = n_+ e \mu = (4 n_+ e^2 A r^2 / kT) \exp(-U/kT) \tag{4}
\]

where \( r \) = distance between neighbouring cation and anion

\( e \) = electronic charge

\( A \) = frequency factor representing the entropy effect of changes in lattice vibrations arising from the formation of vacancies

\( \mu \) = mobility of vacancies

and \( U \) represents activation energy for the motion of the cation vacancy. The numerical factor 4 appears in the expression by consideration of the jumps of a vacancy to any of its 12 nearest neighbours in the fcc cation sub lattice.
In the intrinsic range the effective activation energy consists of two terms, (i) half the energy needed for the formation of a Schottky pair \((W/2)\); (ii) the energy required for the migration of cation vacancy \((U)\). Hence the above general equation can also be written as follows.

\[
\sigma = \sigma_0 \exp \left( \frac{-U+W/2}{kT} \right) \tag{5}
\]

In this equation \(\sigma_0\) is equivalent to the pre-exponential term in equation (4) and represents the extrapolated value of \(\sigma\) at \(T = \infty\).

Similarly at lower temperature \(\sigma\) is given by equations (6) & (7).

\[
\sigma = \sigma_0 \exp \left( \frac{-W/2kT_0}{kT} \right) \exp \left( \frac{-U}{kT} \right) \tag{6}
\]

and

\[
\sigma = \sigma'_0 \exp \left( \frac{-U}{kT} \right) \tag{7}
\]

where \(T_0\) is the effective temperature at which the defect equilibrium becomes frozen. This means that both the activation energy and pre-exponential term will be lower in the lower temperature range, which is experimentally supported\(^4\). \(T_0\) and hence \(\sigma'_0\) will vary according to the thermal history of the sample. Accordingly \(\sigma'_0\) will be greater for a crystal which has been quenched rapidly from high temperature than for one which has been cooled slowly through the range where "freezing" started.

(c) Impurity Effect Concept: A third suggestion\(^6\) for the existence of the low temperature region is made on the basis of the impurity effect concept, the impurity usually being of aliovalent nature. The term aliovalent means that the valency of a cation or an anion
impurity is different from that of an ion in the pure host crystal. This suggestion is based on the fact that the substitution of a divalent cation for a monovalent one, introduces one cation vacancy, in order to maintain the electrical neutrality of the crystal as a whole. Such cation vacancies will be present at all temperatures in the same concentration (provided that the impurity remains in solid solution) and consequently their effect on conductivity will be much more apparent at lower temperature, because at lower temperature the concentration of thermally produced vacancies is lower than that already present. Now if the number of divalent cation impurities is \( n_1 \) per cm\(^3\), this number of vacancies will be present in addition to the vacancies produced thermally, and the conductivity will be enhanced.

The concentration of cation vacancies may be calculated in the doped sample as follows. In an impure crystal as well as in a pure crystal, the defect concentrations must obey equation (2) but in a doped sample, \( n_+ = n_- + n_1 \) \( (8) \)

Substituting the value of \( n_- \) in equation (2), it can be written as,

\[
n_+ (n_+ - n_1) = N^2 \exp(-W/kT) = C \quad (9)
\]

or

\[
n_+^2 - n_+ n_1 - C = 0
\]

or

\[
n_+ = n_1 \pm \sqrt{n_1^2 + 4C}
\]

\[
\frac{1}{2}
\]

(i) At high temperature, \( C \gg n_1 \), then \( n_+ = C^{\frac{1}{2}} = N \exp(-W/2kT) \) .. \( (10) \)

and this corresponds to Region I.
(ii) At low temperature, \( n_1 \gg C \), therefore, \( n_+ = n_1 \).

and this corresponds to Region II.

Most experimental studies in the last twenty years have indicated that, at least for the cations, the impurity effect is predominant in Region II. (Anion diffusion, which also shows Regions I & II, seems to be more complicated). For example, the effect of added divalent impurity \( Sr^{+2} \) ions (in the range of 1000 ppm. to 8000 ppm.) on the electrical conductivity of \( KCl \) in the temperature range of 600-725°C has been studied by Wagner and Hantelmann. The plot of conductivity versus impurity content at 600°C is fairly linear; see Figure (3). Later Etzel and Maurer also studied the effect of \( Cd^{+2} \) ion (in the range 10 ppm. to 688 ppm.) on the electrical conductivity of \( NaCl \) in the temperature range 403 to 256°C. They also have shown that the graph of conductivity versus impurity content does not deviate far from linearity (Figure 4). The deviation may be accounted for by association and precipitation effects which are discussed in the next section.
Fig. 3
Plot of conductivity versus impurity content
(Wagner & Hantlemann)

Fig. 4
Plot of conductivity versus impurity content
(Etzel and Maurer)

KCl-SrCl$_2$ System

NaCl-CdCl$_2$ System

Mole ratio x 10$^5$ ($\text{Cd}^{2+}$)
Association and Precipitation Effects

Recently, low temperature measurements on sodium chloride have been extended down to and beyond room temperature and the existence of other regions of higher activation energies, III and IV, has been established as shown in Figure (5). These are accounted for by association and precipitation effects as follows.

(i) The first is the tendency of oppositely charged divalent impurity ion (which has an effective single positive charge) and the cation vacancy (which has an effective negative charge) to associate to form a neutral complex.

(ii) The second is the precipitation of divalent impurity ion at temperatures where their concentration in solution exceeds the solubility limit.

By the application of Statistical Mechanics (or even by a simple Mass Action treatment as indicated below) the effect of association reaction on conductivity is easily calculated for the dilute solution. The effective energy for the Region III is found to be the sum of $U$ and $E_a/2$, where $E_a$ is the energy needed for the association reaction. Let $A$ be the impurity vacancy complex such that,

\[ A \rightleftharpoons I + \overset{\text{+}}{\text{-}} \overset{\text{-}}{\text{+}} \]  \hspace{1cm} (12)

where $I$ is the divalent impurity ion and $\overset{\text{-}}{\text{+}} \overset{\text{+}}{\text{-}}$ represents the cation vacancy. By the Law of Mass Action, the equilibrium constant $K$, is given by

\[ (n_I n_+ / n_A) = K = K_0 \exp (-E_a / kT) \]  \hspace{1cm} (13)
Fig. 5

Typical conductivity plot for lower temperatures
(NaCl, Dreyfus and Nowick)
where \( n_1' \) is the concentration of dissociated complex and \( n_A \) is the concentration of undissociated complex. This equilibrium is analogous to that for dissociation of a weak electrolyte in aqueous solutions. For the case of a low degree of dissociation, \( n_A \sim n_1 \) (total impurities) and if the temperature is low enough for the assumption to be made that "intrinsic" vacancies can be neglected, then

\[
\begin{align*}
n_1' &= n_+^* \\
n_+^2 &= n_1 K_0 \exp(-E_a/kT) \quad (14)
\end{align*}
\]

and

\[
\begin{align*}
n_+ &= (n_1 K_0)^{1/2} \exp(-E_a/2kT) \quad (15)
\end{align*}
\]

so that the activation energy for conductivity becomes \((U + E_a/2)\). If the impurities in solution are in equilibrium with precipitated impurities, then \( n_1 \) is governed by a solubility equilibrium which makes a further addition of \( \Delta H \) of solution to the activation energy.

On the basis of a simple model of electrostatic attraction between a positive and negative charge in a continuum having the static dielectric constant \( \varepsilon_o \) of the crystal, \( E_a \) is given by the equation (16)

\[
E_a \sim \frac{e^2}{r \varepsilon_o} \quad (16)
\]

where \( r \) is the second nearest neighbour distance. This quantity varies very little from one alkali halide to another, and is roughly 0.6 eV. Detailed calculations taking into account the arrangement of neighbours around the complex generally give somewhat smaller values. Reitz and Gammel\(^{10}\) obtained 0.44 eV for \( \text{Cd}^{2+} \) in NaCl. Some experimental values are given below in table 1.
TABLE 1

Energy of Association for divalent impurity ion and cation vacancy.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Host crystal</th>
<th>Ea(eV.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd⁺</td>
<td>NaCl</td>
<td>0.35</td>
<td>Etzel and Maurer⁸</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lidiard¹¹</td>
</tr>
<tr>
<td>Mg⁺</td>
<td>NaCl</td>
<td>0.54</td>
<td>Dreyfus and Nowick⁹</td>
</tr>
<tr>
<td>Mn⁺</td>
<td>NaCl</td>
<td>0.52</td>
<td>Dreyfus and Nowick⁹</td>
</tr>
<tr>
<td>Cd⁺</td>
<td>NaCl</td>
<td>0.42</td>
<td>Dreyfus and Nowick⁹</td>
</tr>
</tbody>
</table>

The last three values are calculated from the difference of activation energies in Region II and III. Dreyfus and Nowick correlated the Region IV with the occurrence of precipitation and on that basis they concluded that Region III results from association. Also, the fact that no hysteresis occurs in Region III, suggests that probably precipitation is not involved in this region.

However, for regions of types III and IV, it is not yet clearly established which one shows the association effect only and which shows also the precipitation effect.
Previous Work on Potassium Iodide:

From work on electrical conductivity of KI (see also table 3 in the Discussion Section) Lehfeldt\(^1\) reported that in the intrinsic range, the activation energy of conductivity is 0.82 eV. From the result of autodiffusion studies\(^12\) of vacancies in the intrinsic range, the activation energy is 0.67 eV. Ecklin et al.\(^13\) studied the electrical conductivity of pure and doped KI (dopants used were Sr\(^{+2}\) and Ca\(^{+2}\)) as a function of temperature from 560°C down to 20°C. They observed four domains in the conductivity plot. Domains I and II correspond to intrinsic and extrinsic Regions I and II, and they have given the conventional arguments for their existence. Domain III was dominated by association but the transition from II to III is at an unusually high temperature (about 300°C). They reported the activation energy of motion of cation vacancy as U equal to 1.21 ± 0.05 eV. The erratic Domain IV was dominated by surface effects and polarization effects. During comprehensive studies of the electrical conductivity of ammonium salts, Harrington and Staveley\(^14\) measured the conductivity of KI single crystal and pellet as a function of temperature. They found the activation energy of conductivity in temperature range 123-188°C for a single crystal to be about 1.30 eV and that for a pellet 0.86 eV. in the temperature range 38°C - 138°C.

Baijal\(^15\) in this laboratory found that the activation energy of electrical conductivity in the range 330-90°C was in agreement with Lehfeldt's value. Baijal also observed that there is a region (Fig. 6) of exceptionally low activation energy from 90°C down to room temperature. During his investigation of oxidation of KI by halogen gases, he noticed
Fig. 6

Baijal's conductivity plot for KI
that the initial resistance of KI plays an important role and this led him to study the electrical conductivity at low temperature. His apparatus, however, was not designed with such high impedance measurements in mind, and there was some doubt as to whether the effect was a spurious one arising from the rather variable leakage resistance of the apparatus. The work therefore needed to be repeated with apparatus redesigned for this high impedance region.

The Object of the Present Work

The object of the present work was to study the behaviour of electrical conductivity of pure and impure potassium iodide (dopant used was CdI₂) from 200°C down to room temperature, particularly in order to determine whether there exists a region of unusually low activation energy, as previously reported by Baijal.
EXPERIMENTAL
Apparatus

The apparatus was designed a year before use in this work by A. Rantamaa. It consists of a conductivity cell, electrometer, simple high impedance circuit and a non-inductively wound electric furnace (see Fig. 7), all of which were housed in a grounded copper case.

Conductivity Cell

The conductivity cell (see Fig. 7) consists of two electrodes P and Q, both of which are made of platinum in the form of discs. The electrode P is fixed in a circular cavity at the bottom of a teflon cylinder (S). A Pt/Rh(10%) wire T is attached to the other end of the electrode P, thus forming the hot junction of a thermocouple. A circular guard ring G around P is also provided so that the conductivity can be measured with either the bottom electrode or the guard ring or both in circuit, and either part may be grounded when not in circuit. This makes it possible to measure separately any contribution from surface conductivity.

The wires connecting P, T, G and Q pass along the side of a teflon cylinder and have been wrapped in teflon foil. At the top of the teflon cylinder, a metallic hook is provided by means of which the weight of the cylinder together with the electrodes and sample is supported during assembly on a horizontal glass rod, fixed in a glass cone (B-45). The electrodes are held to the sample by the weight of the cylinder (which contains a metal weight of about 250 gm) and thus there is a good contact between electrodes and sample. Near the top of the glass cone, there is an opening through which the cell is connected to the vacuum system for evacuation or introduction of any
Fig. 7
Conductivity cell and guard ring
gas when needed. The four wires namely P, T, G and Q pass through teflon inserts in the glass cone and are vacuum-sealed with dekhotinski cement. The use of teflon and dekhotinski cement makes it possible to use the apparatus for high impedance measurements. For operation the cell was placed in a large cylindrical flat bottomed glass vessel, which contained a few pieces of uniform flat teflon in the bottom in order to support the load of the cylinder.

Circuit:— The conductivity cell was connected in series with a Keithley decade shunt having resistances from $10^3$ to $10^{12}$ ohms, and a potential difference $E_1$ of about 22-1/2 volts was applied by means of a dry cell as shown in Fig. (8). Almost all this potential difference was across the sample. The small potential difference $E_2$ across the shunt was measured with a Keithley model 200B battery operated electrometer (dcvvvm) having an input resistance of $10^{11}$ ohms, residual current at input $5 \times 10^{-14}$ amperes and ranges down to 8 mv. on full scale deflection. Since the electrometer was used in high impedance circuitry every care was taken to shield input leads and the whole circuit by housing in a big copper case which was already grounded. The high impedance part of the circuit, which must be isolated particularly carefully from ground, is the part between letters (PTABCDPE) in the Fig. (8). The operator of the machine is also grounded. For that purpose a long piece of copper is placed in front of the apparatus, which has to be touched while operating the machine.

The voltage $E_1$ was checked at intervals of about 4 hours,
High impedance part of circuit is PTABCDFE and connections inside the Keithley from F to electrometer tube.
either by using an external meter or by turning the switch to short position and using a shunt resistance of $10^4$ ohms. The voltage measured on 20 volt scale is doubled to find out the actual E.M.F. $E_1$ of the battery.

During the measurement of conductance, the thermocouple leads were disconnected at the plugs in the wall of the copper case (CD, Fig. 8), to avoid the leakage to ground which otherwise effectively short-circuits the Keithley shunt and leads to spurious low values for $E_2$.

**Electric Furnace** :- An electric furnace in order to heat the cell was designed with a metallic hollow cylinder which contained an asbestos pipe in which the cell was placed. The winding of the furnace was non-inductive in order to avoid the inductive effect arising from A.C. currents, the furnace being the only A.C. device inside the copper case enclosing the whole apparatus. In between outer and inner walls of the pipe and cylinder respectively, glass wool was filled for insulation. The furnace was usually heated by 15-16 volts for about 3-4 hours for thermal equilibrium.

**Preparation of pellets**

Two kinds of pellets were prepared.

1) Pure KI

2) CdI$_2$-doped KI

(a) Pellets of pure KI: A.R. grade (Fisher Sc. Co.) KI was dried at 120°C for about 2-3 days and then powdered with mortar and pestle. This powder was dried overnight and pressed into pellets of
1.32 cm in diameter and about 1.3 - 3.0 mm in thickness using hydraulic pressure of 7000 lbs. per pellet, after evacuating the apparatus for about 8-10 minutes. The load was allowed to remain for about 2-3 minutes. The pellets were stored in a desiccator before and after use.

(b) Doped KI: In this case CdI₂ was used as dopant and three different compositions were used. The calculated amount of KI and CdI₂ for different compositions were weighed in the previously weighed platinum crucible and the weighed material was fused on the bunsen flame. The melt was made homogeneous by shaking the crucible cautiously. In order to avoid a brown coloration obtained in the first trial, air was blown into the melt through a fine jet while cooling. The solid thus obtained was powdered and dried for 2-3 days at 120°C. Then the pellets were pressed exactly in the same way as for pure KI.

In making the pellets no quantitative procedure was used to check whether or not the size of grains was always the same, but the same grinding procedure was followed in every case. The microscopic observation of the size of grains indicated that the grains were in the range 8μ - 14μ.

Analysis of the pellets to check the impurity content

The doped samples were analysed by a colorimetric method in order to check the impurity content before and after the conductivity runs. The experimental procedure was as follows. The sample solution, 25 ml, containing KI was first treated with 5 ml of 20% Na-K tartrate solution. To the resulting solution an equal volume of 10% NaOH solution was added. The mixture was extracted with 5% dithizone solution in
carbon tetrachloride (Sp. grade.) in a separating funnel, until the last portion became colourless. The extract was collected in a blackened volumetric flask, in order to avoid any photochemical decomposition of Cd-dithizonate. This extract was washed with distilled water and then with carbon tetrachloride and collected in another 25 ml volumetric flask, and the volume was made up to the mark by adding carbon tetrachloride. The transmittancy was measured at 520 μμ with a Cary 14 Spectrophotometer (which was calibrated with a known amount of CdI₂ made up in solution) and by comparing with the calibration curve, the impurity contents were determined. The results are given in table 2.

TABLE 2
Analysis of Impurity Content (Cd⁺²)

<table>
<thead>
<tr>
<th>Impurity Added (mole%)</th>
<th>Impurity present (mole%) Before Conductivity Run</th>
<th>After Conduct. Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.0498</td>
<td>0.0499</td>
</tr>
<tr>
<td>0.100</td>
<td>0.102</td>
<td>0.103</td>
</tr>
<tr>
<td>0.250</td>
<td>0.249</td>
<td>0.248</td>
</tr>
</tbody>
</table>

Experimental Procedure: - D.C. electrical conductivity was measured in this work. The sample was introduced into the conductivity cell and the cell was evacuated for about 20-25 hours, till the resistance of the sample at room temperature was constant. The conductivity cell was then heated till a constant temperature of about 200°C was recorded by
keeping the cold junction at 0°C (ice-water). The applied voltage 
$E_1$ was measured each day before measuring conductivity and was 
checked at intervals of about 4 hours. The potential difference 
$E_2$ across the shunt was measured by Keithley electrometer (see Fig. 8), 
taking an interval of 15 seconds between successive readings. The 
polarity was then reversed, the first reading taken immediately, and 
a similar series of measurements was made. The mean value before and 
after reversing the polarity was taken as $E^\prime$. The conductance of the 
sample was then calculated as follows.

$$\sigma = \frac{E_2}{E_1 - E_2} I \text{ohm}^{-1}$$  \hspace{1cm} (17)

where $\sigma$ is the conductance in ohm$^{-1}$ and $I$ is the current range 
marked on the shunt in amperes (i.e. the reciprocal of the shunt 
resistance). The specific conductivity was calculated by the 
following equation.

$$\sigma_{sp} = (\ell/s) \text{ ohm}^{-1} \text{ cm}^{-1}$$  \hspace{1cm} (18)

where $\ell$ is the thickness of the sample and $s$ is the area of the 
sample.

In these measurements, two types of cooling procedures 
were followed, rapid cooling and slow cooling. 

In rapid cooling the furnace was switched off and the 
measurements were made taking an interval of about 30-35 minutes 
(the temperature range being ~ 200-100°C) and about an hour interval 
below 100°C. In slow cooling the furnace setting was adjusted to 
give some constant temperature and readings were taken after equili-
brium was reached at that temperature (about one hour). The two
procedures appear to give generally similar results. In the majority of the experiments, rapid cooling was used, and it is not known whether slower procedures would show any different effects in the instances in which slow precipitation may occur. (e.g. 0.05 mole% CdI₂ doped sample, in which supersaturation occurs when the rapid procedure is used; see discussion section).

Polarization Effect: It has been observed by several workers\(^{17}\) that after the application of an electric field, an ionic crystal gets polarized, see Fig. (9.a). Qualitatively it is also observed that the polarization decreases with increasing temperature. The conductivity of the sample decreases with time after the application of the electric field until the sample is fully polarized. The variation of apparent E.M.F. with time is shown diagramatically in Fig. (9.b).

The procedure adopted to eliminate polarization effects assumes that the polarization may be represented by an E.M.F. inside the crystal, which is not immediately changed at the instant of reversing the applied E.M.F., so that the polarization E.M.F. is momentarily added to the applied E.M.F. instead of opposing it.

Thus in order to find the conductivity of an unpolarized sample, the mean of the last and first reading (before and after reversing the polarity) was taken in this work.

Blank Run: Using a piece of teflon of about pellet size, blank runs were made from time to time (of about four months interval) in order to check the internal resistance of the apparatus. An illustrative run is shown in Fig. (10).
Fig. 9
Polarization effect in ionic crystal

Fig. (9.a)

Polarization decreases field inside pellet, decreases apparent conductance.

Fig. (9.b)

Polarization increases field, increases apparent conductance.

Time (Min.)
The blank resistance was at room temperature at least 10 times higher than the highest resistance measured for a pellet or a crystal, and at all higher temperatures the ratio was much larger. Thus the limit to which the measurements could be made with this apparatus is about room temperature.
Fig. 10

Conductivity plot for blank run compared with results for pure KI pellet.
RESULTS
Two distinct regions A and B of different activation energies are observed in each type of pure and doped KI, (since, as discussed below, one of these regions does not correspond to any region previously known in an alkali halide, the numerals, I, II, III and IV are avoided in discussing them). Typical graphs for each type of sample studied are shown in Figure (6). Graphs showing the changes in behaviour for various treatments of a single crystal are also shown in Figures (17-19). The results are summarised in table 3. The absolute value of specific conductivity at 300°C from different investigations is tabulated in table 4.

The values of \( \sigma_{sp} \) in region A may in general be given limits of error ± 10%, but doped samples were very sensitive to the history of the pellet, and sometimes show erratic variations well outside this range. The sample containing 0.05 mole% CdI\(_2\) showed a considerable shift in \( \sigma_{sp} \) at 476°K (203°C) on temperature cycling. The value of \( \sigma_{sp} \) increases by a factor of 6 on temperature cycling. Other samples containing 0.10 mole% and 0.25 mole% CdI\(_2\) did not show this behaviour.

The activation energy \( E_A \) is generally reliable to ± 0.02 eV. and \( E_B \) to ± 0.03 eV. \( E_B \) gave rather more scattered values for pure pellets, for which limits of ± 0.06 should be assigned.

The tabulated results are mostly averages of three or four runs on two or three different pellets; for the single crystal, in two runs, the first crystal showed a small change in region A on overnight heating, while the second showed virtually no change.

For the pellets, the region B continued linear on the Arrhenius plot down to room temperature, but for single crystals the conductivity levelled off at about 60°C. Table 3 gives both the actual
conductivity at room temperature and the extrapolated value from the region B plot between 60°C and 23°C, the latter being needed for comparison with the results on pellets.

### TABLE 3

<table>
<thead>
<tr>
<th>KI sample</th>
<th>476 K (10^3/T=2.1)</th>
<th>296 K (10^3/T=3.37)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10^16 \sigma_{sp} (ohm^{-1}cm^{-1})</td>
<td>10^18 \sigma_{sp} (ohm^{-1}cm^{-1})</td>
<td>E_a (eV.)</td>
</tr>
<tr>
<td>Pure crystal, untreated</td>
<td>1.2</td>
<td>3.0</td>
<td>0.54</td>
</tr>
<tr>
<td>Pure crystal, annealed</td>
<td>1.8</td>
<td>1.9</td>
<td>0.038</td>
</tr>
<tr>
<td>Pure crystal, strained</td>
<td>0.66</td>
<td>1.5</td>
<td>0.43</td>
</tr>
<tr>
<td>Pure pellet</td>
<td>5.80</td>
<td>1.2</td>
<td>1.14</td>
</tr>
<tr>
<td>Doped pellet, 0.05 mole% CdI</td>
<td>140</td>
<td>3.0</td>
<td>1.20</td>
</tr>
<tr>
<td>Doped pellet, 0.10 mole% CdI</td>
<td>330</td>
<td>2.9</td>
<td>1.33</td>
</tr>
<tr>
<td>Doped pellet, 0.25 mole% CdI</td>
<td>380</td>
<td>0.5</td>
<td>1.45</td>
</tr>
</tbody>
</table>

### TABLE 4

Comparison with previous results

<table>
<thead>
<tr>
<th>KI sample</th>
<th>Reference</th>
<th>Temperature range °C</th>
<th>\sigma_{sp} (ohm^{-1}cm^{-1}) at 300°C</th>
<th>E_a (eV.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>Lehfeldt</td>
<td>(250 - 378)</td>
<td>1.00 x 10^{-8}</td>
<td>0.82</td>
</tr>
<tr>
<td>Pressed pellet</td>
<td>Baijal</td>
<td>(92 - 330)</td>
<td>3.18 x 10^{-7}</td>
<td>0.817</td>
</tr>
<tr>
<td>Single crystal</td>
<td>Present work</td>
<td>(97 - 203)</td>
<td>5.91 x 10^{-9}</td>
<td>0.96</td>
</tr>
<tr>
<td>Pressed pellet</td>
<td>Present work</td>
<td>(97 - 203)</td>
<td>4.91 x 10^{-8}</td>
<td>1.14</td>
</tr>
</tbody>
</table>
Fig. 11

Conductivity plot for pure KI pellet

\[ \log_{10} (\sigma_{sp} T) \]

\[ 10^3/T(°K) \]
Fig. 12
Conductivity plot for doped KI
(0.05 mole% CdI₂)

Region A

Region B

\[ \log(\sigma T) \]

\[ 10^3/T(°K) \]
Fig. 13
Conductivity plot for doped KI
(0.10 mole% CdI$_2$)
Fig. 14
Conductivity plot for doped KI
(0.25 mole% C:HI₂)
Fig. 15

Summary of conductivity plots

1 - 0.25 mole\% (CdI\textsubscript{2}) Sample
2 - 0.05 mole\% (CdI\textsubscript{2}) Sample
3 - Pure KI Sample
4 - Single Crystal
Fig. 16

Plot of conductivity versus impurity content

(this work)

Conductivity (ohm$^{-1}$cm$^{-1}$) x 10$^9$

mole% Cd$^{+2}$

KI-CdI$_2$ System
Fig. 17
Conductivity plot of single crystal (untreated)
Fig. 18

Conductivity plot of single crystal
(heated overnight)
Fig. 19

Conductivity plot of single crystal (strained)

Log$_{10}(\sigma_{spT})$ vs. $10^3/T(°K)$
DISCUSSION
As mentioned earlier, the conductivity plot of KI in the range 200°C to 23°C divides itself into two distinct regions A and B. Results in region A can be given a conventional interpretation in terms of conduction controlled by cation vacancies whose concentration is governed by aliovalent impurities together with association and precipitation effects.

Region A

(a) Absolute values of $\sigma_{sp}$ and impurity content: The absolute value of conductivity at 300°C is compared with previously obtained values and is given in table 4. Lehfeldt's\(^1\) value of $\sigma_{sp}$ of single crystal is $1 \times 10^{-8}$ ohm\(^-1\)cm\(^-1\). Baijal obtained for $\sigma_{sp}$ for a pure pellet a greater value than Lehfeldt by a factor of 30. In this work the value of $\sigma_{sp}$ at 300°C was calculated from extrapolated line in both samples (single crystal and pure pellet). The value for a single crystal is less by a factor of 6.5 than Lehfeldt's value, and the value for a pure pellet is less by a factor of 6 than Baijal's value. The discrepancies may be attributed to the purity of the specimen, since the region under investigation is the impurity region, similar to the well-investigated impurity region of sodium chloride. The specified impurity limits of my sample along with Baijal's is given in the appendix (tables 8 and 9) respectively, but the purity of Lehfeldt's sample is not known.

The values of $\sigma_{sp}$ at 203°C in different samples (see table 3) of pure and doped KI, suggests saturation at about 0.1 mole% (1000 ppm.). It is also seen from the graph of conductivity versus impurity content (see Figure 16), that the conductivity is linear up to 0.1 mole% Cd\(^{2+}\). From the values of $\sigma_{sp}$ at 203°C of doped and undoped samples, it appears...
that impurity contents in pure pellet and single crystal are about 18 ppm. and 4 ppm. respectively. Comparison of the former figure with specification of AR material indicates that the experimental value is about five times less than maximum impurity limits from the specification (about 100 ppm.).

(b) $E_A$ for pure samples and U: The activation energy of conductivity $E_A$ in region A was calculated from the slopes of corresponding graphs and the values have been tabulated in table 4. In the case of a single crystal $E_A$ is about 0.96 eV. and that of a pure pellet 1.14 eV. within the limits of 0.02 eV., either value being greater than Lehfeldt and Baijal's results. The activation energies given in table 4 have been calculated from the slope of $\log(\sigma_{sp}T)$ versus $T^{-1}$. The same method of calculation raises the Lehfeldt and Baijal's values by about 0.04 eV. $E_A$ in the case of single crystal is probably the energy needed for the motion of cation vacancy (U), since the impurity content in this case is probably low enough for association and precipitation effects to be negligible.

(c) $E_A$ for impure samples; association and precipitation: The effect of association energy and heat of precipitation are probably responsible for the higher activation energy in these samples (see table 3). The $E_A$ values for pure pellet and 0.05 mole% Cd$^{+2}$ doped pellet probably show the effect of association uncomplicated by precipitation and hence give the mean association energy for impurities in AR material as $2(1.14 - 0.96)$ equal to 0.36 eV. and the value for Cd$^{+2}$ in 0.05 mole% sample as $2(1.20 - 0.96)$ equal to 0.48 eV. These are comparable with reported values of association energies in alkali halides as quoted in the introduction to this thesis.
At higher impurity content, there is evidence for precipitation effects.

Thus Figure (15) shows that the line for the 0.25 mole% sample actually crosses that for the 0.05 mole% sample as T decreases. This suggests that the 0.05 mole% solution is saturated at the crossing-point at 140°C and that the slope of the 0.25% line contains the full effect of the heat of solution. We can therefore calculate $\Delta H_{\text{soln}}$ from the difference between this slope and that of the 0.05 mole% sample which shows the full association effect without precipitation.

$$\Delta H_{\text{soln}} = (\Delta H_{\text{soln}} + \frac{E_a}{2} + U) - (\frac{E_a}{2} + U) \quad (19)$$

$$= 1.45 - 1.20 = 0.25 \text{ eV.}$$

The 0.05 mole% sample is evidently supersaturated below 140°C, which probably explains why results at this impurity content were rather more erratic than most other results, as mentioned in the results section.

$\Delta H_{\text{soln}}$ may be estimated in two other ways from the results: -

(a) If the crossing-point of the 0.25 mole% line and the 0.1 mole% line is taken to give the temperature at which the solubility is 0.1 mole%, we have:

188°C, solubility = 0.1 mole%

140°C, solubility = 0.05 mole%

Application of the Van't Hoff equation to these results gives $\Delta H_{\text{soln}} = 0.24 \text{ eV.}$
(b) If it is assumed that there is very little entropy charge on solution (except for configurational entropy) then

\[ \text{solubility} = e^{-\Delta H_{\text{soln}}/kT} = 5 \times 10^{-4} \text{ at } 140^\circ\text{C}, \]

whence \( \Delta H_{\text{soln}} = 0.27 \text{ eV}. \)

**Region B:**

The existence of region B found in this work represents unusual behaviour and has not previously been observed in any alkali halides. There is a sharp decrease in activation energy from region A to region B. The activation energy in region B is considerably less than the energy needed for the motion of cation vacancies in the bulk, which for KI is between 0.86 and 0.96 eV. as discussed above. Now in any temperature range, below the impurity region, the activation energy of conductivity is expected to be greater than this value, since the activation energy below this temperature range is composed of two terms, one energy associated with the mobility of cation vacancies and another energy arising from the association of vacancies with impurities or from the heat of solution of impurities. \( \Delta H_{\text{soln}} \) could of course possibly be negative, but is usually positive and has been fairly clearly established as positive in the present case from the results for region A). Dreyfus and Nowick\(^9\) have observed high activation energy as expected for the conductivity below the impurity region for NaCl doped with CdCl\(_2\), see Figure (5) and have interpreted their results nicely in terms of multivalent cation impurity in the system. Results obtained in this work are not similar to Dreyfus and Nowick's results for NaCl and are not amenable to conventional interpretation in terms of cation vacancies in the bulk.
The considerably lower activation energy observed here may be interpreted in terms of vacancies in a region of unusually high mobility, such as dislocations and grain boundaries. The effect may arise partly from a lower activation energy for motion of vacancies in these regions and partly from a vacancy concentration in these regions which increases with decreasing temperature.

Let the concentration of cation and anion vacancies in the core of the dislocation or grain boundary be \( j_+ \) and \( j_- \) respectively. These concentrations are governed by an equilibrium similar to that for bulk defects,

\[
j_+ j_- = A \exp\left(-\frac{W_j^+ + W_j^-}{kT}\right) \tag{20}
\]

\[
= A \exp\left(-\frac{W_j}{kT}\right) \tag{21}
\]

where \( W_j \) is probably very much less than the value \( W \) for bulk defects. This equilibrium is related to the bulk equilibrium by the "space-charge" effects discussed by Lehovec\(^{18}\) in relation to surfaces and later by Lidiard et al\(^{19}\) for dislocations which, like surfaces, act as sources and sinks of vacancies.

The origin of space-charge may be visualised from the following consideration. Consider an ideal crystal without any lattice defect. Now if the energy of formation of a cation vacancy is less than the energy of formation of an anion vacancy, initially more cation vacancies will be formed and migrate into the interior than anion vacancies. This will leave a positive charge at the surface of the crystal. The resulting space-charge discourages the emission of further cation vacancies and
encourages the emission of anion vacancies. Assuming the bulk of the crystal to be electrically neutral the positive charge \( q \) on the surface is balanced by an equal and opposite negative charge cloud penetrating some distance into the crystal.

Now \( j_- - j_+ = q \) (22)

and combining this with equation (21)

\[
j_+ (q + j_+) = A \exp(-Wj/kT)
\]

(23)

whence \( j_+ = \frac{1}{2} (q^2 + 4A \exp(-Wj/kT))^{1/2} = q \)

If \( q^2 >> 4A \exp(-Wj/kT) \), this reduces to

\[
j_+ = A \exp(-Wj/kT)/q
\]

(24)

From Lehovec's account, one can write \( q \) as

\[
q = (2 \varepsilon \varepsilon_0 kT Z e^2)^{1/2} \exp \left[ \left( V_{\infty}/2 \right) - (W/4) \right]/kT
\]

(25)

where \( V_{\infty} \) is the potential difference between bulk and surface produced by the space-charge effect and is given by

\[
V_{\infty} = (W - W_+)/2
\]

(26)

where \( Z \) is the number of molecules per unit vol, \( W_+ \) is the energy of formation of anion vacancies and \( \varepsilon_0 \) is the dielectric constant; \( \varepsilon \) is the permittivity of material.

Thus

\[
j_+ = A \left( 2 \varepsilon \varepsilon_0 kT Z e^2 \right)^{1/2} \exp \left[ (W/4) - (V_{\infty}/2) - Wj \right]/kT
\]

(27)

\[
= \text{(constant)} \exp(Ej/kT)
\]

(28)

Since for alkali halides \( W/4 \sim 0.5 \text{ eV} \) and \( V_{\infty}^- \) is likely to be negative
(energy of formation of anion vacancy greater than that of cation vacancy), and since $W_j$ may be quite small, it is reasonable to expect $E_j$ to be positive, and hence to make a negative contribution to the activation energy of conduction.

These effects become complicated in doped samples because these structures (grain boundaries and dislocations) interact with impurities. At high temperature there is very little effect, but at low temperature aliovalent cationic impurities may cause the sign of the charge on dislocation and grain boundaries to reverse. Dislocations and grain boundaries probably serve also as places at which precipitates aggregate.

Doping at first raises the conductivity [see table (3)] since the divalent impurity at low temperature reverses the sign of the charge on the grain boundaries leading to a high cation vacancy concentration in the region of unusually high mobility, but heavy doping reduces the conductivity (table 3). The latter effect probably represents the blocking of diffusion paths with precipitates. This is clearly noted in the sample containing 0.25 mole% Cd$^{2+}$. The conductivity at 296°K changes from $3.0 \times 10^{-14}$ ohm$^{-1}$cm$^{-1}$ for 0.05 mole% sample to $0.5 \times 10^{-14}$ ohm$^{-1}$cm$^{-1}$ in 0.25 mole% sample (see table 3).

The value of 0.57 eV. (see table 3) for the region B activation energy in single crystals, probably refers to motion of vacancies in isolated dislocations and low angle boundaries, while the value of 0.38 eV. for a pure pellet corresponds to motion in large angle boundaries.

If it is assumed the $j_+$ is independent of temperature, so that the experimental activation energy is a mobility term, and taking $A \approx 10^{13}$ sec$^{-1}$ in equation (4) ($j_+ = (4 j_+ e^2 r_o^2 A/kT) \exp(-U/kT)$ (with $j_+$ in place of $n_+$) the concentration of charge carriers in a pure pellet is
about $6.5 \times 10^{10}$ per cm$^3$ which leads for a grain size of 10µ to a defect concentration of about $10^7$ defects per cm$^2$ of grain boundary. In a single crystal the charge carriers' concentration is similarly calculated as about $9 \times 10^{16}$cm$^{-3}$. The dislocation density in the crystal is of course very uncertain. If the crystal is assumed to have isolated dislocations at about one per square micron, then the concentrations of jogs in the dislocations becomes more than one per A$\bar{ }$ on this basis; but if the crystal is broken up into mosaic blocks of about 1µ size, then jogs are about 60 A apart in the low angle boundaries. This is still a high value, and probably indicates that the assumption regarding the activation energy is incorrect, and that the value of 0.57 eV. contains an energy effect in the concentration $j_+$.

A strong piece of evidence that region B involves an effect of dislocation is obtained from the conductivity runs on single crystals. As for pure and doped KI pellets, region A and B are identified in single crystals, but region B essentially disappears on overnight heating and is replaced by an extension of region A down to room temperature (see Fig.18); but region B reappears on straining the crystal. In addition to this important effect of straining in region B, it is noted that strain had a very small effect on region A (see Fig. 19 and table 3). These experimental observations suggest that

1) The mechanisms for conduction in region A and B are not identical. Conduction is not governed primarily by dislocation and grain boundaries in region A.
2) Overnight heating reduces the concentration of dislocation so that the activation energy becomes that for bulk motion of vacancies.

3) Straining introduces dislocations and thus restores the migration path of low activation energy.
### TABLE 1
Electrical Conductivity of KI Pellet (23°C - 203°C)

<table>
<thead>
<tr>
<th>$t^\circ C$</th>
<th>$T^\circ K$</th>
<th>$10^3 / T^\circ K$</th>
<th>Log($\sigma_{sp} \cdot T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>476</td>
<td>2.10</td>
<td>7.53</td>
</tr>
<tr>
<td>185</td>
<td>458</td>
<td>2.18</td>
<td>7.07</td>
</tr>
<tr>
<td>154</td>
<td>427</td>
<td>2.34</td>
<td>9.90</td>
</tr>
<tr>
<td>136</td>
<td>409</td>
<td>2.44</td>
<td>9.35</td>
</tr>
<tr>
<td>111</td>
<td>384</td>
<td>2.60</td>
<td>10.35</td>
</tr>
<tr>
<td>101</td>
<td>374</td>
<td>2.67</td>
<td>10.10</td>
</tr>
<tr>
<td>84</td>
<td>357</td>
<td>2.80</td>
<td>11.63</td>
</tr>
<tr>
<td>74</td>
<td>347</td>
<td>2.88</td>
<td>11.45</td>
</tr>
<tr>
<td>56</td>
<td>329</td>
<td>3.04</td>
<td>11.12</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>12.25</td>
</tr>
</tbody>
</table>

### TABLE 2
Electrical Conductivity of KI Doped Pellet (0.05 mole% CdI$_2$) (23° - 215°C)

<table>
<thead>
<tr>
<th>$t^\circ C$</th>
<th>$T^\circ K$</th>
<th>$10^3 / T^\circ K$</th>
<th>Log($\sigma_{sp} \cdot T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>488</td>
<td>2.05</td>
<td>5.287</td>
</tr>
<tr>
<td>187</td>
<td>460</td>
<td>2.17</td>
<td>6.487</td>
</tr>
<tr>
<td>162</td>
<td>435</td>
<td>2.30</td>
<td>7.461</td>
</tr>
<tr>
<td>140</td>
<td>413</td>
<td>2.42</td>
<td>8.827</td>
</tr>
<tr>
<td>115</td>
<td>388</td>
<td>2.58</td>
<td>8.099</td>
</tr>
<tr>
<td>97</td>
<td>370</td>
<td>2.70</td>
<td>9.136</td>
</tr>
<tr>
<td>75</td>
<td>348</td>
<td>2.87</td>
<td>10.363</td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>3.00</td>
<td>11.980</td>
</tr>
<tr>
<td>40</td>
<td>313</td>
<td>3.20</td>
<td>11.599</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>11.000</td>
</tr>
</tbody>
</table>
### TABLE 3

Electrical Conductivity of KI-Doped Pellet (0.1 mole% CdI$_2$) (23° - 212°C)

<table>
<thead>
<tr>
<th>$t^\circ$c</th>
<th>$T^\circK$</th>
<th>$10^3/T^\circK$</th>
<th>Log ($\sigma_{sp}$ T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>212</td>
<td>485</td>
<td>2.06</td>
<td>5.550</td>
</tr>
<tr>
<td>186</td>
<td>459</td>
<td>2.18</td>
<td>6.752</td>
</tr>
<tr>
<td>168</td>
<td>441</td>
<td>2.27</td>
<td>6.058</td>
</tr>
<tr>
<td>145</td>
<td>418</td>
<td>2.39</td>
<td>7.166</td>
</tr>
<tr>
<td>113</td>
<td>380</td>
<td>2.59</td>
<td>9.921</td>
</tr>
<tr>
<td>82</td>
<td>355</td>
<td>2.82</td>
<td>10.084</td>
</tr>
<tr>
<td>65</td>
<td>338</td>
<td>2.95</td>
<td>10.194</td>
</tr>
<tr>
<td>52</td>
<td>325</td>
<td>3.07</td>
<td>11.845</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>12.920</td>
</tr>
</tbody>
</table>

### TABLE 4

Electrical Conductivity of KI Doped Pellet (0.25 mole% CdI$_2$) (23° - 200°C)

<table>
<thead>
<tr>
<th>$t^\circ$c</th>
<th>$T^\circK$</th>
<th>$10^3/T^\circK$</th>
<th>Log ($\sigma_{sp}$ T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>473</td>
<td>2.11</td>
<td>5.150</td>
</tr>
<tr>
<td>185</td>
<td>458</td>
<td>2.18</td>
<td>6.729</td>
</tr>
<tr>
<td>166</td>
<td>439</td>
<td>2.28</td>
<td>7.818</td>
</tr>
<tr>
<td>150</td>
<td>423</td>
<td>2.36</td>
<td>7.166</td>
</tr>
<tr>
<td>129</td>
<td>402</td>
<td>2.49</td>
<td>8.315</td>
</tr>
<tr>
<td>108</td>
<td>381</td>
<td>2.62</td>
<td>9.425</td>
</tr>
<tr>
<td>91</td>
<td>364</td>
<td>2.75</td>
<td>10.662</td>
</tr>
<tr>
<td>74</td>
<td>347</td>
<td>2.88</td>
<td>10.076</td>
</tr>
</tbody>
</table>

Continued ....
### Table 4 (continued)

<table>
<thead>
<tr>
<th>t°C</th>
<th>T°K</th>
<th>10³/T°K</th>
<th>Log ($\sigma_{sp}T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>338</td>
<td>2.96</td>
<td>$\overline{11.784}$</td>
</tr>
<tr>
<td>50</td>
<td>323</td>
<td>3.10</td>
<td>$\overline{11.183}$</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>$\overline{12.600}$</td>
</tr>
</tbody>
</table>

### Table 5

**Electrical Conductivity of KI Single Crystal (Untreated) (23° - 200°C)**

<table>
<thead>
<tr>
<th>t°C</th>
<th>T°K</th>
<th>10³/T°K</th>
<th>Log ($\sigma_{sp}T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>473</td>
<td>2.11</td>
<td>$\overline{8.720}$</td>
</tr>
<tr>
<td>186</td>
<td>459</td>
<td>2.18</td>
<td>$\overline{8.436}$</td>
</tr>
<tr>
<td>162</td>
<td>435</td>
<td>2.30</td>
<td>$\overline{9.664}$</td>
</tr>
<tr>
<td>144</td>
<td>417</td>
<td>2.40</td>
<td>$\overline{9.243}$</td>
</tr>
<tr>
<td>127</td>
<td>400</td>
<td>2.50</td>
<td>$\overline{10.804}$</td>
</tr>
<tr>
<td>111</td>
<td>384</td>
<td>2.60</td>
<td>$\overline{10.413}$</td>
</tr>
<tr>
<td>95</td>
<td>368</td>
<td>2.72</td>
<td>$\overline{10.104}$</td>
</tr>
<tr>
<td>76</td>
<td>349</td>
<td>2.80</td>
<td>$\overline{11.639}$</td>
</tr>
<tr>
<td>65</td>
<td>335</td>
<td>2.98</td>
<td>$\overline{11.253}$</td>
</tr>
<tr>
<td>38</td>
<td>311</td>
<td>3.21</td>
<td>$\overline{11.100}$</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>$\overline{12.950}$</td>
</tr>
</tbody>
</table>

### Table 6

**Electrical Conductivity of Annealed (Overnight) KI Single Crystal (23° - 205°C)**

<table>
<thead>
<tr>
<th>t°C</th>
<th>T°K</th>
<th>10³/T°K</th>
<th>Log ($\sigma_{sp}T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>478</td>
<td>2.09</td>
<td>$\overline{8.500}$</td>
</tr>
<tr>
<td>191</td>
<td>464</td>
<td>2.16</td>
<td>$\overline{8.749}$</td>
</tr>
<tr>
<td>175</td>
<td>448</td>
<td>2.23</td>
<td>$\overline{8.308}$</td>
</tr>
<tr>
<td>151</td>
<td>424</td>
<td>2.36</td>
<td>$\overline{9.572}$</td>
</tr>
</tbody>
</table>

Continued....
Table 6 (continued)

<table>
<thead>
<tr>
<th>T°C</th>
<th>T°K</th>
<th>10^3/T°K</th>
<th>Log (σspT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>137</td>
<td>410</td>
<td>2.44</td>
<td>9.176</td>
</tr>
<tr>
<td>125</td>
<td>398</td>
<td>2.51</td>
<td>10.843</td>
</tr>
<tr>
<td>116</td>
<td>389</td>
<td>2.57</td>
<td>10.572</td>
</tr>
<tr>
<td>109</td>
<td>382</td>
<td>2.62</td>
<td>10.405</td>
</tr>
<tr>
<td>98</td>
<td>371</td>
<td>2.69</td>
<td>10.072</td>
</tr>
<tr>
<td>86</td>
<td>359</td>
<td>2.79</td>
<td>11.631</td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>3.00</td>
<td>12.798</td>
</tr>
<tr>
<td>45</td>
<td>318</td>
<td>3.14</td>
<td>12.550</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>12.770</td>
</tr>
</tbody>
</table>

TABLE 7

Electrical Conductivity of Strained KI Single Crystal

<table>
<thead>
<tr>
<th>T°C</th>
<th>T°K</th>
<th>10^3/T°K</th>
<th>Log (σspT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>474</td>
<td>2.11</td>
<td>8.431</td>
</tr>
<tr>
<td>172</td>
<td>445</td>
<td>2.24</td>
<td>9.775</td>
</tr>
<tr>
<td>152</td>
<td>425</td>
<td>2.35</td>
<td>9.305</td>
</tr>
<tr>
<td>138</td>
<td>411</td>
<td>2.43</td>
<td>9.067</td>
</tr>
<tr>
<td>124</td>
<td>397</td>
<td>2.52</td>
<td>9.680</td>
</tr>
<tr>
<td>107</td>
<td>380</td>
<td>2.63</td>
<td>10.330</td>
</tr>
<tr>
<td>94</td>
<td>367</td>
<td>2.72</td>
<td>11.989</td>
</tr>
<tr>
<td>80</td>
<td>353</td>
<td>2.83</td>
<td>11.698</td>
</tr>
<tr>
<td>61</td>
<td>334</td>
<td>2.99</td>
<td>11.169</td>
</tr>
<tr>
<td>45</td>
<td>318</td>
<td>3.14</td>
<td>12.918</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.37</td>
<td>12.619</td>
</tr>
</tbody>
</table>
TABLE 8

Specification from Fisher Scientific Company of KI used in this work
Certified A.C.S. Potassium Iodide Crystal

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance and odor</td>
<td>Transparent, colorless crystal, odorless</td>
</tr>
<tr>
<td>Insoluble matter</td>
<td>0.001%</td>
</tr>
<tr>
<td>Sulphate (SO₄)</td>
<td>0.0008%</td>
</tr>
<tr>
<td>Loss on drying at 150°C</td>
<td>0.04%</td>
</tr>
<tr>
<td>pH of a 5% solution at 25°C</td>
<td>6.70</td>
</tr>
<tr>
<td>Chloride and bromide (as Cl)</td>
<td>0.005%</td>
</tr>
<tr>
<td>Iodate (IO₃⁻)</td>
<td>0.0003%</td>
</tr>
<tr>
<td>Nitrogen compounds (as N)</td>
<td>0.0005%</td>
</tr>
<tr>
<td>Phosphate (PO₄³⁻)</td>
<td>0.000%</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.000%</td>
</tr>
<tr>
<td>Calcium magnesium and R₂O₃ precipitate</td>
<td>0.000%</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>0.00000%</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.0002%</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.0013%</td>
</tr>
</tbody>
</table>
**TABLE 9**

Specification from Mallinckrodt Chemical Works of KI used in Baijal's work.

Potassium Iodide Ar (ACS) Crystals

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance and odor</td>
<td>Transparent, colorless crystal, odorless</td>
</tr>
<tr>
<td>Insoluble matter</td>
<td>0.005% max.</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td>0.005% max.</td>
</tr>
<tr>
<td>Loss on Drying</td>
<td>0.20% max.</td>
</tr>
<tr>
<td>pH of a 5% solution (25°C)</td>
<td>6.0 - 9.2</td>
</tr>
<tr>
<td>Chloride and bromide as (Cl⁻)</td>
<td>0.10 max.</td>
</tr>
<tr>
<td>Iodate (IO₃⁻)</td>
<td>To pass test (limit about 0.0003%)</td>
</tr>
<tr>
<td>Nitrogen compounds (as N)</td>
<td>0.001% max.</td>
</tr>
<tr>
<td>Phosphate (PO₄³⁻)</td>
<td>0.001% max.</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>0.002% max.</td>
</tr>
<tr>
<td>Calcium magnesium and R2O3 precipitate</td>
<td>0.005% max.</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>0.005% max.</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.0003% max.</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.005% max.</td>
</tr>
<tr>
<td>Sieve test #20 U.S. standard</td>
<td>25% max. through</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY
