CHAPTER I

INTRODUCTION TO RED OX REACTIVITY SOLID ELECTROLYTES
Solid electrolytes are ionic materials with high electrical conductivity comparable to those of liquid electrolytes. These materials are also termed as "superionic solids" or "fast ion conductors". Typically a superionic solid has the following characteristics (Chandra 1, to be published):-

(i) Crystal bonding is ionic
(ii) Electrical conductivity is high
\[ \sim 10^{-1} - 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \]
(iii) Principal charge carriers are ions which means that the ionic transference number \( t_{\text{ion}} \) is almost equal to 1. Here \( t_{\text{ion}} \) refers to the fraction of charge transferred by all types of ions taken together with reference to the total charge transferred.
(iv) The electronic conductivity is small.

Generally materials with electronic transference number \( t_e \) less than \( 10^{-4} \) are considered satisfactory superionic solids.

The values of electrical conductivity of a few ionic and superionic solids are shown in Figure 1.1. The highest conductivity at room temperature obtained so far is for \( \text{RbAgI}_5 \) which is \( 0.27 \text{ ohm}^{-1} \text{ cm}^{-1} \). This is many orders
Fig. 14: Ionic conductivity of various silver-ion containing solids as function of inverse of absolute temperature. The ends of solid lines represent the temperature range of the measurements. The vertical bars after the temperatures were not the melting points.
of magnitude higher than those of the more commonly known ionic solids KCl, NaCl etc., which have room temperature conductivity $\approx 10^{-12} - 10^{-16}$ ohm$^{-1}$ cm$^{-1}$. It may be noted that most of the superionic materials attain high electrical conductivity after undergoing a phase transition at a certain temperature which may or may not be well defined.

(1.1) **Types of ionic solids**

From the crystallographic point of view a perfect crystal of an ionic compound would be an insulator (Lidiard $^2$). The presence of defect or disorder is a necessity to sustain meaningful ionic transport. It is natural to classify the ionic solids according to the types of defect or disorder responsible for ionic transport. These solids are principally of two types (Chandra $^1$, to be published):

1. **Point defect type**
2. **Molten sublattice type**

In the 'point defect type' solids, the transport is through Frenkel or Schottky defect pairs which are thermally generated. As a result, the number of defects (and hence charge carriers) are a function of temperature. The activation energy is generally high $\approx 1$ eV or more. 'Point defect type' solids can further be subdivided according to
defect concentration density as follows:

(a) **Dilute**: Example - $\text{AgCl, BiI₃, KCl}$ etc.

(b) **Concentrated**: Example - stabilised zirconia or Hafnia, $\text{CaF₂}$ etc.

In 'molten sublattice type' solids, the number of a particular ion is less than the number of sites available for it in its sublattice. As a result, all these ions can 'hop' or 'move like a free-ion' from one position to another. Since all these ions are available for transport, the conductivity is large and activation energy is low. These materials/ions possess an 'average structure' rather than a rigid structure.

Nica & Roth ³ has suggested another scheme of classification of ionic solids based on the parameters of his 'free-ion like theory' of superionic solids which is essentially the same as above. According to this scheme, ionic solids are of three types:

**Type I**: These are conventional ionic solids in which the defect concentration is low. The number of mobile defects is $\sim 10^{18} / \text{cm}^3$ or less. This is the case of 'dilute point defect type' ionic solid discussed above.
Type II: They contain a large concentration of defects which have coalesced into coherent substructure or 'extended defects' of submicroscopic dimension. These are the same as 'concentrated point defect type' solids. The defect concentration is \( \sim 10^{20}/\text{cm}^3 \).

Type III: This is the case of 'liquid like molten sublattice' in which practically all the ions in a sublattice are available for movement. The number of mobile charge carriers is \( \sim 10^{22}/\text{cm}^3 \). These are generally marked by a channelled or layered structure.

Types II & III are superionic solids or solid electrolytes while Type I are essentially Insulating Ionic solids like alkali halides.

(1.2) Insulating Ionic Solids

They possess conductivities lower than \( 10^{-10} \text{ ohm}^{-1}\text{cm}^{-1} \) at room temperature. A great majority of the ionic solids belong to this class viz. alkali halides, silver halides (\( \text{AgCl} \) and \( \text{AgI} \)) etc.

In an ideally perfect ionic crystal the movement of ions under the action of an electric field is not possible if we assume that transport of charge could only
take place via union - cation exchange. This process involves a very high energy of the order of 15 eV i.e. in one gram-molecule such an event would occur only once in \(10^{30}\) years. From extensive series of measurements of ionic conductivity as a function of temperature, two facts stand out clearly:

(i) The existence of two main regions in conductivity curve as a function of temperature, and

(ii) In both the regions the \(\log (\sigma)\) vs \(T^{-1}\) is approximately linear.

The high temperature conductivity above the transition region or 'knee' in general is an intrinsic property of the crystal and measurements in this region are quite reproducible. On the other hand, low temperature conductivity (or extrinsic conductivity) displays a smaller slope in \(\log \sigma\) vs \(T^{-1}\) curve but it depends on the purity of the sample. To explain the low but finite temperature dependent ionic conductivity the existence of thermally generated point defect has been invoked.

In general electrical conductivity is given by

\[
\sigma = \sum n_i q_i \mu_i, \quad (1.1)
\]

where \(n_i\) is the number of charge carriers, \(q_i\) is the
charge and \( \mu_i \) is the mobility of the charge carrier of \( \text{i} \text{th} \) species. It is now well recognized that predominant types of charge carriers in ionic solids are either Frenkel defects or Schottky defects.

In case of Frenkel defect, an ion (cation or anion) from a normal lattice site is activated to a nearby interstitial site, creating an interstitial ion and an ion vacancy. If this pair of defect becomes thermally dissociated to beyond the range of their Debye–Hückel charge clouds, they will migrate independently in an electric field, in general, with different mobilities. If the temperature is high enough to assure ion defect equilibrium (and impurity effects be ignored), there will be a fixed and equal concentration of the two types of defects given by the following expression.

\[
n_f = (\frac{NN'}{2})^{1/2} \exp \left(-\frac{E_f}{2kT}\right), \quad (1.2)
\]

where \( E_f \) is the energy required to form a thermally dissociated Frenkel defect pair, \( N \) is the number of normal lattice sites and \( N' \) is the number of interstitial sites per unit volume. Silver bromide and chloride are the classic examples of this class.
Schottky defects (cation and anion vacancies) are assumed to be introduced in pairs into the crystal lattice from the surface sites or from vacancy sinks such as dislocations or grain boundaries. Fixed and equal concentrations of the two types of vacancies result at each temperature assuming ionic equilibrium and negligible impurity effects. Again dissociated defects may migrate independently in an electric field. In general Schottky defects occur in crystals with comparable cationic and anionic radii. The number of vacancies \( n_s \) of each type is given by

\[
    n_s = N \exp \left( - \frac{g_s}{2kT} \right),
\]

where \( g_s \) is the amount of energy required to form a Schottky defect pair.

Ionic mobility in such solids occurs as a result of random, thermally activated jumps, either of an interstitial ion into an adjacent unoccupied interstitial site, or of an ion on a normal lattice site into an adjacent vacancy for that type of ion. Another migration mechanism is that in which an interstitial ion replaces alike ion on normal lattice site, pushing it into an unoccupied adjacent interstitial site. The latter is known as 'interstitialcy' mechanism. In any event, each jump process is assumed to
involve an activation energy of \( \Delta E \), such that the jump frequency is given by

\[
\omega = y \exp \left( - \frac{\Delta E}{kT} \right),
\]

where \( y \) is the vibrational frequency. The above expression is the jump frequency when there is no applied electric field. Suppose an uniform electric field \( E \) acts along one of the axes (say \( x \)-axis). The applied electric field can be regarded as adding a term \(-eEx\) in the potential energy of the interstitial. The net effect is that a jump in the direction of field would take place with an increased probability

\[
\omega' = y \exp \left( - \frac{1}{kT} \left( E - \frac{1}{2} eE_x \right) \right),
\]

and a jump in a direction opposite to the applied field takes place with a reduced probability

\[
\omega'' = y \exp \left[ - \frac{1}{kT} \left( \Delta E + \frac{1}{2} eE_x \right) \right].
\]

If \( eE \ll kT \), this would result in a current density (Lidiard 2)

\[
J = \frac{n e^2 e^2 E}{kT} y \exp \left( - \frac{\Delta E}{kT} \right),
\]
The mobility \( \mu_1 \) is then given by

\[
\mu_1 = \frac{v}{nea^2} = \frac{ea^2}{kT} y \exp\left( - \frac{\Delta E}{kT} \right), \tag{1.8}
\]

Hence the partial conductivity (from Eq. 1.1) due to mechanism considered above is

\[
\sigma = \frac{n e^2 a^2}{kT} v \exp\left( - \frac{\Delta E}{kT} \right), \tag{1.9}
\]

where \( e \) is the charge on a particular ion participating in conduction mechanism and \( n \) is given by Eq. 1.2 or Eq. 1.3. Hence a plot between \( \log \sigma \) and \( 1/T \) would be linear if one type of defect mechanism is responsible for the conductivity.

In actual experiment, broadly speaking, the log \( \sigma \) vs \( 1/T \) plot shows two distinct regions. The high temperature conductivity is independent of purity of the crystal (if the impurity concentration is not too large) but the low temperature conductivity is strongly impurity sensitive. The former is known as intrinsic conductivity and the latter as the extrinsic. Intrinsic conductivity is due to thermally generated defects while the extrinsic conductivity is due to vacancies created by impurity doping (allovalent cation or anion). A few more variations in
slope can be seen in the conductivity curve due to association and precipitation of impurities. For alkali halides, it is now well established that both the positive and negative ion vacancies are mobile. The transport parameters can be obtained either by following Chandra and Wolfe's 4 procedure (from electrical conductivity measurement on pure and divalent cation and anion doped samples) or by the method of Fuller et al 5 (from diffusion and electrical conductivity measurements on pure and divalent cation doped samples).

(1.3) **Superionic Materials**

In general both cations and anions can move in a solid lattice. The cations have relatively small ionic radii as compared to anions. For example, the Pauling ionic radii of alkali metal ions are: Li+(0.60 Å), Na+(0.95 Å), K+(1.33 Å) and Rb+(1.48 Å) while the ionic radii of halide ions are: F− (1.36 Å), Cl− (1.86 Å), Br− (1.95 Å) and I− (2.16 Å). As such the number of conducting solids with alkali metal ions are expected to be more. The possibility of halide ion conductors is much less except that for the smallest ion F−. In fact, the materials available so far confirm this statement. The more common ions showing high mobility are
Li$^+$, Na$^+$, K$^+$, Ag$^+$, Cu$^+$, F$^-$ and O$_2^-$ Most of the compounds of the latter two ions (F$^-$ and O$_2^-$) show high conductivity only at high temperatures. Leaving oxygen ion conductors, most of the superionic solids involve a monovalent ion. There are no di- and trivalent ions reported showing high mobility though reports for small ionic conduction exist. This is somewhat expected since the coulombic energies involved in jumping/hopping of di- or trivalent ions would be more than those for monovalent ions. However, the above description is an oversimplification of the actual situation. The structure is probably the most important factor (Niedersich & Geller$^5$). Structural principles governing the formation of solids showing fast ion transport has not yet been studied in detail though the beginning has been made by Phillips$^6$ and Raleigh$^7$.

Table 1.1 gives some of the important high conductivity solid electrolytes or superionic solids. Amongst these, the highest conductivity has been reported for silver ion conductors out of which RbAg$_4$I$_5$ is the best. This thesis is concerned with silver ion conductors and hence some of the salient features of silver ion conductors are reviewed below.
Table 1.1  Some important Superionic Solids
(see Chandra 1, to be published)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mobile ion</th>
<th>Conductivity (ohm^{-1} cm^{-1})</th>
<th>Temperature (°C)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
</tr>
</tbody>
</table>

**Alkali metal ion conductors:**

- LiI + (40% Al_{2}O_{3})  
  Li^+  
  1.2x10^{-5}  
  25  
  0.43
- Li_{2}SiO_{4}  
  Li^+  
  1.6x10^{-3}  
  400  
  0.68
- Lithium β-alumina  
  Li^+  
  1.3x10^{-4}  
  25  
  0.37
- Sodium β-alumina  
  Na^+  
  1.4x10^{-2}  
  25  
  0.16
- Na_{2}SiO_{4}  
  Na^+  
  5.2x10^{-2}  
  300  
  -
- Sodium β-gallate  
  Na^+  
  3.0x10^{-2}  
  300  
  0.27
- Potassium β-alumina  
  K^+  
  6.5x10^{-5}  
  300  
  0.29

**Silver ion conductors:**

- KAg_{4}I_{5}  
  Ag^+  
  0.21  
  22  
  0.1
- PbAg_{4}I_{5}  
  Ag^+  
  0.21  
  (pellet)  
  0.27  
  (crystal)
- NH_{4}Ag_{4}I_{5}  
  Ag^+  
  0.19  
  22  
  0.1
Table 1.1 (contd)

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>α -AgI</td>
<td></td>
<td></td>
<td>1.0</td>
<td>150</td>
<td>0.06</td>
</tr>
<tr>
<td>α -CuI</td>
<td></td>
<td></td>
<td>0.02</td>
<td>25</td>
<td>0.16</td>
</tr>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td></td>
<td>0.09</td>
<td>25</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Copper ion conductors:**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Cu^{+}</th>
<th>0.09</th>
<th>450</th>
<th>0.13</th>
</tr>
</thead>
<tbody>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>Cu^{+}</td>
<td>0.6</td>
<td>280</td>
<td>0.22</td>
</tr>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>Cu^{+}</td>
<td>1.1x10^{-1}</td>
<td>150</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**Oxygen ion conductors:**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>O^{2-}</th>
<th>5.5x10^{-2}</th>
<th>1000</th>
<th>1.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>O^{2-}</td>
<td>4.8x10^{-3}</td>
<td>1000</td>
<td>1.10</td>
</tr>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>O^{2-}</td>
<td>1.1x10^{-1}</td>
<td>1000</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Fluorine ion conductors:**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>F^{-}</th>
<th>1</th>
<th>500</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>F^{-}</td>
<td>6x10^{-4}</td>
<td>200</td>
<td>0.26</td>
</tr>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>F^{-}</td>
<td>4x10^{-2}</td>
<td>700</td>
<td>0.2</td>
</tr>
<tr>
<td>α -Cu_{2}I_{5}</td>
<td></td>
<td>F^{-}</td>
<td>4x10^{-3}</td>
<td>100</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Silver ion conductors are the most extensively studied group of superionic solids and have been very well reviewed by Friedersich & Geller \(^5\); Takahashi \(^6\); Unke \(^7\); Halfi \(^8\) and Chandra \(^1\) (to be published).

The earliest good high temperature silver ion conductor probably reported in literature is silver sulfide, \(\text{Ag}_2\text{S}\), by Paraday \(^11\) who had also surmised the presence of many other such compounds — "there is no other body with which I am acquainted, that like sulphuret of silver can compare with metals in conducting power for electricity when hot, but which .... during cooling lose in power .... Probably, however, many others may, when sought for, be found". \(\text{Ag}_2\text{Se}\) and \(\text{Ag}_2\text{Te}\), compounds similar to \(\text{Ag}_2\text{S}\), have been later found to have high conductivity at high temperatures (Tubandt \(^12\)).

However, the measurement of conductivity in silver halides by Tubandt & Lorenz \(^13\) may well be taken as the starting point for the present day effort to understand and search for new silver ion conduction.

They reported that the conductivity of AgI abruptly increases by more than 3 orders of magnitude at 147°C. This high conductivity phase is known as \(\alpha\)-AgI (cubic) and the low conductivity phase is \(\beta\)-AgI (wurtzite). Since then, a large number of silver ion conducting
Most of the silver ion conductors are based on AgI. These conductive phases have been obtained by partially:

(i) Substituting different cations for Ag$^+$
(ii) Substituting different anions for I$^-$ or 
(iii) Substituting both cations and anions

The first reported room temperature good silver ion conductor is cation substituted and was obtained by solid solution AgI + 4AgI ($' = \text{Ag, Pb, } \text{Bi}_4$) independently by Bradley & Greene 14 and Owens 15. The compounds $\text{H}_4\text{Ag}_4\text{I}_5$ are known to decompose according to the following solid state disproportionation reaction (Owens 16) below a certain temperature -

$$2\text{Ag}_4\text{I}_5 \rightarrow \text{Ag}_2\text{I}_3 + 7\text{AgI}$$

The disproportionation temperatures for $\text{Ag}_4\text{I}_5$, $\text{Bi}_4\text{Ag}_4\text{I}_5$ and $\text{H}_4\text{Ag}_4\text{I}_5$ are 37, 28, 32$^o$C respectively. The presence of water vapour seems to catalyse the disproportionation reaction rate.

Chandra & Kohabey 17 have studied the above reaction by observing the rate of growth of AgI exciton peak. These results are given in Chapter VI as a subsidiary matter of this thesis.
Ion transport and dynamics have been studied in silver ion conductors using a wide variety of techniques. As a result of these studies, more or less a common picture is emerging out for the AgI-type superionic solids (Funke 9; Chandra 1 to be published).

(a) The cations are structurally disordered and the cation sublattice is "liquid-like". The number of cations is less than the number of sites (voids) available for them and these sites are occupied at random.

(b) The anions are arranged in such a way that the local potentials are rather flat along certain lines which interconnect neighbouring sites. Along these lines the difference in potential energy is of the order of thermal energy. According to Geller 13 "the common structural motif in the conductive compounds is the existence of passage ways of face-shared iodide ion polyhedra".

(c) As a consequence of (a) and (b) all or a large fraction of the cations can move from one site to another site with a very low activation energy of the order of thermal energy and thus, in general, participating in the cation diffusion process. The diffusion path is channel like and not exactly liquid-like.
(d) The disordering process may be first-order or second-order. At the first-order transition temperature the conductivity changes abruptly and generally involves a change in lattice symmetry and latent heat. In second order phase transition, there is no abrupt change in conductivity — only the slope changes slightly. Generally, there is no or small change in lattice symmetry and is accompanied by a power law divergence in specific heat.

(e) Ion-Ion correlation is an important factor in bringing about disorder (e.g. Huberman 13; Rice et al 19; Radeé & Mahan 20; Mahan 21; Vergas et al 22; Solomon 23; Welch & Dienes et al 24; Lederman et al 25).

(f) The ion transport is possibly by a jump-diffusion process on which an additional cation local motion is superimposed (diffusive and/or overdamped oscillatory local motion).

Unusual structure is the single most important factor responsible for high Ag⁺ ion transport. There are more sites available than the number of ions per unit cell giving the ions a 'free-ion like state'. The number of available sites and number of ions per unit cell are given in Table 1.2 to illustrate this point.
Table 1.2  Structural parameters of some Ag ion conductors

<table>
<thead>
<tr>
<th>Superionic Solid</th>
<th>Structure</th>
<th>Lattice constant $\text{Å}^0$</th>
<th>Number of Ag per unit cell</th>
<th>No. of Ag sites available</th>
<th>Stability range/Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-AgI</td>
<td>b.c.c.</td>
<td>5.06</td>
<td>2</td>
<td>12 or 42</td>
<td>147-555°</td>
</tr>
<tr>
<td>($\text{CH}_3)_4$ $\text{Ag}_2\text{I}_5$</td>
<td>Hexagonal</td>
<td>a 12.77 c 26.54</td>
<td>39</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>($\text{C}_6\text{H}_5\text{NH})\text{Ag}_5\text{I}_6$</td>
<td>Hexagonal</td>
<td>a 11.97 c 26.54</td>
<td>10</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>RbAg$_4$I$_5$</td>
<td>Cubic</td>
<td>11.24</td>
<td>16</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ag$_3$I</td>
<td>b.c.c. (disordered)</td>
<td>4.99</td>
<td>3</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Ag$_3$I</td>
<td>b.c.c. (ordered)</td>
<td>4.90</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ag$_3$Br</td>
<td>b.c.c. (ordered)</td>
<td>4.81</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ag$_2$S</td>
<td>b.c.c.</td>
<td>4.89</td>
<td>4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ag$_2$Se</td>
<td>b.c.c.</td>
<td>5.0</td>
<td>4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Ag$_2$Te</td>
<td>f.c.c.</td>
<td>6.57</td>
<td>8</td>
<td>24s</td>
<td></td>
</tr>
</tbody>
</table>

*4 are at tetrahedral sites and the remaining mixed conductor is 179°C. 4 distributed are 20 positions 3-, 4- and 6-coordinated.
(1.5) **Superionic phase transitions**

It has been found during the electrical conductivity vs temperature studies for most superionic solids that the high ionic conductivity is attained only after the material has undergone some phase transition. Two typical examples are given in figure (1.2) for RbAg$_4$I$_5$ and AgI. It is seen that at $T_1$ the conductivity rises by order of magnitude. This transition is referred to as Class I (or Insulator-Electrolyte phase transition). The values of $T_1$ for RbAg$_4$I$_5$ and AgI respectively are $-151^\circ$C and $147^\circ$C. There is yet another type of transition in which the conductivity does not change rapidly but at the transition only the slope of $\sigma$ vs $\frac{1}{T}$ curve changes. The temperature $T_2$ ($=64^\circ$C) marked in Figure 1.2 for RbAg$_4$I$_5$ refers to such a transition. Many theories have been put forward to account for the above two types of transitions outlined below.

A phenomenological model was proposed almost simultaneously in 1974 by Huberman$^{18}$ and Rice, Strassler and Toombs$^{19}$ (hereafter referred as RST model). Welch & Dienes$^{24}$ have suggested a general phenomenological model of which Huberman's and RST models come out as a special case. It is well known that the ionic conductivity depends upon the number of Frankel or Schottky defect pairs which is an exponential function of the activation energy for their formation. In
Fig 1.2: Electrical conductivity of RbAg₄I₅ and AgI as a function of temperature showing the variation of conductivity at phase transition. At T₁, the conductivity changes abruptly while at T₂, the change is slow and only the slope changes.
the phenomenological models, it is assumed that the activation energy for formation is concentration dependent due to defect interactions. Without going into the details of defect interaction, Welch & Diens\textsuperscript{24} wrote the concentration (c) dependent term for free energy per ion, F(c), as under:

\[ F(c) = E(c) - kT \left\{ -2c \ln c - (1-c) \ln (1-c) \right\} \]

\[ \left( \alpha - c \right) \ln \left( \alpha - c \right) \alpha \ln \left( \alpha \right) - TS_{vib}(c) \] \hspace{1cm} (1.10)

Where E(c),

is the concentration dependent energy required for pushing an atom into an interstitial site;

\( \alpha \) is the ratio of number of interstitial "cells" to the number of ions;

\( S_{vib} \) is the vibrational contribution to the entropy.

Welch & Diens\textsuperscript{24} considered two approximate forms for \( E(c) \). In the 'Quadratic form',

\[ E(c) = E_1 c - E_2 c^2 \]

or, \( \frac{\partial E(c)}{\partial c} = E_1 - 2E_2 c \)

and, \( S_{vib}(c) = \Delta S_1 c - \Delta S_2 c^2 \) \hspace{1cm} \text{ (1.11)}

In this approximation, Welch & Dienes model reduces to Huberman or RST models. Welch & Dienes formulation is quite arbitrary while Huberman & RST arrived at their equations using a physical model for defect interaction. Huberman assumed an 'attractive interaction' between an interstitial ion and a vacancy while RST considered the
interaction of interstitial cation defects with the strain field they induce.

One more form of $K(c)$ other than equation 1.11 has been taken by Selch & Dienes which is based on 'Wott-Littleton type' calculations. This is given as,

$$
\frac{\partial E}{\partial c} = E_1(1-2E_2c) - \beta c \left[ 1 - (1+c)^{1/2} \right] c^2
$$

(1.12)

The equilibrium defect concentration (on whose number the conductivity depends) can be obtained by minimising $F(c)$ with respect to $c$, i.e.

$$
\frac{\partial F(c)}{\partial c} = 0
$$

where $F(c)$ is given by equation 1.10 under approximation of equation 1.11 or equation 1.12. Theoretical calculations show that both class I (Temperature $T_1$ of Fig. 1.2) or class II (Temperature $T_2$ of Fig. 1.2) transitions can be simulated by taking different strength of interaction terms (i.e. values of $E_1$, $E_2$, etc.).

Lattice gas theories form another approach to understand the superionic phase transition. In these theories it is assumed that the mobile ions within the superionic solids can be considered as a 'lattice-gas' hopping from one lattice point to another. The hopping 'lattice-gas' particles interact with each other and modify
the ion diffusion or transport activation energy. This is referred to as 'cooperative hopping' of interacting ions. Sato & Kikuchi\textsuperscript{26} did first statistical calculation for $\beta$-alumina using the Path Probability Method. More recently Murch & Thorn\textsuperscript{27} reported the above calculation using a Monte Carlo Method. Both the above calculations could simulate class II type phase transitions successfully.

Another interesting approach has been suggested by Parde\textsuperscript{a} & Mehan\textsuperscript{20} and Mehan\textsuperscript{21} which is referred as Ionic Polaron Theory. It is considered that an ion polarises the host crystal, and when hopping must carry this polarising cloud with it called 'ionic polaron'. This is similar to the theory of conduction by hopping electrons (small polaron) developed for metals and semiconductors. The ionic polaron interaction has been considered by Mehan\textsuperscript{21} quantum mechanically through explicit use of phonon co-ordinate and introducing coupling parameter for the coupling of ion hop to the surrounding lattice vibrations. Ionic polaron theory could also simulate class II transitions but fails to account for class I transitions.

(1.6) Dynamics of ion transport

The various microscopic theories proposed for the ion dynamics in superionic solids can broadly be classified as:
(1) Free-ion model
(2) Domain model
(3) Hopping or jump diffusion model

In free-ion model, it is assumed that an ion is thermally excited from a localised state to a state in which the ion moves translationally through the solid to another localised state. Historically, this was the first theory proposed by Rice & Roth\(^3\) but it is no more accepted (see Hase\(^2\)). It has been shown that it is not necessary to invoke 'free-ion theory' and the same results can be obtained by conventional 'hopping models'.

Van Gool\(^2\) and Van Gool & Bottelberghs\(^3\) have given a 'domain-model'. As pointed out earlier, the high conductivity in superionic solids is marked by low values of activations. There are two important possibilities for low values of activation energy: (a) cooperative jump of a number of ions as taken by Sato & Kikuchi\(^2\) or (b) movement of walls between domains of ordered configurations. The possibility (b) was considered by Van Gool et al\(^3\). In most superionic solids, the number of sites or lattice position is much larger than number of ions available. It is assumed that in one domain ions are occupying one type of positions while in an adjacent domain another set of positions is occupied. Considering the domain as a "defect", the energy per ion necessary to create the "defect" has been
found to be low in an idealised calculation by Van Cool et al.\textsuperscript{30} for $\beta$-alumina. This accounts for low activation energy of ion migration in them. So far, no experimental evidence has been reported either to prove or disprove 'domain model'.

It is now well recognised that deeper and new insight into fast diffusion in superionic conductors could be gained by investigating the full dynamics of ionic motion including the host lattice (see Chand	extsuperscript{1}, to be published). The first microscopic theory in this direction was attempted by Huberman and Sen\textsuperscript{31} in which the mobile ions are assumed to have two basic degrees of freedom (i) an oscillatory motion in the harmonic potential provided by the rigid lattice and (ii) a random-walk process through which they can diffuse throughout the crystal. The jump process was assumed as occurring "instantaneously" and being uncorrelated with the oscillatory motion. This theory could successfully predict the peak in conductivity at 60 cm\textsuperscript{-1} for $\beta$-alumina but detailed structure could not be explained. Recently in a series of papers from Brown Baveri Research Centre Group (Bruesch et al\textsuperscript{32}, Fulde et al\textsuperscript{33}, Zeller et al\textsuperscript{34}, Bruesch et al\textsuperscript{35}) have investigated the Brownian motion in a periodic lattice including the effects of polarisability of lattice and correlated jumps of ions relevant to the problem of superionic conductors.
Various physical mechanisms for diffusion are shown in Fig. 1.3. The physical jump diffusion model shown in Fig. 1.3(b) has been proposed by Clemen & Funke\textsuperscript{36}, Funke\textsuperscript{9} to explain the microwave conductivity data of superionic conductors. The ion jumps are characterised by a mean duration of the jumps ($\tau_1$) and a mean residence time ($\tau_0$). In classical jump diffusion $\tau_1 \ll \tau_0$ but for superionic solids the experimental results indicate that $\tau_1 \approx \tau_0$. So, a superposition of jump diffusion and a local type motion was considered by Clemen & Funke\textsuperscript{36} as a good first approximation. The concept developed by Clemen & Funke to understand physically the microwave conductivity data is interesting and deserves some mention though it does not give the microscopic detail of ion dynamics. During conductivity measurements, the applied electrical field is assumed to give rise to two effects referred to as "start effect" and "acceleration effect". The "start effect" can be visualised as in the conventional theory of conductivity of alkali halides. The electrical field slightly supports or hinders the 'start' of jumps in or against the instantaneously preferred direction. At low frequencies ($\tau_1 \ll \frac{1}{\omega}$) the phase of the field is practically constant while an ion is performing a jump giving a constant value of $-\omega \varepsilon(\omega)$ or $-\varepsilon(\omega)$ at low frequencies. At slightly higher frequencies, a cation starting jump with the help of the electrical field is still on its way while the field is already changing its sign and this would try to
(a) SIMPLE DIFFUSION IN LIQUID

(b) LOCAL MOTION + JUMP DIFFUSION
   \( T_0 \approx T_i \ll 10^{11} \text{ sec.} \)

(c) JUMP DIFFUSION \( T \ll T_0 \)

FIG. 13 VARIOUS POSSIBLE DIFFUSION MECHANISMS.
reverse the ion jump direction consequently leading to
decrease in conductivity. In the high frequency limit
$\tau_i \gg \frac{1}{\omega}$, the applied field changes its sign many
times during the flight of an ion and the overall conductivity tends to zero. This explains the decreasing experimental microwave conductivity with the increase in frequency but an "acceleration effect" has to be invoked to explain the conductivity peak $\sim 1 \text{ cm}^{-1}$. During flight of the ion, friction is expected because the coulomb interactions with the other moving cations cause rapid fluctuations of the local potentials. Funke\textsuperscript{9} assumed that the jump lengths of the ions are fixed, being given by the geometry of the anion lattice and not being affected by the electrical field. The jump distances being constant, the effect of acceleration or retardation of the moving ions by the field changes their times of flight but cannot give any contribution to $\mathcal{O}(0)$, as this does not change the jump rates.

The complex conductivity is given by,

$$\mathcal{O}(w) = q \cdot \hat{\mathcal{I}}(w,t)/(\varepsilon_0 e^{-i\omega t})$$

where $\hat{\mathcal{I}}$ is the complex ionic flux in the direction of the electric field $E_0 \exp(-i\omega t)$. Clemens and Funke\textsuperscript{36} gave a detailed expression for $\mathcal{I} = \mathcal{I}_{\text{start}} + \mathcal{I}_{\text{accel}}$. The flux $\mathcal{I}_{\text{start}}$ was a function of change in ion number densities.
while \( I_{\text{accel}} \) depend upon velocity variation at different times. The calculated values have a good fit with experimental data confirming that the jump diffusion model superimposed by local motion is a good phenomenological description of ion dynamics in superionic conductors.
References


