Part D : Experimental
Experimental determination of ionic conductivity of pure, Mg-doped and Al doped NaCl crystals and determination of different defect energies from the conductivity plots.
9.1 Introduction

Electrolytic conductivity has furnished the key, for understanding the basic disorder in the alkali halides. Defect formation energies, such as, Schottky pair formation energy, migration and activation energies of cation diffusion, solution enthalpy of divalent cation defect and impurity-vacancy association energy have been extensively studied by means of ionic conductivity and self diffusion measurements. There is a relation between the ionic conductivity \( \sigma \) and the self diffusion coefficient \( D \) as follows

\[
\frac{\sigma}{D} = \frac{N e^2}{kT}
\]

where \( N \) is the number of cation vacancy per unit volume of the crystal.

This is known as Einstein equation or Wannier-Einstein equation.

There are enough measurements of electrical conductivities of alkali halide crystals, pure and doped with divalent impurities, and calculation of defect energies of divalent defects (Ca\(^{2+}\), Mg\(^{2+}\), Cd\(^{2+}\), Sr\(^{2+}\)) in NaCl type alkali halides from the conductivity plots. On the other hand there are a few experiments with trivalent defects in alkali halides. The reason may be (i) the difficulty in preparing these systems because of large ionic radii of the defects and (ii) the large charge compensation involved. Also according to some early calculations, trivalent impurity ions may not be very common in NaCl or KCl. However, recent experimental evidences suggest that trivalent impurities can be doped in NaCl type alkali halides. There is also no theoretical calculation of the defect properties with trivalent impurities in alkali halide crystals. In this thesis, in Chapter 6, one method
of theoretical calculation of defect energies of trivalent impurities in alkali halides has been discussed and also in Chapter 3 the substitution energies and solution enthalpies of trivalent defect in NaCl type alkali halides have been calculated and explained from the physical point of view. One experimental datum has only been found in the work of Benier and Bokhani \[125\] and this is not far from corresponding theoretical value calculated by us. So calculation of these theoretical values in this thesis, needs also the experimental determination of some trivalent defect energies in alkali halides.

Again chemical analysis of pure NaCl crystals (even Harshaw type) shows the predominance of Al as an impurity. Also it has already been suggested that the presence of such impurities (Al\(^{3+}\) or Fe\(^{3+}\)) could be responsible for the anomalous self-diffusion of the cation in the extrinsic range of the undoped sample \[115, 125\]. The ionic radius of Al\(^{3+}\), being equal to 0.051 nm is very small compared to both Na\(^{+}\) (0.12 nm) and Cl\(^{-}\) (0.162 nm) ions in NaCl crystal. Thus it is a point to study the behaviour of Al doped NaCl- type alkali halide crystals experimentally. Such experiment may also reveal the charge nature of the defect ions. So it was decided to measure the ionic conductivities of different concentrations of Al doped NaCl crystals and to evaluate some defect energies like, Schottky defect formation energy and migration energy and activation energy of Al defect in NaCl crystal from the conductivity plots.

In this chapter the experimental measurements of conductivities of Al-doped NaCl crystal of different concentrations, and determination of some defect energies from the conductivity plots are discussed. For the purpose of comparison, the conductivities of pure and Mg\(^{2+}\) doped NaCl crystals also have
been measured, and the corresponding conductivity plots and evaluation of
defect energies from the plots are also discussed in this chapter.

9.2 Theory

Any dielectric material corresponds in its electrical behaviour to a
capacitor connected parallel by a resistor. Therefore, when a dielectric
material is placed in an a.c. circuit within two parallel plates the total
current traversing through it is

\[ I = I_c + I_R \]
\[ = (i\omega c + G) V \quad \ldots \quad (9.2) \]

where \( G \) is the conductance of the dielectric and \( V \) is the applied voltage
across it. The dissipation factor is given by

\[ D = \tan \phi = \frac{I_R}{I_c} = \frac{1}{\omega RC} \quad \ldots \quad (9.3) \]

Introducing a complex permittivity

\[ \varepsilon^* = \varepsilon' - i\varepsilon'' \]

the total current may be written as

\[ I = (i\omega \varepsilon' + \omega \varepsilon'') \frac{Q_0}{\varepsilon_0} V \quad \ldots \quad (9.4) \]

where \( Q_0 \) is the capacity in air medium and \( \varepsilon_0 \) is the dielectric constant in
vacuum.

If \( J \) be the current density flowing through the polarised crystal
under the action of a field \( E \), the complex dielectric constant will be found
from eqn (9.4) as below
The applied field strength \( \mathbf{F} \) is given by

\[
\mathbf{F} = \frac{\varepsilon''}{\varepsilon'} \mathbf{D} = \frac{\varepsilon''}{\varepsilon'} \mathbf{E} \exp \left( i \omega t \right) 
\]

where \( \varepsilon'' \) is the dielectric loss factor. In eqn (9.5), the complex representation has been used for both \( \mathbf{F} \) and \( \mathbf{J} \) and

\[
\mathbf{F} = \mathbf{E} \exp \left( i \omega t \right) \]

The loss angle is now given by

\[
\tan \delta = \text{Dissipation factor} \quad \tan \delta = -\frac{\varepsilon''}{\varepsilon'} \quad \text{... (9.7)}
\]

As the contribution of the unassociated and the associated defects to \( \tan \delta \) is additive, the part of the current density not due to dipolar complexes is

\[
\mathbf{J}_u = \sigma \mathbf{E} \exp \left( i \omega t \right) = \frac{\omega \varepsilon''}{4 \kappa} \mathbf{E} \exp \left( i \omega t \right) \quad \text{... (9.8)}
\]

Therefore

\[
\sigma = \frac{\varepsilon''}{4 \kappa} \quad \text{... (9.9)}
\]

Elimination of \( \varepsilon'' \) from equation (9.7) and (9.9) gives

\[
\sigma = \frac{\varepsilon''}{4 \kappa} \quad \text{... (9.10)}
\]

For a parallel plate condenser the capacitance is given by

\[
c = \frac{\varepsilon'}{4 \kappa} \quad \text{... (9.11)}
\]

where \( A \) is the surface area of the dielectric and \( d \) is its thickness. From equation (9.10) and (9.11)

\[
\sigma = \frac{\varepsilon''}{4 \kappa} \cdot \frac{d}{A} \cdot c_d \quad \text{... (9.12)}
\]
Conductivity of the sample, by the bridge measurement method, has been obtained with the help of this formula.

9.3 Experimental Apparatus

(a) Crystal growing unit:

The alkali halide crystals, pure and doped, were grown by Czochralski method. The schematic diagram of the apparatus used for growing the crystals are shown in Fig. 9.1. F is the cylindrical vertical furnace having a cylindrical space of diameter 12 cm and height 30 cm, where in the middle position a platinum crucible (P) having upper end dia 7 cm, bottom dia 4 cm and height 6 cm is kept with the charge material. Within this space a continuous flow of Argon gas is maintained through a quartz tube, Q. The source of heating the furnace is a resistance (cathode wire) winding. The temperature of the furnace is controlled manually by means of a variac through voltage change. The furnace is enclosed by a radiation shield. R is the pull rod with a chuck arrangement to hold the crystal seed at its lower end. This rod is water cooled by passing water through pipes I & O and is positioned above the crucible and is rotated by means of a clock motor (C) with a speed of 60 rev/min. P₁, P₂ and P₃ are three pulleys which are connected with the pull rod and a dragging unit (D) by means of a flexible and nonextensible metal chord, M. The speed of the dragging unit is controlled by suitable use of the gear system. Temperature of the material in the crucible is noted by a Pt-Pt thermocouple T. S is a scale used to note the length of the growing crystal.

(b) Balance: A common balance was used to weigh the charge material and a single pan semi-microbalance of 'Adeco Dhama type', having resolutions 0.00001
Fig. 9.1 - A sketch of crystal growing unit.
ga was used to weigh the solute.

(o) Arrangement for annealing: Annealing of the sample was done in a horizontal furnace, F (Fig. 9.2) prepared by Laksan Industries of Calcutta, having 45 cm length and a heating space of 5 cm diameter. The temperature range of the furnace was up to 1200°C. The furnace is also provided with an arrangement to maintain a fixed temperature for any interval of time. Through the heating space of the furnace, a silica tube S' of length 50 cm. and dia 2.4 cm. is pushed. The samples, S, are placed on a quartz boat, B, and the boat is placed in the middle position of the silica tube, S'. The middle position of the silica tube is made to coincide with the middle position of the furnace and this position of the furnace is considered to be of constant temperature zone. The temperature of this position of the furnace is indicated by a dial reading by means of a thermocouple. Two ends of the silica tube are fitted with two glass circuits G₁ and G₂ to pass pure and dry nitrogen from a gas cylinder with the help of a flowmeter and a gas pipe.

(d) Conductivity cell and heating arrangement: It consists of two stainless steel electrodes of diameter 1.6 cm, E₁ and E₂ (Fig. 9.3) which form a parallel plate circular condenser. The specimen, S is placed in the space between them. In order to avoid the stray capacitances and disturbances from a.c. used in the heating coil of the furnace, a stainless steel cylinder, S'' is placed surrounding the electrodes as an electrical screen. This cylinder is earthed and kept insulated from the electrodes. Thus the capacity between the electrodes, when sample is not placed, is made only equal to that of the existing air gap between them. The whole system is placed within a cylindrical furnace, F of dia
Fig. 9.2 - A sketch of annealing set up
Fig. 9.3 - A sketch of conductivity measuring cell.
28 cm and height 24 cm with two faces open. A ceramic disk, C<sub>2</sub>, is fitted at the lower end of the furnace. The lower electrode of dia 1.6 cm and length 18 cm is then fixed at the central position of the disk, such that the upper end of the electrode remains at the central heating zone of the furnace. Allowance is given to the upper electrode, E<sub>1</sub> having same dimension to move up and down within the cylinder along its central line. Allowance was also made for its removal from the furnace. Removing the upper electrode from the system, the sample, S (alkali halide crystal having surface area nearly equal to 1 cm x 1 cm and thickness nearly equal to 1 mm with silver paint on two opposite surfaces) is placed on the lower electrode, E<sub>2</sub> with silver painted surface in contact with the electrode, with the help of a long forceps and then the upper electrode is placed on its another silver painted surface. It is fixed by giving a slight pressure on its top end by a spring S′ which is fixed with a stand, S′′. Electrical connections are done from both the lower and upper electrodes to a bridge (Badart 0.1 per cent universal bridge type 1204) or to a lock-in-Amplifier (model 124A), for the measurement of conductivity of the sample. Two calibrated crosem-alumel thermocouples of which only one, T has been shown in Fig. 9.3, are introduced within the screened cylinder with beads of couples very close to the sample. The thermo e.m.fs are measured by the common method of a potentiometer arrangement. The temperature of the furnace is controlled manually by varying voltage of the variac. Inert gas is flown in the cell by the stainless steel tube G.

(e) Temperature measurement arrangements: The temperature of the sample was measured by two thermocouples (crosem-alumel), placed on the two sides and very close to the sample within the conductivity measuring cell, Fig. 9.3. It
is obvious that if the thermal mass of the thermocouples is too large, it will influence the measurement of the temperature change in the sample. So, very small thermocouple wire of chromel-Alumel—one having 0.5 mm dia and another 0.75 mm dia were used. The temperature was determined from the measurement of thermo e.m.f.s of the two thermocouples and the calibration chart given by Procon Engineers of Calcutta. Thermo e.m.f.s of the thermocouples were measured by a potentiometer arrangement (OSAU slide wire potentiometer, cat. no 360068 of Oriental Science Apparatus Workshops, Ambala, India). The potentiometer was first calibrated with a standard cell (Weston cadmium cell). The dial readings (1 smallest div = 0.0002 volts) of the potentiometer which give the null point of a galvanometer (spot galvanometer) denote the thermo e.m.f.s.

(f) Conductivity measuring instruments:

(i) "Radart" 0.1 per cent universal bridge type 1204.

This bridge is a general purpose impedance bridge with 0.1 per cent measurement accuracy over a wide range of inductance, capacitance and resistance values. It offers exceptional discrimination and resettability, wide range loss balancing and facilities for using an external oscillator and a detector. A front panel view of the bridge is given in Fig. 9.4.

For L, C and R measurements, the balance control comprises of a coarse balance, displayed in digits x 1 and x 0.1 through windows on the front panel, and a fine balance having calibrated dial to give required x 0.1 decade covers the one step of x 1 control and x 0.1 fine dial continuously covers one step of 0.1 with some overlap. The variable and non-linear sensitivity of the detector facilitates easy measurement of completely unknown components. An external audio
oscillator can be plugged in where L and C measurements are required at frequencies other than the internally provided 1 kHz and 10 kHz. The detector output is available externally to allow an oscilloscope to be used for balance indication.

A.C. conductivity of a sample can be measured by the bridge on measuring capacity and loss of the system.

The bridge measures the resistive and capacitive components of a capacitor as a series network when the D-Q switch is set to D and as a parallel network when set to Q. The equivalent parallel ($C_p$) and series ($C_s$) capacitance are related by the expressions,

$$C_p = \frac{C_s}{1+D^2} \quad \ldots \ (9.13)$$

and

$$C_s = \frac{1+Q^2}{Q^2} \cdot C_p \quad \ldots \ (9.14)$$

where $D = \frac{1}{Q}$ is the dissipation factor and $Q$ is the loss factor. From the value of $C_p$ and $D$ the conductivity $\sigma$ of the samples are calculated from eqn. 9.12. Thus using this bridge the dissipation factor $D$ and capacity $C_p$ of a sample and hence the conductivity of the sample can be measured.

(ii) **Lock-in Amplifier model 124 A** (make EG & G TAFC)

The r.m.s. amplitude and phase of weak signals buried in noise signals in the range of picovolts up to 500 millivolts, and frequencies from 0.2 Hz to 210 kHz can be measured quickly and precisely. Voltage outputs are provided for the amplitude and the phase of the signal may be read from a dial. A front panel
Fig 9.5
Model 124A
Precision Lock-In Amplifier
view is given in Fig. 9.5. These measurements are with reference to a synchronizing signal supplied to or supplied by, the model 124A. In either of the external f or external f/2 mode of operation, the instrument will accept any reference waveform that crosses its mean twice each cycle and will lock to and track that signal over a 100:1 frequency range. In the internal mode the frequency is determined by front-panel dials or by an externally derived voltage.

A selection of plug-in-preamplifiers is available for providing optimum low-noise performance over a wide range of input frequencies and source resistances. After preamplification, noise and harmonics accompanying the signal are attenuated in the signal channel by filtering out all frequencies except the band in which the signal lies. Flat, band pass, band rejected high pass and low pass filtering modes may be selected. The remaining band of frequencies is converted to an equivalent band width about d.c. by a synchronous detector which is locked to the synchronizing signal. A low pass filter eliminates frequency components about d.c., so that the detector output is a d.c. voltage proportional to the in phase component of the fundamental signal. Proper selection of signal channel and output channel filtering parameters can render the final noise bandwidth extremely narrow. The r.m.s. value of the fundamental signal is indicated on the panel meter when the synchronous detection phase is adjusted for maximum detector output. A switch is provided that allows drift to be traded for dynamic reserve. In addition an output d.c. off set feature is provided to allow higher sensitivity settings for relatively steady signals. These features permit selection of the optimum operating mode for each experimental situation.

Other design features include selection of output filter time constants
1 ms to 300 sec, optional digital panel meter with BCD output, a built-in calibrator and independent use of the phase-lockable oscillator and tuned amplifier for general purpose laboratory work. The model 124A may also be used as a conventional wideband laboratory voltmeter.

The input impedance of the lock-in-amplifier depends on the preamplifier used. With the preamplifiers available at our disposal, the maximum impedance offered at the input of the lock-in-amplifier is about 100 MΩ. It is found that beyond resistances of the order of few megohms, the measurement with the apparatus becomes unreliable for precision measurement. Measurements of impedance in the higher range are therefore not considered with lock-in-amplifier.

The real and imaginary components of an a.c. waveform are defined with respect to source reference waveform. The real component is in phase with the reference waveform and the imaginary component also referred to as the "quadrature component" is exactly 90° out of phase.

An a.c. supply from an oscillator through a step down transformer is given to the sample, taking the sample within the conductivity measuring cell, with a standard resistance, r(= 1 ω) in series. The voltage across the sample was measured with respect to reference voltage from the same oscillator directly. The voltage was found exactly 90° out of phase with the reference voltage.

Then the voltage (V2) across the resistance r was measured in phase with, and 90° out of phase with V1. The component of the current in phase with the supply voltage is given by

\[ I' = \frac{E'2}{r} \]

... (9.15)
and the component of the current 90° out of phase with the supply voltage is given by

\[ I'' = \frac{E_2'}{r} \]  \hspace{1cm} (9.16)

where \( E_2' \) and \( E_2'' \) are the inphase and 90° out of phase components of voltage \( E_2 \).

In electrical behaviour, an ionic crystal can be regarded as a parallel combination of a capacitive and a resistive part. The current through the resistive part is \( I' \) and the resistance is given by

\[ R = \frac{E'}{I'} = \frac{E_2'}{E_2''} \]  \hspace{1cm} (9.17)

Therefore

\[ \sigma = \left( \frac{A}{d} \right)^{-1} \left( \frac{A}{E_2''} \cdot \frac{E_1}{E_2''} \cdot r \right)^{-1} \]  \hspace{1cm} (9.13)

Thus the conductivity of the sample can be obtained by the lock-in-amplifier.

iii) Oscilloscope:

One oscilloscope of 'systronics 5053' was used sometimes for balance indication with the bridge measurements and also to obtain a lock in condition in lock-in-amplifier.

iv) Oscillator:

An external oscillator of Hadart (type 2142) having frequency range 20 Hz to 2000Hz was also used to provide the supply voltage across the sample in the case of measurements with lock-in-amplifier and also in the case of measurements with bridge at different frequencies provided by the inner oscillator of the bridge (i.e., 1 kHz and 10 kHz).
(g) Apparatus for colour center test:

(i) X-ray generator

For the purpose of irradiation of the crystals, X-rays from a 4 window 1.5 kW X-ray generator (Make: Radha House, India) working at 30 kV and 10 mA were used.

(ii) U.V. Spectrometer: Absorption was measured by a UV spectrometer of Hitachi model 200-20.

9.4 Experimental Procedure

Single crystals of pure and doped (Mg and Al) NaCl were grown in the laboratory from the melt of E-Merck CR sodium chloride (99.5 per cent pure and containing many nonvalent and divalent impurities) by the czeochralski method under an inert atmosphere of Argon using a platinum crucible. As a divalent impurity, weighed amount of magnesium was added in the form of anhydrous chloride to the weighted charge. Anhydrous magnesium chloride was prepared in the laboratory just before the addition to the charge material, from the hydrous magnesium chloride (MgCl₂, 6H₂O). The hydrous magnesium chloride is mixed with equimolecular amounts of analar grade ammonium chloride. A solution of the mixture was made in double distilled water. The solution was concentrated by boiling and then cooled. Double salt of MgCl₂, NH₄Cl, H₂O was crystallised and filtered. On heating this double salt to dryness, anhydrous magnesium chloride was prepared.

\[
\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O} \xrightarrow{\text{Heat}} \text{MgCl}_2 + \text{NH}_4\text{Cl} \uparrow + 6\text{H}_2\text{O} \uparrow
\]
Confirmation tests for both magnesium and chloride were also made before mixed with charge material.

Aluminium chloride has a melting point of 190°C at a pressure of 2.5 at atmospheric and sublimates at 177.3°C under normal atmospheric pressure. So the normal method of mixing the elements and melting does not give Al-doped NaCl crystal.

To prepare aluminium doped crystals, anhydrous aluminium chloride, in finely powdered form was weighted and poured in the charge material (pure sodium chloride) in the molten state and stirred by a quartz rod as soon as possible. Thus, some amount of AlCl₃ before sublimation may mix with the molten NaCl and form solid solutions. A solid solution of aluminium chloride in sodium chloride was thus prepared.

The charge material was maintained at a temperature just above its melting point adjusting the temperature of the furnace through adjustment of the voltage of the variac. A seed crystal of dimension 0.3 cm x 0.4 cm x 2 cm were chosen. The small cross-sectional area of the seed crystal helps to reduce dislocation that originates from the seed crystal. The seed with (100) face horizontal was then attached to the end of the pulling rod by means of a chuck arrangement and dipped into the melt. The rotation (60 rev/min) of the pull rod was started. The flow of water through the pull rod was first kept slow, so that a small part of the seed was melted off. This produces a good solid to liquid contact and thus helps to prevent the formation of unwanted dislocations and twinned structures. After insertion of the seed, the input power to the furnace and the rate of flow of water through the pull rod were adjusted, until
growth was started. The diameter of the growing crystal was then gradually allowed to increase from that of the seed crystal upto about 4 cm to 5 cm dia. The pulling was then started with a controlled rate such that the initial diameter of the growing crystal was maintained or a slight tapering was carried out gradually to avoid the generation of growth defects. The pulling rate was kept equal to the rate of growth of crystals and this was about 5 mm/hour. During normal growth of crystal a temperature gradient was applied across the growing interface between the liquid and the solid, such that heat flows from the melt to the crystal, where it is dissipated by conduction and radiation. A part of the heat escaped from the surface of the melt and from the crucible itself, by radiation to such thermal sinks as the furnace walls and the inert gas stream flowing through the heat chamber. At the same time, the latent heat of crystallisation was generated at the growing front. The rate at which the extra heat was dissipated governed the rate of growth of the crystal. To maintain the practical conditions of removing the latent heat and preserving the single crystal structure, the growth rate was restricted to very low value of the order of 5 mm/hour. The isothermal surface, constituting the liquid-solid interface was assumed to be at the melting point of the material. The conditions in the furnace were carefully controlled in such a way that this interface remained stationary throughout the growth of the crystal i.e., the pulling rate was equal to the growth rate. Under these circumstances, the heat input to the system was exactly balanced by the heat losses i.e., heat out. In this way about 4 cm to 5 cm diameter and 7 to 8 cm length crystals were grown in the laboratory.

The surface of these crystals were marked with very fine circular
ridges of unequal growth. These were formed due to oscillation between the hotter and cooler parts of the furnace, for unsymmetrically centered specimens or by periodic changes in the thermal pattern, caused by variations in the power input or the flow of gas. The crystals of circular diameter were formed due to surface tensional forces. These surface tensional forces might be overcome by using high speed in the rotation of the pulling rod. But in this process the melt might become super cooled. The rotation helped to stir the melt and to ensure a more homogeneous distribution of the doping impurities and it tended to reduce the radial temp. gradients at the growing interface, and hence, to minimise thermal asymmetries.

The labgrown single crystal (pure and doped) was then cleaved into cubes, approximately of size 1 cm x 1 cm x 0.1 cm, from regions of good cleavage in the lower third of the ingot. The cleaved crystals were then separately set on a quartz boat and placed inside the silica tube in the annealing furnace, Fig. 9.2. The furnace was switched on and very pure and dry nitrogen named lolar 2 nitrogen (analytical reagent grade) was passed through the silica tube containing the boat with samples. The temperature of the furnace was increased slowly (6°C/min) to 750°C. The temperature of the furnace was then kept constant at 750°C for an hour and then decreased to room temperature very slowly (3°C/min.). Thus the samples were annealed. This process helps to dissolve any dislocations that may be formed during the growth process.

The two opposite faces (1 cm x 1 cm) were then painted with silver paint carefully, so that, no other faces were attacked by the paint. The painting of the samples were done in an airconditioned room just before the measure-
ments. After nearly half an hour the sample was dried. The area and thickness of the sample was measured accurately by a travelling microscope.

The electrodes were cleaned before starting every experiment. The silver painted sample was then placed within the cleaned electrode of the conductivity measuring cell. Argon gas (standard 1) was flown through the cell and the temperature of the surrounding furnace was increased slowly (6°C/min) to nearly 250°C. The temperature of the furnace was then made steady at the temperature for half an hour and then capacity loss of the system was measured by the a.c. bridge, Fig. 9.6. The real and quadrature components of the voltage across the sample and of the current through it were also measured by the lock-in-amplifier, Fig. 9.7. Readings of this temperature were taken from the thermocouples from the measurements of their o.m.f. by the potentiometer arrangement. The temperature was then increased slowly by nearly 25°C and again made steady for half an hour. The reading of the temperature, capacity and loss were again taken. The procedure was repeated until the temperature of the sample attains nearly 730°C. The temperature of the furnace was then decreased slowly to room temperature. The whole procedure was repeated with another two samples from the same ingot (i.e., with the same concentration of same type of impurity). Again the whole procedure was repeated with samples from different ingots (containing different concentration of Al impurity for Al-doped NaCl sample, pure NaCl and Mg-doped NaCl samples). Some annealed samples were coloured by irradiating in X-rays for half an hour and then colour centers were also measured by measuring absorption in spectrometer both in visible and ultraviolet ranges.)
Fig. 9.6 - A block diagram for conductivity measurement at different temperature by a Bridge.
Fig. 9.7 — A block diagram for conductivity measurement at different temperature by an lock-in-Amplifier.
9.5 Calculations:

(a) Determination of mol. percent of the defect

mol. percent of an impurity is defined as,

\[
\text{mol. percent of impurity} = \frac{\text{amount of impurity in g}}{\text{molecular weight of the impurity}} \times \frac{\text{amount of solvent in g}}{\text{molecular weight of the solvent}} + \frac{\text{amount of impurity in g}}{\text{molecular weight of impurity}}
\]

(b) Determination of conductivity:

Calculation of conductivities of different samples at different temperatures were done using eqn. (9.12) in the bridge method and eqn. (9.13) in the lock in Amplifier method.

9.6 Experimental results

From the weight of AlCl\textsubscript{3} added to the weight of \textit{NaCl} the concentrations of the impurity ions in NaCl crystals were estimated to be around 0.003, 0.012 and 0.015 mol per cent. The amount of actual aluminium ions incorporated in the lattice may be lower than this. All the defect crystals were transparent and no absorption (when compared to a pure crystal) was found in the visible region, while in the UV region one absorption peak was observed around 190 nm for all the three defect crystals, the absorption wave lengths slightly changing for the three different doped crystals. Similarly, the magnesium doped crystals having defect concentration 0.007 mole per cent was found to be transparent and
only one absorption peak was found in the UV around 190 nm. These absorption peaks in the UV region proved qualitatively the existence of the defects in NaCl crystals [121].

The measurement of absorption of the irradiated Al-doped crystals showed that the peak height and half-width of the absorption curve were due to V-centre and number of V centres, increased substantially from pure to both Al and Mg doped crystals.

For every defect concentration, conductivity was measured with three different samples cleaved from the different regions of a defect crystal. Separate curves of \( \lg(\sigma T) \) vs \( 10^3/T \) were drawn for the three samples and it was seen that all the curves were similar. This proved beyond doubt the reproducibility of the conductivity values. Observed values of \( \lg(\sigma T) \) as a function of \( 10^3/T \) were shown in Fig. 9.3 for all the five crystals— one pure, one Mg-doped and three crystals with different amounts of Al doping. The F. Merck CR grade sodium chloride crystal contained 40 ppm of various divalent defects. So all this experimental specimens contained this impurity as a background. The conductivity plots for pure crystal (curve 2 in Fig. 9.3) agreed quite well with other values obtained from BDH anar sodium chloride [121].

As expected theoretically, the conductivity plots in the intrinsic region (known as region I) is a straight line for all the samples having different concentrations of Al and Mg and also for the pure crystal and its slope yields a value of \( E_I = E_F + \frac{E_S}{2} \) where \( E_I \) is the activation energy in the intrinsic region, \( E_F \) is the energy of formation of a separated pair of Schottky pair.
Fig. 9.8 - Observed plots of $\lg (\sigma T)$ as a function of $10^3/T$ for pure and doped sodium chloride crystals. (1) The plot for NaCl - Mg$^{2+}$ (0.007 mol per cent), (2) the plot for E. Merck NaCl pure crystal, (3) to (5) are the plots of NaCl doped with different concentrations of aluminium 0.008, 0.012 and 0.015 mol per cent respectively.
vacancies and \( E_m \) is the energy of activation of migration for the cation vacancy in the extrinsic region (known as region II). The value of \( E_T \) is found to be 2.117 eV.

The effect of adding impurity (both Al and Mg) can be seen by studying the conductivity curves in region II which is known as the region controlled by impurity. The slope of all the curves in this region is nearly the same, slightly varying for the different systems. Combining this value of \( E_m \) with the value of \( E_T \) obtained from region I, we find \( E_g = 2.65 \text{ eV} \) and \( E_m = 0.80 \text{ eV}, 0.31 \text{ eV}, \) and \( 0.87 \text{ eV} \) for the three Al-doped crystals having defect concentrations \( 0.008, 0.012 \text{ and } 0.015 \text{ mol per cent respectively } \) (curves 3, 4 and 5 in Fig. 9,8).

The value of \( E_g \) for pure and Mg-doped crystal 2 & 1) is \( 0.79 \text{ eV} \) and \( 0.83 \text{ eV} \) respectively. However, the conductivity of the Al-doped crystals comes out to be less than the values for the pure crystals in this region. Furthermore, the plot in the \( \lg (\sigma T) Vs \frac{1}{T} \) curve decreases with increase of the donor concentration of Al in NaCl. From Fig. 9,8 it is found that the knee of the conductivity curve occurs at a higher temperature for the crystals having lesser concentration of impurity ions- a behaviour opposite in nature to that found with divalent ions. Thus, it can be said, as the amount of Al in NaCl increases, the conductivity decreases. To check whether it was a deficiency of this experimental arrangement that conductivity values higher than those of pure crystals could not be obtained, the conductivity of a Mg doped NaCl crystal was measured and it was found that the plots for NaCl-Mg\(^{2+}\) lie above the line for pure crystal. Thus it is found that conductivity of Mg-doped NaCl crystal is higher than that of pure crystal whereas, the conductivity of Al-doped NaCl crystals are lower than those of pure crystals. For the purpose of checking these findings
and comparing the values so obtained from bridge measurements, the lock-in-amplifier was utilised for measuring the conductivities of these systems. The readings taken by the bridge measurements and lock-in-amplifier were simultaneous i.e., when a sample was kept fixed at a particular temperature then its reading was taken first by the bridge measurements and next by the lock-in-amplifier and then the temperature was changed to another value. In region I, the conductivities obtained by the lock-in-amplifier exactly coincided with the values obtained from the bridge measurements. With the lock-in-amplifier the conductivity values of the samples could not be obtained throughout region II but it was found to agree with the behaviour as revealed by the bridge measurements up to 440°C only thus confirming that the slope was the same for all the samples and that the conductivities of the Al-doped crystals were less than those of the pure crystals, decreasing more with increasing dopant concentrations.

At the end of region II, the slope of the curves again changes, but it does not seem that this change arises from the starting of region III, whose energy $E_{III}$ would give the association energy for the vacancy-doped impurity complex where $E_{III} = E_a + \frac{E_g}{2}$, $E_a$ being the association energy for the vacancy impurity complex. Rather, it seems that the activation energy obtained from this region gives the association energy between different vacancy complexes and the background impurity ions present in the pure solid. The reason is that $E_a$, calculated from this region, gives nearly same values for the pure and the Al-doped crystals which are equal to 0.66 eV and 0.63 eV, 0.61 eV and 0.53 eV considering the crystals in the increasing order of dopant concentrations. For Mg-doped crystal, its value comes out to be 0.37 eV which may give the association energy.
between the cation vacancy and the doped Mg ion and the other background ions.

9.7 Discussion

From the conductivity curves in Fig. 9.3, it is seen that the conductivity of Al-doped and Mg-doped NaCl crystals agrees quite well with the values of the pure crystal, in the high temperature region, thereby confirming the general result that in the high temperature intrinsic region, it is the Schottky pair vacancies which are responsible for the conduction in this type of ionic crystal. The activation energy $E_a$ is found to be 2.65 eV, while Rowell and Sangster [85] have given the theoretical value to be 2.53 eV and experimental value lying over a range of $2.20 - 2.75$ eV. In this thesis also the Schottky defect formation energy for NaCl lattice has been calculated in Chapter 5 and is found to be 2.55 eV. Thus it can be said that this experimental value agrees well with other theoretical and experimental values. Also for pure NaCl crystal, the values of $E_a$ comes out to be 0.79 eV which is very similar to the theoretical values 0.72 eV calculated in Chapter 5 of this thesis.

To explain the region II of the conductivity curves of Al doped NaCl crystals, two possibilities that might occur when Al enters a NaCl crystal are given.

First possibility: When anhydrous aluminium chloride is mixed with the melt of NaCl and single crystals are pulled, Al enters the NaCl crystal substitutionally as a triply charged ion. As a result two extra cation vacancies are created (Fig. 9.9). The possible sites from where two $Na^+$ ions will be removed are the twelve next-nearest-neighbour-sites ($A$, $B$, $C$, $D$, etc.) of the central
defect \( \text{Al}^{3+} \) ion. The two cation vacancies at A and B will have effective negative charge and they will be attracted towards the defect \( \text{Al}^{3+} \) ion. From the behaviour of divalent doped \( \text{NaCl} \) crystal, it is natural that the conductivity of \( \text{Al}^{3+} \) doped \( \text{NaCl} \) crystal would increase more than that of the divalent-doped crystal, for here the number of cation vacancies created is higher. For each \( \text{Al}^{3+} \) ion doped, two cation vacancies are created and conductivity would increase with the increase of cation vacancies. \( \text{Itzel and Maurer} \) \( [113] \) from their observation that the increase in \( \sigma \) of \( \text{NaCl} \) containing \( \text{CdCl}_2 \) was not quite proportional to the amount of \( \text{CdCl}_2 \) added suggested that a small degree of association between the divalent ion and the vacancy might be responsible for the decrease. \( \text{Seitz} \) \( [115] \) mentioned that \( \text{Lidiard} \) had given a simple expression for finding the association energy between a divalent ion and a vacancy which was equal to \( \frac{e^2}{E_{\text{p}}} \) where \( e \) was the excess charge, \( K_s \) was the static dielectric constant and \( r \) was the separation which was restricted to the discrete values permitted by the lattice geometry. Taking \( K_s \) to be equal to 5.62, \( \text{Lidiard} \) calculated this association energy to be 0.6 eV. 

If we extend this expression for the case of a trivalent ion an impurity complex is obtained with the triply charged ion \( \text{Al}^{3+} \) at \( P \) and the two cation vacancies either (i) at A and B or (ii) at B and C (Fig. 9.9). The expression for the association energy for this trivalent ion-bivacency complex, including repulsion between the two cation vacancies, is:

\[
\begin{align*}
\varepsilon_a^\text{II} & = \frac{4e^2}{K_s \sqrt{2} r_0} - \frac{e^2}{K_p 2 r_0} \\
\text{for case I when the vacancies are formed at A and B}
\end{align*}
\]
Fig. 9.9 - The $\text{Al}^{3+}$ ion • in a substitutional position with a pair of created cation vacancies at A and B or at B and C.
Substituting proper values of $K_a$, $r_o$ etc., the association energy for the impurity complex comes out to be 2.114 eV or 2.25 eV for case I or case II respectively i.e., the average energy with which a cation vacancy remains associated with the triply charged ion becomes 1.057 eV or 1.125 eV as the case may be. The radius of $\text{Al}^{2+}$ ion is 0.051 nm - much smaller than that of the host ion - $\text{Na}^+$ (0.120 nm). The relaxation of the nearest neighbours will be greater for a defect of smaller radius and in case of $\text{Al}^{2+}$ ion, this relaxation is found in Chapter 6 to be 0.05 nm, Table 8.5. Considering this relaxation, the distance between the $\text{Al}^{2+}$ ion and the cation vacancies will change and considering these changes of distance, the association energy of the impurity-vacancy complex will be 2.32 eV or 2.47 eV for case I or case II respectively. That is considering the relaxations of the nearest neighbours, the average association energy of a cation vacancy with the triply charged $\text{Al}^{2+}$ ion increases and becomes 1.16 eV or 1.23 eV depending on the positions of the vacancies created. These values are nearly twice the corresponding value for a divalent ion and as such, it seems that this association energy may be sufficient in restricting the motion of the generated cation vacancies.

Second possibility: The second possibility is that $\text{Al}$ enters the $\text{NaCl}$ lattice as a triply charged ion and takes an interstitial position. Energetically the interstitial at the cube centre position is more favourable than that at the square centre position. Let us see, if this is geometrically possible. The radius
of a Na$^{+}$ ion is 0.120 nm and that of a Cl$^{-}$ ion is 0.162 nm, Table 4.1. The distance covered by a Na$^{+}$ ion and a Cl$^{-}$ ion along the body diagonal is 0.232 nm whereas the length of the body diagonal is $\sqrt{3}$ $r_0$ or 0.4334 nm, thereby keeping a hole of diameter 0.2064 nm where an Al$^{3+}$ ion takes a cube centre position, the neighbouring ions will be inwardly relaxed due to the strong electrostatic attraction. As a result, the available space at the centre of the cube will be decreased, but the relaxation may not be so high as to restrict the entry of a small Al$^{3+}$ ion having a radius of 0.05 nm only. But now the condition of charge neutrality requires the formation of three cation vacancies around the Al$^{3+}$ ion. The possible sites for these three cation vacancies are three of the four equivalent sites A, B, C, D in Fig. 9.10. The distances of these three cation vacancies from the cube centre position are equal and are equal to $\frac{\sqrt{3}}{2}$ $r_0$. Therefore, the expression for the association energy for this triply charged ion-trivacency complex, $E_{III}$, will be

$$E_{III} = \frac{9 e^2}{k_B \frac{\sqrt{3}}{2} r_0} - \frac{3 e^2}{k_B \sqrt{2} r_0}$$

$$= 7.51 \text{ eV}.$$ 

Therefore, the average association energy of a cation vacancy with the triply charged Al$^{3+}$ ion comes out to be 2.50 eV, nearly five times the value for a divalent ion - vacancy complex. Of course this association energy 2.50 eV will further increase when we consider the inward relaxations of the neighbouring ions and the cation vacancies. With such a large association energy, it may be possible for the created cation vacancies to remain associated with the triply
Fig. 9, 10 - The Al$^{3+}$ ion in an interstitial position with three created cation vacancies at A, B and C.
charged Al$^{2+}$ ion and hence the conductivity may be decreased for want of free and mobile cation vacancies.

However, even if all the created vacancies remain bound with the defect ion, then also, one cannot explain why the conductivity of the Al doped crystal would have less values than those for pure crystal. It is known, when cation defects are introduced in a NaCl crystal, the number of thermally produced cation and anion vacancies decreases. This fact was also pointed out by Etsel and Maurer [113] that the equilibrium concentration of positive ion vacancies in the impure crystal is less than the sum of the original concentration in the pure crystal and the concentration of the aliovalent impurity ion. Thus, as the number of trivalent defects increases in a NaCl crystal, the number of thermally produced cation and anion vacancies decreases from even the values found in the pure crystal. As ionic conductivity proceeds through cation vacancies, so for Al doped crystal, if the created extra cation vacancies remain bound, then as the number of thermally produced cation vacancies decreases, so the conductivity decreases with increased dopant concentration. But when a Mg$^{2+}$ ion enters NaCl lattice substitutionally, then also the number of thermally produced cation and anion vacancies decreases but as the extra created cation vacancies are free, so, the net effect is the increase in the number of mobile cation vacancies and as such conductivity of divalent doped crystals increases.

Deniere and Rehbani [125] experimentally obtained the conductivity of Y$^{3+}$ doped NaCl crystal, but their values were higher than the values for pure crystals. Y$^{3+}$ having a radius of 0.0393 nm is a larger ion and cannot possibly take an interstitial position. If Y$^{3+}$ occupies a substitutional position, then the associated vacancies may be loosely bound and with increase of temperature,
the created cation vacancies may be free and thus the conductivity may increase. Similarly the behaviour of Cr$^{3+}$ and Bi$^{3+}$ doped NaCl crystals can be explained on the basis of large ionic radii, though for these defect ions do not have inert gas configurations, rather, they contain relatively loosely bound electrons in the outermost shell. For Cr$^{3+}$, the energy of the outermost electrons in the d shell is $-0.65$ at. units (18 eV), while for Al$^{3+}$ it is $-3.52$ at. units (56 eV), for Y$^{3+}$ it is $-1.63$ at. units (44 eV) and even for Ba$^{+}$ it is $-1.79$ at. units (49 eV). Thus the behaviour may not be exactly same with that of trivalent or divalent defects having closed shell inert gas electron configurations.

Considering all aspects of the problem, it seems that due to very small ionic radius, Al$^{3+}$ might have been trapped in an interstitial position and thus the conductivity of aluminium doped NaCl is decreased.