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SELF DIFFUSION OF THE SODIUM ION IN PURE SODIUM CHLORIDE

Harry L. Downing, Jr.

June, 1964

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Department of Physics & Astronomy

THE UNIVERSITY OF KANSAS

Lawrence, Kansas

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Point Defects in Ionic Crystals

Robert J. Friauf
Principal Investigator

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I. INTRODUCTION

Electrical conductivity and self diffusion in the alkali halides are made possible by defects in the perfect crystal structure. These vacancy defects can be caused by thermal agitation or by the presence of divalent impurity ions in the lattice. Several proposed defects are shown in Figure 1. Theoretical work by Jost¹ and Mott and Littleton² has shown that the Schottky defect in the alkali halides is the most predominant defect. This has been confirmed by recent experimental work in NaCl by Mapother, Crooks and Maurer³; Bean⁴; Aschner⁵; and Laurance⁶. By comparing the work done by Maurer³ on self diffusion of the sodium atom to the work of Laurance⁶ on self diffusion of the chlorine atom, it is found that the positive ion vacancy contributes more to the diffusion and conductivity than the negative ion vacancy. In the low temperature region, the contribution of the negative ion vacancy can be neglected, but at the higher temperatures this contribution is considerable.

The temperature dependence of the self diffusion coefficient and electrical conductivity can be represented by⁷

$$D = D_0 \exp(-W/kT), \quad (1)$$

$$\sigma = \frac{\sigma_0}{T} \exp(-W/kT). \quad (2)$$

The quantities D and σ are the self diffusion coefficient and conductivity, D_0 and σ_0 are constants, and W is the activation energy.

The work by Maurer³ has shown that the conductivity and self diffusion curves for pure NaCl have well-defined high and low temperature regions. The high temperature region, above 550°C, has a greater slope, therefore, a larger activation energy. By adding divalent impurities to the crystal, it is possible to identify these two temperature regions. The high temperature region is not affected by the addition of impurities. The low temperature region, however, shows a dependence on the impurity concentration. Therefore at the lower temperatures the concentration of vacancies is proportional to the number of divalent impurities, whereas at the higher temperatures the concentration of thermally produced vacancies predominates. Therefore the activation energy in the high temperature region is given by $W = (U + E_f/2)$, whereas in the low temperature region the activation energy is simply $W = U$. U represents the activation energy for a jump of an ion into a vacancy, and E_f is the energy required to form a positive and a negative ion vacancy well separated from each other. Tables I and II give the actual values of the activation energies found experimentally and theoretically.

Since the electrical conductivity and the self diffusion are due to the same basic process, namely, motion of defects in the crystal lattice, a relationship should exist between the two. This is given by the Einstein relation⁷

$$\frac{D\sigma}{\sigma} = \frac{kT}{Nq^2}, \quad (3)$$

where σ is the conductivity, D_σ is the corresponding self diffusion coefficient, N is the concentration of atoms of charge q , k is the Boltzmann constant, and T is the absolute temperature. This relationship will be valid only if the conductivity and diffusion are produced by the same defect mechanism.

In the experimental procedure the electrical conductivity and the self diffusion are measured independently in order to test the Einstein relation. The conductivity σ is found by placing the crystal in an electric field and measuring the current. Then by using the above Einstein relation, an equivalent self diffusion coefficient D_σ is calculated. The self diffusion coefficient $D^*(\text{Na})$ is measured directly by using a radioactive tracer technique. When the values of these two independent measurements are compared by forming the ratio $f^*(\text{Na}) = D^*(\text{Na})/D_\sigma$, it is found that the above Einstein relation is only approximately satisfied.

There are several effects that may cause deviations from this relation. In the first place the measured conductivity has contributions from both the positive and negative ions; therefore, it is necessary to consider both sodium and chlorine diffusion in calculating the experimental correlation factor

$$f^* = \frac{D^*(\text{Na}) + D^*(\text{Cl})}{D_\sigma} \quad (4)$$

Also there are correlation effects between successive jumps of the tracer atoms; these effects reduce the self diffusion coefficients

$D^*(\text{Na})$ and $D^*(\text{Cl})$ but do not affect the self diffusion coefficient D_0 calculated from the observed conductivity. There may also be an electrically neutral defect complex, such as a vacancy pair or a divalent ion-vacancy complex (Figure 1), that would not contribute to the conductivity but would contribute to the diffusion. Therefore, by comparing the results of these two kinds of experimental measurements, it is possible to obtain information about the different types of defect motion.

The purpose of this present experiment is, then, to compare the two observed self diffusion coefficients D_0 and $D^*(\text{Na})$ for pure sodium chloride crystals. This experiment will be limited to the high temperature (intrinsic) region where the effect of impurities can be neglected. In this intrinsic region only two types of defect mechanisms are expected to occur: (1) separated positive and negative vacancies, (2) vacancy-pair complexes. Compaan and Haven⁸ have found theoretically the correlation factor for separated vacancies in the NaCl structure to be $f_v = 0.781$. The contribution of vacancy pairs to the tracer diffusion would have the effect of increasing the observed values $f^*(\text{Na})$ and $f^*(\text{Cl})$ above the predicted value for separated vacancies.

II. THEORY

A. Conductivity and Diffusion

It has been established that the predominant defect in the alkali halides is the Schottky defect. The number of vacancies (n_v) present at temperature T when the crystal is in thermodynamic equilibrium is given by⁹

$$n_v = C_0 \exp(-E_f/2kT), \quad (5)$$

where C_0 is a constant and E_f is the energy required to form a pair of separated vacancies. For sodium chloride crystals it has been found experimentally by Etzel¹⁰ that the concentration of vacancies at room temperature is approximately 10^{+6} per cm^3 while near the melting point $n_v \approx 10^{+18}$ per cm^3 .

The conductivity caused by the positive ion vacancies is given by⁹

$$\sigma_p = en_v \mu_p = \frac{e^2 C_0 \nu_{op} a^2}{6kT} \exp \left(- \frac{U_p + E_f/2}{kT} \right), \quad (6)$$

where a is the jump distance and ν_{op} is the vibration frequency of a Na atom next to a vacancy. The conductivity will contain contributions from both the positive and negative vacancies; therefore, the total conductivity σ can be written

$$\sigma = \sigma_p + \sigma_n;$$

$$\sigma = \frac{e^2 C_o V_{op} a^2}{6kT} \exp\left(-\frac{U_p + E_f/2}{kT}\right) + \frac{e^2 C_o V_{on} a^2}{6kT} \exp\left(-\frac{U_n + E_f/2}{kT}\right). \quad (7)$$

The "microscopic" self diffusion coefficient caused by positive ion vacancies is given by

$$d_p = \frac{1}{6} V_{op} a^2 \exp(-U_p/kT). \quad (8)$$

By considering the probability of a positive ion vacancy being next to a radioactive Na ion and comparing to Fick's first law of diffusion, the "macroscopic" self diffusion coefficient for a radioactive Na ion is given by

$$D_p = \frac{n_v}{N} d_p = \frac{a^2 C_o V_{op}}{6N} \exp\left(-\frac{U_p + E_f/2}{kT}\right). \quad (9)$$

The contribution for the radioactive Cl atom will have a similar form; hence

$$D_p + D_n = \frac{a^2 C_o V_{op}}{6N} \exp\left(-\frac{U_p + E_f/2}{kT}\right) + \frac{a^2 C_o V_{on}}{6N} \exp\left(-\frac{U_n + E_f/2}{kT}\right). \quad (10)$$

B. Einstein Relation

A relationship between conductivity and diffusion becomes apparent when they are considered experimentally since both diffusion

and conduction are able to take place because of defects in the perfect crystal structure. Diffusion represents a mixing up of ions in a crystal by thermal fluctuations, and the conduction of charge represents a drift superimposed on this random motion by the applied electric field. The quantitative relationship is given by the Einstein relation⁷

$$\frac{\mu_i}{d_i} = \frac{q_i}{kT}, \quad (11)$$

where d_i is the microscopic diffusion coefficient of a defect of type i and μ_i is the mobility. In order to compare experimentally observable quantities, the conductivity σ_i and macroscopic diffusion coefficient $D_{\sigma i}$ are given by

$$\sigma_i = n_i q_i \mu_i \quad \text{and} \quad D_{\sigma i} = (n_i/N) d_i, \quad (12)$$

where n_i is the defect concentration and N is the concentration of the kind of atoms involved in the defect motion. Combining these relations, the macroscopic Einstein relation is given by

$$\frac{D_{\sigma i}}{\sigma_i} = \frac{kT}{N q_i^2}. \quad (13)$$

This same relation can be found by comparing the equations found in Section A for the conductivity σ_i and the tracer diffusion coefficient D_i .

C. Correlation Factor and Vacancy Pairs

Correlation effects become evident when it is considered that the conductivity experiment measures the displacement of the vacancy, whereas the diffusion experiment measures the displacement of the tracer atom, which is able to move by means of the vacancy. The tracer atom does not move in a random manner since there are certain preferred directions for successive jumps because of the position of the tracer relative to the vacancy causing the first jump in a sequence. Therefore the observed amount of diffusion is less than expected from the jump frequency of the vacancy. But the conductivity is not affected by these correlation effects since it depends on the motion of the vacancy and not the tracer. The correlation factor is found theoretically by considering the geometry of the lattice and the type of defect mechanism. Compaan and Haven⁸ found a correlation factor of $f_v = 0.781$ for the vacancy mechanism in the face centered cubic lattice of sodium chloride. Since both the positive and negative vacancies move on a face centered cubic lattice, the radioactive diffusion coefficients are given by

$$D_p^* = f_v(n_v/N)d_p \quad \text{and} \quad D_n^* = f_v(n_v/N)d_n. \quad (14)$$

The electrically neutral vacancy pair complex has the effect of increasing the ratio of D^* to D_σ since it can contribute to the diffusion but not to the conductivity. The effect of vacancy pairs on the observed correlation factor can be seen by the following theoretical

considerations which have been presented by Friauf¹². Let ν_p' and ν_n' represent the jump frequencies for positive and negative vacancies in a vacancy pair. The contribution of the vacancy pair to the diffusion of the positive Na ions will be

$$D_{p'}^* = f_{pr} \left(\frac{\nu_p'}{\nu_n'} \right) \frac{n_{pr}}{N} d_{p'} \quad (15)$$

where $d_{p'} = \frac{1}{6} \nu_p' a^2$ and $f_{pr}(\nu_p'/\nu_n')$ ⁸ is a frequency dependent correlation factor. The observed correlation factor caused by both the positive Na ions and the positive part of the vacancy pair is given by

$$f_p = t_p \left\{ f_v + f_{pr} \left(\frac{\nu_p'}{\nu_n'} \right) \frac{n_{pr} \nu_p'}{n_v \nu_p} \right\}, \quad (16)$$

where $t_p = \sigma_p/\sigma$. Therefore the "total" correlation factor caused by both positive and negative ions and including the vacancy pair complex contribution can be represented by the following relation

$$f = f_p + f_n$$

$$f = f_v + \frac{n_{pr}(\nu_p' + \nu_n')}{n_v(\nu_p' + \nu_n')} \left\{ t_p' f_{pr} \left(\frac{\nu_p'}{\nu_n'} \right) + t_n' f_{pr} \left(\frac{\nu_n'}{\nu_p'} \right) \right\}; \quad (17)$$

where

$$t_p' = \frac{\nu_p'}{(\nu_p' + \nu_n')} \quad \text{and} \quad t_n' = \frac{\nu_n'}{(\nu_p' + \nu_n')}.$$

Theoretical considerations by Tosi and Fumi¹³ have predicted that the ratio of the concentration of vacancy pairs to the concentration of Schottky defects in NaCl is of the order of 10% to 20% between 500°C to 700°C.

D. Solution of Diffusion Equation

The diffusion coefficient is found by considering the diffusion equation and its solution from a macroscopic treatment. The mathematical formulation of the diffusion of atoms in solids is based on Fick's first law, that the net flow of atoms is proportional to the gradient of the concentration

$$\vec{F} = - D \text{ grad } n^*. \quad (18)$$

Where $\vec{F}$ is the flux of radioactive atoms crossing a unit area per unit time, D is the diffusion coefficient, and n^* is the concentration of radioactive atoms. The conservation of atoms is represented by the continuity equation

$$- \frac{\partial n^*}{\partial t} = \text{div } F. \quad (19)$$

Fick's second law is found by combining these two equations to give

$$\frac{\partial n^*}{\partial t} = D \nabla^2 n^*. \quad (20)$$

In this experiment a very thin film of radioactive material was deposited on one end of a crystal in the form of a semi-infinite rectangular parallelepiped. Therefore all the diffusion is in the positive x direction, and a solution to the time dependent diffusion equation which meets the above initial and boundary conditions is given by

$$n^*(x, t) = \frac{Q}{\sqrt{\pi Dt}} \exp(-x^2/4Dt). \quad (21)$$

At $t = 0$ the quantity Q of the radioactive substance is concentrated in the plane $x = 0$, and for $t > 0$ the solution gives the resulting distribution of concentration for the radioactive material.

The root mean-square displacement gives an estimate of the depth of penetration of the radioactive material after a time t . The mean-square displacement is given by

$$\langle x^2 \rangle = \frac{\int_0^{\infty} x^2 n^*(x, t) dx}{\int_0^{\infty} n^*(x, t) dx} = 2Dt; \quad (22)$$

hence

$$x_{\text{rms}} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}. \quad (23)$$

III. EXPERIMENTAL PROCEDURE

A. Crystals

Pure sodium chloride crystals purchased from the Harshaw Chemical Company were judged to be very impure for three reasons.

(1) An indication of impurity content was given by the great difficulty encountered in cleaving the crystals; added impurities usually have the effect of embrittling ionic crystals. (2) When an optical absorption curve was run on these crystals, the characteristic hydroxide band seen for pure crystals was absent; presumably the hydroxide ions were associated with the impurities. (3) The conductivity of these crystals was found to be greater than the conductivity of pure crystals measured in other experiments. Therefore it was decided to grow our own crystals by a technique similar to the Kyropoulas method. See Figure 2.

The sodium chloride salt used in growing the crystals was a very pure reagent grade from the Fisher Scientific Company. The salt had the following certificate of analysis:

Barium	0.001%	Iodide	0.000%
Calcium & Magnesium	0.000%	Bromide	0.01%
Heavy Metals	0.0000%	Insoluble Matter	0.001%
Iron	0.0000%	Chlorate & Nitrate	0.000%
Potassium	0.005%	Nitrogen Compounds	0.0003%
		Phosphate	0.0003%
		Sulfate	0.000%

A 2.5 by 2.5 inch quartz crucible was filled to the brim with this NaCl. The crucible was then placed into a 1.7 kilowatt open ended Hevi-Duty furnace. The crucible was set on asbestos blocks so that it was placed in the middle of the heating coils. Then a piece of 0.001

inch platinum foil in the form of a cylinder was placed around the crucible as a heat conductor and shield against impurities. A thick iron cylinder was used at one time, but the crystals with this arrangement were very impure because of iron oxide scale falling into the melt. The top of the furnace was covered with an asbestos sheet, in which holes were cut to let light in and also to observe the melt. To eliminate convection currents, quartz plates were placed over these holes. The furnace was controlled by using a Brown recorder with the thermocouple placed between the platinum foil and the coils of the furnace. A platinum wire tip on one end of a double-walled Inconel tube was inserted into the melt. The other end was fastened to an electric motor assembly that could move the tube in a vertical direction. Compressed air was passed through the tube cooling the platinum tip to give a temperature gradient in order to crystallize the salt.

The tip was inserted and air turned on before the furnace was heated. The crucible was heated past the melting point (800°C) until all the salt was melted. Then the platinum tip was inserted $1/4$ inch into the melt, and the temperature was lowered in 5°C intervals and left for 10 to 20 minutes at each interval until a seed started to form on the platinum wire tip. With this particular arrangement the thermocouple reading was 916°C when the seed started to form and was lowered to 901°C at the end of the operation. After the seed was approximately $1/4$ inch in diameter, it was raised vertically at the rate of 0.13 inch/hour. As the crystal got longer, it was necessary to lower the

temperature of the melt in 1°C intervals so that the crystal would not pull out of the melt. Care was taken not to lower the temperature so low that the melt would crystallize around the edge of the crucible. When most of the melt was gone, the crystal was raised clear of the melt and allowed to cool very slowly to room temperature. Using this technique, it was possible to obtain very pure crystals 3 inches long by 1 inch in diameter.

The conductivity curves for these crystals were compared to conductivity curves measured by Aschner⁵. It was found that our conductivity curves lie in the region between the curve for pure NaCl and the curve for five parts per million impurity as shown in the results by Aschner.

Then it was necessary to cleave these large crystals into 1 cm X 1 cm X 1/2 cm plates. The cleavage plane was found to be at approximately 45 degrees with respect to the wire tip in the top of the crystal. Once this plane was found, the crystal was cleaved into 5 mm thick plates. Then these plates could be cleaved to the proper size. It was a very difficult and tedious job to get a perfect crystal with no cracks or broken corners. It was best to use a razor blade with the top metal strip removed. The blade was struck with several light taps with a hammer until the crystal cleaved. One hard blow was found to be completely unsatisfactory because it was difficult to find the exact cleavage plane with the eye. By using the light taps, it was possible to let the blade itself alter its position until the correct cleavage plane was found.

B. Apparatus

The furnace used for the diffusion and conductivity measurements was a Leeds and Northrup thermocouple calibration furnace. The heating coils were 3 1/2 feet long and 4 inches in diameter. The space between the crystal and the coils was filled with a metal alloy (Inconel) to obtain good thermal conduction. Temperature gradients over the crystal were eliminated by placing the very small crystal (1 square cm) in the middle of the very long coils.

The same crystal holder was used for both the conductivity and diffusion measurements, and conductivity measurements were taken during the diffusion run. See Figure 3. The holder was made from a metal alloy (75% nickel) with the brand name of Inconel. Great care was taken to design the holder without screws in the high temperature region because screws could not be removed due to oxidation at these high temperatures (600°C - 750°C). A nickel brazing compound was used to connect all necessary parts since the high temperatures prevented using the normal silver solder.

The crystal was held between two thick Inconel plates, which had 0.01 inch platinum sheets micro-brazed to their inner surfaces. Pieces of thin platinum foil (0.001 inch) cut to the size of the crystal were inserted between the crystal and the heavier platinum sheets. Quartz plates surrounded the crystal on all four sides to prevent electrical contact to the sides of the holder. A light pressure was applied to the crystal by a spring outside the high temperature region acting through a 1/4 inch diameter Inconel rod. This rod also served

as the electrical high lead and was insulated by thick quartz cylinders. The chromel-alumel thermocouple was micro-brazed into the Inconel plate which held the crystal in order to obtain the most accurate temperature reading of the crystal.

The holder was designed to be vacuum tight and was evacuated to 4×10^{-5} mm Hg at room temperature before each experiment. It was then filled with pure helium gas so that the pressure would be approximately one atmosphere at the measurement temperatures.

C. Conductivity

A sample was prepared by painting both sides with a suspension of graphite in isopropyl alcohol. It was sometimes necessary to add a few drops of isopropyl alcohol to obtain a suitable consistency. Care was taken not to let any of the graphite run onto the sides of the crystal. When this did happen, the graphite was removed by scraping gently with a razor blade. When applied properly, the graphite made a very thin uniform electrode on the surface of the crystal. These graphite electrodes proved quite stable even when held at 750°C for several hours.

The dimensions of the samples were measured with a measuring microscope that could be read to five figures. This was usually done before the electrodes were applied so as not to scratch the surface of the graphite. Since the crystal samples were not perfect, each dimension was measured at three different locations on the crystal. To get the correct cross sectional area, both sides of the crystal were

measured in this manner. The average value was used in determining the conductivity.

In order to make sure the crystals were pure, it was necessary to make a conductivity check on each crystal grown. A plate was used from the top and the bottom of each crystal to insure that the whole crystal was pure. In this experiment it was necessary to grow two large crystals. Therefore a total of four conductivity runs were made. An average conductivity curve was established by combining these four curves. The conductivity curves were taken from 525°C to 750°C in 25°C intervals. To insure equilibrium, the sample temperature was regulated by a Brown controller to $\pm 1/2^\circ\text{C}$ for 30 minutes. The temperature was then read to five figures with a Leeds and Northrup millivolt potentiometer.

To measure the conductivity, an A.C. bridge technique was used as shown in Figure 4. The instrument was a General Radio 716-C Capacitance Bridge with a General Radio 1231-B amplifier and null detector. The oscillator used was a General Radio 1304-A beat frequency oscillator or a General Radio 1330-A bridge oscillator, so that resistance measurements could be read at 1,000 cps and 100,000 cps. A General Radio 1432-M Decade Resistance Box was used in parallel with a variable capacitor. An oscilloscope was used as the detector to determine when the bridge was balanced. The two upper arms of the bridge were kept at a 1:1 ratio so that when the bridge was balanced, the resistance of the sample was read directly from the resistance box (R_v).

Now that the resistance and the dimensions of the crystal are known, the conductivity σ can be found from the relation

$$\sigma = L/AR = G/R, \quad (24)$$

where L is the thickness of the crystal of cross sectional area A .

D. Diffusion

Only the most perfect crystals with cross sections of one square cm or greater were used for the diffusion measurements. The large cross section was desirable to minimize the error in weighing.

The radioactive Na^{22} (half-life 2.58 years) was purchased from the Nuclear Science and Engineering Corporation in carrier free form as NaCl in HCl solution. The activity of the solution was greater than 0.5 mc/ml. A thin layer ($0.3 \mu\text{c}$) of this radioisotope in the form of NaCl was deposited on one side of each crystal by evaporation in a vacuum. Scotch tape was applied to the edges of each crystal to prevent any radioactive material from getting on these edges. The crystals were then taped to a special holder which was placed 4 cm above the platinum evaporation boat. The radioisotope solution was transferred to the evaporation boat, powdered dry ice was added to freeze the radioisotope solution, and the excess water and HCl were removed by evaporation. Current was then passed through the platinum boat until it was red hot and left at this temperature for approximately one minute. The thickness of the layer deposited onto the crystal was

estimated to be approximately 6×10^{-4} Å thick by geometrical considerations.

Radioactive sodium was evaporated only on one face of the diffusion crystal. The cross sectional area of this face was used in calculating the diffusion coefficient. This differed from the cross sectional area used in finding the conductivity of this crystal since both faces were considered in the conductivity calculation.

Since the conductivity was measured during the diffusion run, it was necessary to apply graphite electrodes on the radioactive diffusion crystals. Then the crystal was placed in the holder with the radioactive side down, next to the thermocouple junction. The heating and cooling times were approximately 1 1/2 hours from room temperature to the diffusion temperature. The sample temperature was read every one minute while the temperature was changing rapidly, and every hour at the equilibrium diffusion temperature. The furnace temperature was controlled by a Brown Recorder to $\pm 1/2^\circ\text{C}$, and the inside thermocouple (crystal temperature) had a drift of only $\pm 1/2^\circ\text{C}$ if the control temperature was adjusted every four hours to correct for any long time drifts from the diffusion temperature. It was found that these long time drifts were almost completely eliminated if the open end of the furnace were packed with new pyrex wool before each run.

Diffusion measurements were made only in the intrinsic temperature region from 575°C to 700°C at approximate 25°C intervals. The time for the diffusion run was determined by requiring the rms distance ($x_{\text{rms}} = \sqrt{2Dt}$) to be approximately 100 microns. The diffusion

times varied from 48 hours at the lower temperatures to 12 hours at the higher temperatures.

E. Slicing, Weighing, and Counting

The crystals were removed from the diffusion holder and sectioned with a microtome. The microtome was equipped with a ball joint vise which made it possible to orient the crystal surface in two dimensions. The crystal was mounted on a small table with black wax, and this was then placed in the ball joint vise such that one side of the crystal was parallel to the knife edge. The crystal was removed by dissolving the black wax in benzene.

It was very important that the slices be taken parallel to the crystal surface. By first taking several slices on a dummy crystal, the plane of motion of the knife blade was determined. Then an optical flat mirror was placed on top of the crystal, and its orientation was determined by focusing an object onto a piece of graph paper. By adjusting the surface of the diffusion crystal to the same orientation, it was possible to get a complete full cut over the surface of the crystal by the second slice. Misalignment was estimated from the cutting pattern on the crystal surface, and a correction due to Shirn, Wajda, and Huntington¹¹ was applied.

Without any preparation of the crystal surface, the slices were in the form of a fine powder. By blowing lightly on the crystal surface so that it absorbed moisture, the slices came off in small rolls. These were collected by carefully brushing them into planchets. The usual slice thickness was 8 microns, and up to 30 slices were taken

with two slices in each planchet. To determine the slice thickness more accurately, each slice was weighed on a balance with a sensitivity of 0.01 milligrams. The slices were placed in a drying oven and dried for two hours before weighing in order to remove any moisture. Since the diffusion crystal had graphite on its surface, the first planchet contained salt and graphite. The mass of the graphite was approximately 0.3 mg, as determined by weighing the crystal before and after application, and this mass was subtracted from the mass of the salt in the first planchet.

After each slice had been weighed, the slices were prepared for counting. It was desirable to have the salt evenly distributed over the bottom of the planchet in order to insure consistent counting from each planchet. This was accomplished by dissolving the salt with water and then freezing this solution. The water was removed by evaporation in a vacuum, leaving a very thin, uniform film of radioactive salt on the bottom of each planchet. To prevent the frozen salt solution from jumping out of the planchets, silk cloth was placed over the top of the planchets and held in place by an O-ring. Metal lids with and without holes were tried but were unsatisfactory.

After the water had been completely evaporated, the slices were ready to be counted. Each planchet was placed beneath the window of a geiger tube and counted until a minimum of 10,000 counts had been registered in a minimum time of two minutes. This assured that the statistical counting error was held below 1%. The geiger tube was shielded on all sides with a thick wall of iron, and it gave a fairly

consistent background count of 30 cpm. The planchet distance from the geiger tube was adjusted so that the maximum counting rate of 15,000 cps need not be corrected for the dead time of the counter.

The total time taken in counting the 15 planchets was around five hours. To further insure a consistent count, the second planchet was chosen as a standard, and it was counted after every three planchets. The variance in the standard count was then used to adjust the counts for the other planchets.

F. Analysis of Data

A diffusion profile was obtained for each diffusion crystal by plotting the log of the counts against the square of the penetration depth. The count rate was converted to a concentration by multiplying by the ratio m_0/m_i , where m_0 is the mass of the average slice and m_i is the mass for the particular slice. To eliminate any error obtained by variation of counting due to the geiger tube, a standard count rate G_0 was taken at the beginning and then checked after every third slice (G_i). Also the counts were corrected for the background count rate (B_0). Therefore the count rate per slice (C_i) was represented by

$$C_i = \left(\frac{G_0}{G_i} \frac{P_i}{t_i} - B_0 \right) \frac{m_0}{m_i}, \quad (25)$$

where P_i is the count registered by the geiger tube in time t_i .

Since the slices have a finite thickness, the radioactivity of a slice was considered to be concentrated at the center of the slice. Also, since the penetration distance x is proportional to the mass of

each slice, the log of the counts C_i was actually plotted against W_i^2 , where

$$W_i = \sum_{j=1}^{i-1} r_j + \frac{1}{2} r_i, \text{ with } r_i = m_i/m_o. \quad (26)$$

Since the counts and penetration distance have been referred to masses, it is necessary to correct the solution of the diffusion equation,

$$\ln n^* = \text{const.} + x^2/4Dt, \quad (27)$$

to the following equation,

$$\ln C_i = \text{const.} + \frac{(m_o/\rho A)^2}{4Dt} \left(\frac{m_i}{m_o} \right)^2, \quad (28)$$

where ρ is the density of NaCl and A is the cross sectional area of the diffusion crystal. Therefore when the slope of the diffusion profile, $\ln C_i$ vs $(m_i/m_o)^2$, is obtained, the diffusion coefficient is found from the following relation,

$$D = \frac{(m_o/\rho A)^2}{4t (\text{slope})}, \quad (29)$$

Since the temperature was not constant throughout the total diffusion run, it is necessary to calculate an effective time of diffusion. The effective time is calculated from

$$t_{\text{eff}} = \int_0^{\infty} \frac{D(T)}{D(T_0)} dt, \quad (30)$$

where $D(T_0)$ is the diffusion coefficient at the equilibrium temperature T_0 . In the first analysis, this value was approximated by using the activation energy found from the conductivity measurements, but a second analysis for t_{eff} was made using the activation energy found from the radioactive diffusion measurements $D^*(\text{Na})$.

A program for the IBM 1620 computer was written by Dr. Friauf to analyze the raw data. Since there was some scatter in the data, the computer calculated a straight line by a least-squares calculation, giving the slope and per cent error in the slope for the diffusion profile. The integral for the effective time was evaluated graphically by the computer by considering the measured variation of temperature T with time t .

Twice during the slicing operation, one of the crystal corners broke off after the second slice. Since the computer considers the cross sectional area to be constant for each slice, it was necessary to enter a correction factor. For the first two slices, the mass (m_1 and m_2) had to be changed to a reduced mass m_1' and m_2' ,

$$m_1' = \frac{A}{A'} m_1, \quad (31)$$

where A' is the area before the corner broke and A is the area after the corner broke. A is the area that the computer considers to be constant

and is used in the calculation of D^* . Therefore, it was necessary to punch two sets of data cards, (1) original data, (2) masses of slices 1 and 2 corrected, as stated above. A new set of data cards was then constructed by using the counts of Set 1 and the x 's of Set 2.

The experimental values obtained for the conductivity were converted to an equivalent diffusion value D_σ by means of the Einstein relation

$$\frac{D_\sigma}{\sigma} = \frac{kT}{Ne^2} \quad (32)$$

It is shown in Appendix II that

$$D_\sigma(\text{cm}^2/\text{sec}) = 2.412 \times 10^{-8} \sigma(\text{ohm-cm})^{-1} T(^{\circ}\text{K}). \quad (33)$$

G. Errors

In the measurement of the diffusion coefficient, there are two sources of error: those connected with measuring T and those involved in evaluating D from the counting measurements. The exact errors for each diffusion run are given at the end of this thesis.

1. Errors in Temperature

The absolute calibration error of the chromel-alumel thermocouple was $+0.07$ mv (1.8°C). The conductivity and diffusion measurements were made on the same crystal using the same thermocouple. Therefore, in the comparison of these measurements, the error for the individual calculation would cancel out.

2. Errors in the Diffusion Time

Because of the very long diffusion times in this experiment, these errors were very small. They were estimated to be from 0.1% to 0.3% over the temperature region by taking 1/5 of the time correction. The time correction was found from the effective time curve by considering the difference in area of the approximated square curve and the actual time curve.

3. Errors in the Slope B

Random errors in the slope come from two sources: statistical errors in counting and random errors in weighing. The counting error was kept below 1% by requiring a minimum of 10,000 counts per slice. The error in weighing was also kept to a minimum by keeping the mass per slice to a maximum. The error in the slope as determined by a least-squares calculation was around 1%.

There was some loss in crystal mass in the slicing procedure. Therefore it was necessary to correct the slopes of the counting profiles since losing mass had the effect of increasing the value of the slope. To correct for this loss, the crystal was weighed before and after slicing, and this mass was compared to the total mass of the slices. If the loss of mass was assumed to occur uniformly over all the slices, as seemed likely from observations during slicing, the maximum correction would be twice the per cent loss of mass since the mass is squared in the relation used in calculating $D^*(Na)$. Since this loss of mass may not be uniform, however, only half the maximum correction was used in adjusting the slopes. This uncertainty was included in the experimental error and varied from 3% to 0.9%.

4. Errors in Cross Section of Crystal

The error in the crystal cross section was kept to a minimum by using crystals with cross sections of approximately 1 square cm. They were measured very accurately with a measuring microscope that could be read to five figures. This error was in the neighborhood of 1/2%, but this error was doubled since the area is squared in the equation for D.

5. Errors in Slicing

This error was caused by the finite slice thickness and from misalignment of the microtome knife. A correction factor from Shirn, Wajda, and Huntington¹¹ was used.

$$\Delta D/D = \frac{1}{12} (s/x_{rms})^2 + \frac{1}{12} (m/x_{rms})^2 \quad (34)$$

where s is the slice thickness and m is the error in misalignment. This correction varied from 1/2% to 2%, depending on how flat the crystal surface was.

In the measurement of the conductivity, there were two sources of errors.

1. Errors in the Measurement of the Crystal Dimensions

The error in the cross section was less than 1/2% since the crystals were approximately 1 square cm. Since the thickness of the crystals was small (2 mm to 5 mm), this measurement gave the largest error. It was usually around 1%.

2. Error in the Resistance

The resistance measurement was read to five figures. The accuracy of this measurement was restricted to the accuracy of the resistance box. The General Radio resistance box had an error of 0.1%.

The error in the diffusion measurements varied from $\pm 1.8\%$ to $\pm 4.6\%$ and the error in the conductivity measurements varied from $\pm 0.53\%$ to $\pm 1.07\%$. This gives a total error of $\pm 1.98\%$ to $\pm 4.70\%$ for the experimental correlation factor.

IV. EXPERIMENTAL RESULTS

A. Conductivity

Figure 5 shows the result of the conductivity measurements on four crystal plates taken from two pure sodium chloride crystals. The diffusion samples also came from these same large crystals. One plate was taken from near the top and one from near the bottom of each crystal in order to check against an impurity gradient. The numerical experimental data for each run is given in Appendix III.

When the crystal plate was held at a constant temperature for 24 to 48 hours, a decrease in resistance from 5% to 10% was observed. This decrease in resistance varied from plate to plate and no consistent correlation could be made. See Figure 6 for an actual representation of the change in resistance with time for several crystals. Work by Bean⁴ and Aschner⁵ did not show this change in resistance for pure crystals. However, both Bean and Aschner held the temperature constant for only approximately 30 minutes. It is believed that this change in resistance may be due to contamination of the crystal plate from the presence of the Inconel metal surrounding it.

The values of the parameters in the equation for the conductivity,

$$\sigma = \frac{\sigma_0}{T} \exp(-W/kT), \quad (35)$$

were found by a least-squares calculation. In the temperature region

from 575°C to 700°C, the activation energy W was found to be $W = 1.99 \pm 0.01$ ev. and the constant $\sigma_0 = 2.63 \times 10^{+9} \pm 0.02$ °K/ohm-cm. Figure 5 also shows the conductivity results of Maurer³ and Bean⁴ using pure sodium chloride crystals. Table I shows that the activation energy found in this experiment compares very well with the activation energy found by Bean ($W = 1.99$ ev.) and Maurer ($W = 1.89$ ev.).

B. Diffusion

Figure 7 represents a profile of the radioisotope concentration as a function of the square of the penetration depth for one diffusion run. The solid line is the least-squares fit of the experimental points. In all eight diffusion runs, the points were very consistent. When the deviation of a point from the least-squares line was more than twice the root mean-square deviation, the point was dropped and a new least-squares fit was made without this point. It was only necessary to drop one to two points in each profile.

There were a total of eight diffusion runs, using four different samples from each of the two larger crystals. Tables of the numerical data for each run are given in the Appendix.

Figure 8 shows the results of diffusion of sodium in pure sodium chloride as a function of a temperature. The heavy straight line is a least-squares fit of the diffusion equation,

$$D = D_0 \exp(-W/kT), \quad (36)$$

to the experimental diffusion points. The activation energy calculated

from the least-squares line is $W = 1.80 \pm 0.02$ ev. and the constant $D_0 = 3.90 \pm 0.04$ cm²/sec for the temperature range of 585°C to 695°C. These values compare very well with the results found by Maurer³ ($W = 1.80$ ev. and $D_0 = 3.1$) as shown in Table I.

The thin line is the average diffusion coefficient curve found from the measured conductivity data using the Einstein relation. At the beginning and the end of the diffusion run, the conductivity of the diffusion crystal was measured. The self diffusion coefficients D_{σ}^b (beginning) and D_{σ}^f (final) were calculated by using the Einstein relation. These values are represented by $\triangle (D_{\sigma}^b)$ and $\nabla (D_{\sigma}^f)$. All but two of the initial (D_{σ}^b) points were along the average D_{σ} curve. These two points were the first two diffusion runs, and it was believed that in these two runs the crystals touched the grounded sides of the holder, and therefore gave an incorrect resistance reading. This was eliminated for all the following runs by placing quartz plates between the crystal and the sides of the holder.

V. DISCUSSION

The most outstanding feature of the diffusion measurements is the consistency of the points. The diffusion measurements made by Maurer on pure NaCl showed a great deal of scatter. The most disappointing feature is the decrease in resistance with time.

The change in resistance is not expected to occur since it is not predicted by the theory. It is believed this decrease might be caused by two factors. At these high temperatures (600°C to 700°C), the crystal could become contaminated from the metal holder around it. Also, since the crystal was grown in the atmosphere, it is possible that this might have some effect on its electrical properties.

This experiment was limited to the intrinsic region. Therefore only two mechanisms of ion motion seem possible, either by separated vacancies or by vacancy pairs. Therefore the total self diffusion coefficient D_T^* , which is calculated from the tracer diffusion experiments as

$$D_T^* = D^*(\text{Na}) + D^*(\text{Cl}), \quad (37)$$

contains not only the diffusion of both separated positive and negative ions but also the contribution of vacancy pairs to the diffusion.

The diffusion coefficient D_σ calculated from the measured conductivity would not contain the vacancy pair contribution since the vacancy pair is electrically neutral. Therefore, the total diffusion

coefficient from the conductivity measurements is represented by

$$D_{\sigma} = D_p + D_n. \quad (38)$$

The D_{σ} curve is represented in Figure 8, and the parameters for this curve are given by

$$D_{\sigma} = 63.5 \text{ cm}^2/\text{sec} \exp(-1.99 \text{ ev.}/kT). \quad (39)$$

But the diffusion curve found from using the Na^{22} tracer gives only the positive ion contribution to the total diffusion curve D_T^* . Therefore, to get the total diffusion curve it is necessary to add the negative ion contribution found with radioactive chlorine. The results for the chlorine diffusion will be taken from the thesis by Laurance⁶ since his experimental procedure was identical to this experiment. The parameters for the total diffusion coefficient curve D_T^* as shown in Figure 9 are given by

$$D_T^* = 14.2 \text{ cm}^2/\text{sec} \exp(-1.88 \text{ ev.}/kT). \quad (40)$$

In the theory section it was shown that the tracer did not move in random manner, but there were certain preferred directions for jumping caused by its relation to available vacancies. This correlation factor is $f_v = 0.781$ for separated positive and negative ion vacancies in the NaCl lattice structure. The effect of this correlation is also shown in Figure 9 by the curve $0.781 D_{\sigma}$.

If the assumption be made that in the intrinsic region the vacancy pairs do not contribute to the diffusion, then the total diffusion coefficient D_T^* would lie along the line $0.781 D_v$. This would mean that only separated vacancies are present. From Figure 9, the experimental D_T^* does not lie along $0.781 D_v$, but in fact it lies above it and has a somewhat different slope. Therefore, this seems to imply that there is a contribution due to vacancy pairs in this temperature region.

The possible effect of the vacancy pair contribution to the diffusion becomes even more evident by considering the concentration and energy of motion of vacancy pairs. By using the theoretical binding energy of a pair calculated by Tosi¹³ and the experimental concentration of Schottky defects measured by Etzel¹⁰, Tosi shows that the concentration of vacancy pairs relative to Schottky defects should be of the order of 10% to 20% between 500°C to 700°C in sodium chloride. Furthermore in the study of chlorine diffusion in sodium chloride, Laurance⁶ obtained indications that as divalent positive ion impurity is added to the pure crystal the concentration of free negative ion vacancies is reduced until the vacancy pair becomes the dominant mechanism of motion.

The activation energy for diffusion by vacancy pairs would have the form

$$W_{pr} = E_f - E_b + U_m = E_{pr} + U_m, \quad (41)$$

where E_f is the formation energy of a Schottky defect, U_m is an

appropriate energy of motion of a pair (saddle point energy), and E_b is the binding energy of a pair. Laurance⁶ measured an activation energy of 2.49 ev. for diffusion of chlorine in sodium chloride crystals containing 5×10^{-4} mole fraction of calcium. This measured activation energy for the doped crystals of 2.49 ev. can be equated to the total vacancy pair energy W_{pr} by the assumption that the vacancy pair is the dominant mechanism of motion for these doped crystals. Therefore the energy of motion for a vacancy pair U_m can be calculated by using $W_{pr} = 2.49$ ev. and deducing from $E_{pr} = E_f - E_b$ an appropriate value for the formation energy of a vacancy pair. The binding energy of a vacancy pair has been calculated theoretically by Tosi¹³ to be $E_b = 0.6$ ev. The formation energy of a Schottky defect has been calculated theoretically by Tosi¹⁷ to be $E_f = 2.12$ ev. The formation energy of a Schottky defect has also been measured experimentally and shows some disagreement, Etzel¹⁰ ($E_f = 2.02$ ev.), Maurer³ ($E_f = 2.12$ ev.), and Bean⁴ ($E_f = 2.42$ ev.). It would seem that the value given by Bean should be the most accurate, since it is the most recent work using an A.C. field, whereas Etzel and Maurer used a D.C. field. Also the activation energy W in the high temperature region found by Bean is confirmed by the present experiment. With this value of $E_f = 2.42$ ev. for the formation energy of a Schottky defect, a value of $U_m = 0.67$ ev. is deduced for the energy of motion for the vacancy pair. By using the value measured by Etzel, $E_f = 2.02$ ev., a value of $U_m = 1.07$ ev. is obtained. It is difficult to say which value is the more correct, but it does appear that the energy of motion of a pair should lie in the region between 0.67 ev. to 1.07 ev.

It has been calculated theoretically by Tharmalingam and Lidiard²¹ that the saddle point energy for a positive ion jumping into a vacancy pair is $U_p' = 1.46$ ev. and for a negative ion $U_n' = 1.27$ ev. The energy of motion for a vacancy pair calculated experimentally would be expected to lie somewhere between these two values, since both positive and negative ions must jump into the vacancy pair before the vacancy pair can diffuse through the crystal. The values calculated experimentally are lower than the values predicted theoretically, but are in the right neighborhood.

Both the experimental and theoretical calculations indicate that the energy of motion for a vacancy pair is equal to or larger than the energy of motion for a separated positive ion (0.87 ev.) or negative ion (1.11 ev.) jumping into separated vacancies. This is a surprising result since often it has been assumed that an ion is much less restricted in jumping into a vacancy pair because of the absence of the ion of opposite sign. In fact, Dienes¹⁹ (1948) calculated a value of 0.38 ev. in KCl for the saddle point energy for the Cl^- ion jumping into a vacancy pair.

The theoretical calculations by Tharmalingam and Lidiard²¹ show that the activation energy for a jump into a vacancy pair is composed of three terms,

$$\Delta E = \Delta E_c + \Delta E_R + \Delta E_p, \quad (42)$$

where E_c is the coulomb interaction, E_R is the closed-shell repulsion, and E_p is the polarization term. These calculations do indeed show that

the closed-shell repulsions ΔE_R are relatively unimportant for the vacancy pair, but the coulomb contribution ΔE_C is positive for the vacancy pair instead of negative for single vacancies since one of the two barrier ions is absent in the vacancy pair. Therefore the vacancy pairs become less mobile than single vacancies as shown in the following table of calculations from Tharmalingam and Lidiard²¹. The upper values represent vacancy pairs, and the values in parentheses are for the separated vacancies from Tosi²².

Moving Ion	$\Delta E(\text{ev})$	$\Delta E_C(\text{ev})$	$\Delta E_R(\text{ev})$	$\Delta E_p(\text{ev})$	Dipole Correction
Na ⁺ in NaCl	1.46 (0.87)	1.46 (-1.32)	-0.02 (1.83)	0.02 (0.36)	0.00
Cl ⁻ in NaCl	1.27 (1.11)	1.67 (-1.60)	0.24 (2.29)	-0.87 (0.42)	0.23

To get a better look at the correlation factor $f = D^*/D_\sigma$, see Figure 10. In this figure the line $f_v = 0.781$ again represents the contribution caused only by separated vacancies. Immediately there is trouble since in this experiment the conductivity changed with time. Therefore, what value for D_σ is the correct value to use in finding the correlation factor $f = D^*/D_\sigma$? In this figure the correlation for the conductivity at the beginning and the end of the diffusion run and the average of these two are represented. Also the correlation for the average conductivity taken from other crystals is represented. These correlations were found by using the results of this experiment, and the Cl⁻ contribution measured by Laurance⁶. Since the properties of "pure" crystals vary even in crystals grown by the same method in the same

laboratory, the correlation factors found from Laurance may not represent the correct Cl^- contribution for the crystals used in this experiment. But the values should give a fairly accurate approximation, much better than neglecting the Cl^- contribution altogether, as has been done in the past.

The chlorine contribution increases all the correlation factors above the vacancy correlation factor $f_v = 0.781$. Therefore, this does indicate the possibility of vacancy pair contribution. But a precise calculation cannot be made because of the increasing conductivity with time. Since the diffusion measurements were extremely consistent, it seems that it would be possible to get precise measurements by redesigning the apparatus such that only quartz and platinum would be used in the high temperature region. For such an arrangement, see the thesis by Aschner⁵. Crystals with an even smaller impurity content can be grown in the future since a crystal grower that can be evacuated is now being built. Also it would be very desirable to make diffusion measurements using both radioactive sodium and chlorine on the same crystals. With these modifications and using the techniques developed in this thesis the correlation factor could be determined with precision, and the effect of the vacancy pair could be measured.

TABLE I - EXPERIMENTAL ACTIVATION ENERGIES FOR PURE SODIUM CHLORIDE

	Temperature Range °C	W (ev.)	D_0 (cm ² /sec)	U [#] (ev.)	E _f [#] (ev.)
<u>Conductivity</u> - $D_{\sigma} = D_0 \exp(-W/kT)$					
This Work	575-700	1.99	63.5		
Lehfeld ¹⁸ (1933)	High Temp. Low Temp.	1.98 0.78	63.	0.78	2.40
Etzel ¹⁰ (1950)	550-700 250-400	1.86 0.85	8.93	0.85	2.02
Maurer ³ (1950)	520-720 350-500	1.89 0.83	14.	0.83	2.12
Bean ⁴ (1952)	550-680 350-500	1.99 0.78	55.	0.78	2.42
<u>Sodium Diffusion</u> - $D^* = D_0 \exp(-W/kT)$					
This Work Na ²²	585-695	1.80	3.90		
Maurer ³ (1950) Na ²⁴	520-720 350-500	1.80 0.77	3.1	0.77	2.06
Laurent ¹⁴ (1957) Na ²²	600-795	1.61	0.5		
<u>Chlorine Diffusion</u>					
Patterson ¹⁵ (1955)	358-510	1.67	0.10		
Harrison ¹⁶ (1957)	450-690 306-537	2.29 1.61	490.		
Laurent ¹⁴ (1957)	600-795	2.23	110.		
Laurance ⁶ (1960)	520-745	2.12	56.6		

[#] It is assumed that in the high temperature region $W = U + E_f/2$ while in the low temperature region $W = U$ as explained in Section I.

TABLE II - THEORETICAL ACTIVATION ENERGIES IN PURE NaCl

Formation energy of separated positive and negative vacancies:

Mott and Littleton ² (1938)	$E_f = 1.86 \text{ ev}$
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Fumi and Tosi ¹⁷ (1957)	$E_f = 2.12 \text{ ev}$
------------------------------------	-------------------------

Saddle point energy for ions jumping into separated vacancies:

Guccione and Tosi ²² (1959)	$U_p = 0.87 \text{ ev}$
--	-------------------------

	$U_n = 1.11 \text{ ev}$
--	-------------------------

Binding energy for a vacancy pair:

Reitz and Gammel ²⁰ (1951)	$E_b = 0.89 \text{ ev}$
---------------------------------------	-------------------------

Tosi and Fumi ¹³ (1958)	$E_b = 0.6 \text{ ev}$
------------------------------------	------------------------

Formation energy of a vacancy pair:

Tharmalingam and Lidiard ²¹ (1961)	$E_f(\text{pair}) = 1.27 \text{ ev}$
---	--------------------------------------

Saddle point energy for ions jumping into a vacancy pair:

Dienes ¹⁹ (1948) KCl	$U_n' = 0.38 \text{ ev}$
---------------------------------	--------------------------

Tharmalingam and Lidiard ²¹ (1961)	$U_p' = 1.46 \text{ ev}$
---	--------------------------

	$U_n' = 1.27 \text{ ev}$
--	--------------------------

CALCULATION OF THE EINSTEIN RELATION

The numerical values for the parameters in the Einstein relation used in calculating D_{σ} from the measured conductivity and the density used in calculating $D^*(\text{Na})$ are given below.

$$\frac{D_{\sigma}}{\sigma} = \frac{kT}{Ne^2}$$

The lattice parameter a_0 for NaCl was taken from:

Wyckoff, Crystal Tables, Vol. I, Chapter III, Table 14C

$$a_0 = 5.63978 \text{ }^{\circ}\text{A} \text{ (18}^{\circ}\text{C)}$$

$$a_0 = 5.64056 \text{ }^{\circ}\text{A} \text{ (26}^{\circ}\text{C)}$$

N = concentration of Na or Cl atoms

$$N = \frac{4 \text{ sites}}{(5.640 \text{ }^{\circ}\text{A})^3} = 2.230 \times 10^{22} \text{ atoms/cm}^3$$

$$\rho \text{ (density)} = N \frac{\text{molecular weight}}{\text{Avogadro's number}}$$

$$\rho = 2.230 \times 10^{22} \frac{58.45}{6.025 \times 10^{23}}$$

$$\rho = 2.163 \text{ g/cm}^3$$

$$\frac{D_{\sigma}(\text{cm}^2/\text{sec})}{\sigma(\text{ohm-cm})^{-1}} = 2.412 \times 10^{-8} T(^{\circ}\text{K})$$

TABLE III - NUMERICAL DIFFUSION DATA

Crystal	Temperature		$D^*(Na)$ (cm ² /sec)	Error %	D_{σ}^b (cm ² /sec)	D_{σ}^f (cm ² /sec)
	T°C	1000/T°K				
B2-D	585.05	1.165	1.052X10 ⁻¹⁰	2.55	1.237X10 ⁻¹⁰	1.317X10 ⁻¹⁰
B2-B	602.45	1.142	1.647X10 ⁻¹⁰	4.64	2.107X10 ⁻¹⁰	2.431X10 ⁻¹⁰
B5-C	622.02	1.117	3.046X10 ⁻¹⁰	1.80	3.910X10 ⁻¹⁰	4.264X10 ⁻¹⁰
B2-C	632.62	1.104	3.782X10 ⁻¹⁰	1.91	5.384X10 ⁻¹⁰	6.260X10 ⁻¹⁰
B5-B	645.95	1.088	5.183X10 ⁻¹⁰	2.30	7.179X10 ⁻¹⁰	7.556X10 ⁻¹⁰
B2-A	660.65	1.071	7.582X10 ⁻¹⁰	3.04	1.052X10 ⁻⁹	1.108X10 ⁻⁹
B5-A	677.92	1.051	1.167X10 ⁻⁹	2.29	1.676X10 ⁻⁹	1.741X10 ⁻⁹
B5-T	695.15	1.033	1.624X10 ⁻⁹	2.58	2.677X10 ⁻⁹	2.852X10 ⁻⁹

TABLE IV - NUMERICAL CONDUCTIVITY DATA

<u>Crystal</u>	<u>Temperature</u>		σ <u>(ohm-cm)⁻¹</u>
	<u>T^oC</u>	<u>1000/T^oK</u>	
B2-T	499.6	1.2940	4.52X10 ⁻⁷
	527.0	1.2498	1.023X10 ⁻⁶
	549.8	1.2151	2.032X10 ⁻⁶
	574.8	1.1793	4.41X10 ⁻⁶
	599.7	1.1456	9.05X10 ⁻⁶
	624.6	1.1139	1.792X10 ⁻⁵
	649.9	1.0833	3.53X10 ⁻⁵
	675.1	1.0545	6.83X10 ⁻⁵
	701.5	1.0259	1.424X10 ⁻⁴
	724.6	1.0022	2.574X10 ⁻⁴
B2-B	500.7	1.2922	4.82X10 ⁻⁷
	527.6	1.2488	1.059X10 ⁻⁶
	550.0	1.2148	2.085X10 ⁻⁶
	574.3	1.1799	4.469X10 ⁻⁶
	599.9	1.1454	9.22X10 ⁻⁶
	624.5	1.1139	1.806X10 ⁻⁵
	649.9	1.0833	3.62X10 ⁻⁵
	674.9	1.0548	6.96X10 ⁻⁵
	701.0	1.0265	1.359X10 ⁻⁴
	724.8	1.0020	2.400X10 ⁻⁴

TABLE IV - NUMERICAL CONDUCTIVITY DATA

(Continued)

<u>Crystal</u>	<u>Temperature</u>		σ <u>(ohm-cm)⁻¹</u>
	<u>T^oC</u>	<u>1000/T^oK</u>	
B5-B	526.7	1.2502	1.109X10 ⁻⁶
	549.9	1.2150	2.128X10 ⁻⁶
	574.4	1.1798	4.32X10 ⁻⁶
	598.5	1.1472	9.22X10 ⁻⁶
	624.2	1.1144	1.817X10 ⁻⁵
	650.8	1.0823	3.67X10 ⁻⁵
	674.2	1.0556	6.70X10 ⁻⁵
B5-D	605.0	1.1388	1.034X10 ⁻⁵
	624.1	1.1146	1.752X10 ⁻⁵
	648.8	1.0847	3.48X10 ⁻⁵
	675.1	1.0546	6.74X10 ⁻⁵

TABLE V - GENERAL NUMERICAL DATA

<u>Crystal</u>	<u>B2-D</u>	<u>B2-B</u>	<u>B5-C</u>	<u>B2-C</u>
<u>Temperature Data</u>				
T ₀ (°C)	585.05	602.45	622.02	632.62
1000/T(°K)	1.165	1.142	1.117	1.104
V ₀ (mv)	24.272	25.018	25.851	26.301
W ₀ (ev)	1.81	1.81	1.81	1.81
H ₀ (°C/μv)	0.02347	0.02347	0.02358	0.02358
G ₀ (%/μv)	0.06696	0.06432	0.06183	0.06039
<u>Diffusion Coefficient Data</u>				
A(cm ²)	1.4072	1.2713	1.3146	1.2981
m ₀ (mg)	3.60	4.83	5.10	4.65
slope	0.01718	0.02587	0.01472	0.01073
time(eff)(min)	3190.79	3125.13	3018.36	2842.84
<u>Conductivity Data</u>				
A(cm ²)	1.4040	1.2818	1.3439	1.3162
L(cm)	0.3757	0.2243	0.3706	0.3500
G(cm ⁻¹)	0.2676	0.1750	0.2758	0.2659
R(initial)(ohms)	44,790	17,541	15,226	10,793
R(final)(ohms)	42,047	15,200	13,964	9,282
σ(initial)(ohm-cm) ⁻¹	5.974X10 ⁻⁶	9.977X10 ⁻⁶	1.811X10 ⁻⁵	2.464X10 ⁻⁵
σ(final)(ohm-cm) ⁻¹	6.364X10 ⁻⁶	11.51X10 ⁻⁶	1.975X10 ⁻⁵	2.865X10 ⁻⁵
D _σ (initial)(cm ² /sec)	1.237X10 ⁻¹⁰	2.107X10 ⁻¹⁰	3.910X10 ⁻¹⁰	5.384X10 ⁻¹⁰
D _σ (final)(cm ² /sec)	1.317X10 ⁻¹⁰	2.431X10 ⁻¹⁰	4.264X10 ⁻¹⁰	6.260X10 ⁻¹⁰
<u>Slicing Data</u>				
x(rms)(μ)	63.8	77.2	104.	127.
slice thickness(μ)	10.	16.	16.	16.
tilt error(μ)	30.	40.	32.	32.
loss of mass(mg)	0.61(gain)	2.21	0.78	0.65
<u>Errors</u>				
slicing(%)	2.05	2.59	0.99	0.67
cross section(X2)(%)	0.60	1.23	0.61	0.48
slope(%)	0.85	0.68	0.86	1.45
time correction(%)	0.12	0.12	0.13	0.17
loss of mass(%)	1.09	3.50	0.98	0.91
Total error in D*(%)	2.55	4.64	1.80	1.91
Total error in σ(%)	0.86	0.74	1.07	0.53
Total combined error(%)	2.69	4.70	2.09	1.98

TABLE V - GENERAL NUMERICAL DATA

(Continued)

<u>Crystal</u>	<u>B5-B</u>	<u>B2-A</u>	<u>B5-A</u>	<u>B5-T</u>
<u>Temperature Data</u>				
$T_0(^{\circ}\text{C})$	645.95	660.65	677.92	695.15
$1000/T(^{\circ}\text{K})$	1.088	1.071	1.051	1.033
$V_0(\text{mv})$	26.858	27.476	28.207	28.936
$W_0(\text{ev})$	1.81	1.81	1.81	1.81
$H_0(^{\circ}\text{C}/\mu\text{v})$	0.02364	0.02370	0.02375	0.02381
$G_0(\%/ \mu\text{v})$	0.05880	0.05711	0.05517	0.05336
<u>Diffusion Coefficient Data</u>				
$A(\text{cm}^2)$	0.8295	0.8831	1.0820	1.0682
$m_0(\text{mg})$	3.55	4.62	4.00	5.10
slope	0.01972	0.02241	0.01375	0.01428
time (eff) (min)	1624.89	1466.98	772.81	893.61
<u>Conductivity Data</u>				
$A(\text{cm}^2)$	0.8298	0.8829	1.0836	1.0098
$L(\text{cm})$	0.3572	0.1897	0.3831	0.4783
$G(\text{cm}^{-1})$	0.4304	0.2149	0.3535	0.4736
$R(\text{initial})(\text{ohms})$	13,290	4,600	4,839	4,134
$R(\text{final})(\text{ohms})$	12,629	4,366	4,657	3,878
$\sigma(\text{initial})(\text{ohm-cm})^{-1}$	3.238×10^{-5}	4.672×10^{-5}	7.305×10^{-5}	1.146×10^{-4}
$\sigma(\text{final})(\text{ohm-cm})^{-1}$	3.408×10^{-5}	4.922×10^{-5}	7.591×10^{-5}	1.221×10^{-4}
$D_{\sigma}(\text{initial})(\text{cm}^2/\text{sec})$	7.179×10^{-10}	1.052×10^{-9}	1.676×10^{-9}	2.677×10^{-9}
$D_{\sigma}(\text{final})(\text{cm}^2/\text{sec})$	7.556×10^{-10}	1.108×10^{-9}	1.741×10^{-9}	2.852×10^{-9}
<u>Slicing Data</u>				
$x(\text{rms})(\mu)$	99.6	114.	103.	130.
slice thickness (μ)	16.	24.	16.	24.
tilt error (μ)	32.	40.	24.	40.
loss of mass (mg)	0.95	1.57	1.05	1.59
<u>Errors</u>				
slicing (%)	1.08	1.42	0.66	1.08
cross section (X2)	0.52	1.20	0.96	1.04
slope (%)	0.85	0.93	0.77	0.51
time correction (%)	0.06	0.12	0.32	0.30
loss of mass (%)	1.77	2.22	1.79	2.01
Total error in $D^*(\%)$	2.30	3.04	2.29	2.58
Total error in $\sigma(\%)$	0.66	0.88	0.53	1.04
Total combined error (%)	2.40	3.17	2.35	2.78

Perfect Lattice

Frenkel Defects

Schottky Defects

Divalent Ion-Vacancy Complex

Vacancy Pairs

FIGURE 1. DIFFUSION MECHANISMS IN IONIC CRYSTALS

- A - Double Wall Inconel Tube
- B - Asbestos Shield
- C - Furnace
- D - 0.01" Platinum Foil
- E - Platinum Wire
- F - Single Crystal
- G - Quartz Crucible
- H - NaCl Melt
- I - Asbestos Block
- J - Thermocouple

FIGURE 2. CRYSTAL GROWING APPARATUS

- A - Spring (Low Temperature End)
- B - Lavite Insulator
- C - 1/4" Inconel Rod - High Lead
- D - 1/2" Dia. Quartz Insulator
- E - Thermocouple (Chromel-Alumel)
- F - Ceramic Thermocouple Insulator
- G - 1.30" Inconel Rod
- H - Quartz Plates
- I - 1/4" Inconel Plates
- J - 0.05" Platinum Electrodes
- K - NaCl Crystal
- L - 0.001" Platinum Electrode
- M - Thermocouple Junction

FIGURE 3. CRYSTAL HOLDER

- A - General Radio Beat Frequency Oscillator
B - General Radio Decade Resistance Box
C - NaCl Sample

FIGURE 4. SCHEMATIC DIAGRAM OF BRIDGE CIRCUIT

FIGURE 6. PER CENT CHANGE IN RESISTANCE WITH TIME

FIGURE 7. LOG OF ACTIVITY VS SQUARE OF PENETRATION DEPTH FOR 602°C

FIGURE 8.

Measured Self Diffusion Coefficients $D^*(\text{Na})$ of Radioactive Na^{22} and
 Calculated Self Diffusion Coefficients D_σ in Pure Single Crystals of
 NaCl as a Function of the Inverse Absolute Temperature. D_σ was
 Calculated by Using the Einstein Relation and the Measured Conductivity.

- D_σ calculated from the measured conductivity from
Figure 5
- Δ D_σ calculated from the initial conductivity of
the diffusion crystal
- ∇ D_σ calculated from the final conductivity of
the diffusion crystal
- I self diffusion coefficients $D^*(\text{Na})$ measured by
radioactive tracer method

FIGURE 8. DIFFUSION OF SODIUM IN PURE SODIUM CHLORIDE

FIGURE 9

Measured Self Diffusion Coefficients of Radioactive Sodium $D^*(\text{Na})$
and Chlorine $D^*(\text{Cl})$ in Single Crystals of Pure NaCl.

$D^*(\text{Na})$	diffusion of radioactive Na^{22} from present work
$D^*(\text{Cl})$	diffusion of radioactive Cl from work by Laurance ⁶
$0.781 D_\sigma$	calculated from the average con- ductivity curve given in Figure 5

FIGURE 9. DIFFUSION OF SODIUM AND CHLORINE IN PURE SODIUM CHLORIDE

FIGURE 10

Correlation Factors Calculated by Using the Measured Diffusion Coefficients of Radioactive Na^{22} from this Work and Radioactive Cl from Work by Laurance⁶.

$$\Delta \quad D^*(\text{Na})/D_{\sigma} \text{ (initial)}$$

$$\nabla \quad D^*(\text{Na})/D_{\sigma} \text{ (final)}$$

$$\square \quad D^*(\text{Na})/D_{\sigma} \text{ (average of initial and final)}$$

$$\circ \quad D^*(\text{Na})/D_{\sigma} \text{ (average from Figure 5)}$$

$$\blacktriangle \quad [D^*(\text{Na}) + D^*(\text{Cl})]/D_{\sigma} \text{ (initial)}$$

$$\blacktriangledown \quad [D^*(\text{Na}) + D^*(\text{Cl})]/D_{\sigma} \text{ (final)}$$

$$\blacksquare \quad [D^*(\text{Na}) + D^*(\text{Cl})]/D_{\sigma} \text{ (average of initial and final)}$$

$$\bullet \quad [D^*(\text{Na}) + D^*(\text{Cl})]/D_{\sigma} \text{ (average from Figure 5)}$$

FIGURE 10. CORRELATION FACTORS

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