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SELF-DIFFUSION OF THE SILVER ION IN PURE SILVER CHLORIDE

Max D. Weber

Nov., 1964

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Lawrence, Kansas

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Point Defects in Ionic Crystals

Robert J. Friauf
Principal Investigator

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TABLE OF CONTENTS

	page
I. Introduction.	1
II. Theory.	4
A. Conductivity and Diffusion.	4
B. Einstein Relation	5
C. Correlation Effect for the Vacancy Mechanism.	6
D. Displacement and Correlation Effects for the Interstitial Mechanisms	6
E. Total Tracer Diffusion.	9
F. Conductivity in Doped Crystals.	10
1. Teltow's Equations.	10
2. Kurnick's Analysis.	12
III. Experimental Procedure.	14
A. Crystals.	14
B. Conductivity.	15
C. Diffusion	16
D. Slicing and Counting.	18
E. Analysis of Data.	19
F. Errors.	21
IV. Experimental Results.	24
A. Conductivity.	24
B. Diffusion	24

TABLE OF CONTENTS (CONT)

	page
V. Analysis of Results.	26
A. Mobility	26
B. Comparison of Conductivity and Diffusion	27
C. Interstitialcy Mechanisms.	28
IV. Discussion of Results.	31
Appendix I	
Numerical Analysis of the Einstein Relation.	34
Appendix II	
Numerical Data	35-44
Bibliography	45

I. INTRODUCTION

It has been established through early theoretical calculations^{1,2} and later experimental work^{3,4,5,6} that Frenkel defects exist in AgBr and AgCl. Tubandt⁷ and Kurnick,⁸ who did transport experiments on these substances, found that the contribution to the total conductivity of the negative ion defects is negligible compared to the contribution coming from defects in the positive ion lattice.

Since the ionic conductivity and self-diffusion both occur because of these imperfections, one would expect the two quantities to be related. This can be seen by noting that diffusion represents a thermally induced random motion of ions, whereas conduction represents a drift superimposed upon this random motion by an electric field. The quantitative relationship is given by the normal (or macroscopic) Einstein relation:

$$\frac{D_{\sigma}}{\sigma} = \frac{kT}{Ne^2} \quad (1)$$

where D_{σ} is the diffusion coefficient calculated from the conductivity σ , k is Boltzman's constant, N is the number of atoms of charge e , and T is the absolute temperature.

If the conductivity σ and the radioactive self-diffusion coefficient D_T^* are now measured independently, it is found that the Einstein relation is not completely rigorous. Miller,⁹ Compton and Maurer,¹⁰ and Friauf¹¹ measured these quantities on AgBr and

AgCl, and found that D_T^* was appreciably less than D_G . It thus appears necessary to introduce a correction factor f into the Einstein relation. The quantity f is obtained experimentally by forming the ratio $f = \frac{D_T^*(Ag)}{D_G}$. The interpretation of this factor can be accomplished by making a microscopic investigation of the motion of the positive ion vacancies and interstitial silver ions through the silver half of the crystal lattice.

A number of experiments have shown that the defect mechanisms existing in AgBr are (1) positive ion vacancies, and (2) collinear and noncollinear interstitialcy jumps. These same diffusion mechanisms are proposed to occur in AgCl and are shown in figures 1a, 1b, 1c, and 1d.

Fig. 1: Defect mechanisms in AgCl; (1a) positive ion vacancy; (1b) collinear interstitialcy; (1c) noncollinear interstitialcy; (1d) direct interstitial jump.

A detailed discussion of these defect mechanisms and their effect on the quantity f will be discussed in the theory section.

The purpose of this thesis then is: (1) to measure the ionic conductivity σ and the radioactive tracer diffusion coefficient of the silver ions in pure AgCl crystals in the intrinsic temperature

region, and (2) to verify the existence of the proposed defect mechanisms in this substance; i.e. positive ion vacancies, and collinear and noncollinear interstitialcy mechanisms. It is also hoped that it will be possible to determine the activation energy for each of the two interstitialcy jumps shown in Fig. 1.

II. THEORY

A. Conductivity and Diffusion

The concentration of Frenkel defects existing in thermal equilibrium in pure AgCl at a certain absolute temperature T is given by

$$n_v = n_i = c_0 \exp\left(-E_F / 2kT\right), \quad (2)$$

where C_0 is a constant, E_F is the energy required to form a defect pair, and k is Boltzmann's constant. The preservation of electrical neutrality at equilibrium requires that n_v , the concentration of positive ion vacancies, be equal to n_i , the concentration of interstitial ions.

The conductivity σ_v due to the positive ion vacancies is given by¹²

$$\sigma_v = en_v \mu_v = c_0 \nu_{ov} e^2 a^2 \exp\left(-\frac{U_v + E_f/2}{kT}\right), \quad (3)$$

where ν_{ov} is the vibrational frequency of a silver ion next to the vacancy, and a is the jump distance. A similar contribution to the conductivity comes from the interstitial ions.

The microscopic diffusion coefficient for a certain type of defect j is given by:

$$d_j = \frac{1}{6} \nu_j a^2 \exp\left(\frac{U_j}{kT}\right). \quad (4)$$

The macroscopic diffusion coefficient is found by considering the probability of a defect being next to a tracer ion and using Fick's first law of diffusion. Thus

$$D_j = \frac{n_j}{N} d_j = a^2 \nu_{oj} c_o \exp\left(-\frac{U_p + E_F/2}{kT}\right), \quad (5)$$

where N is the concentration of silver ions in the crystal. The total diffusion coefficient D includes the effect of both positive ion vacancies and interstitial silver ions.

B. Einstein Relation

By considering the nature of electrical conductivity and self-diffusion, it is seen that these two quantities are related. The quantitative relationship is given by the Einstein relation.

$$\frac{\mu_j}{d_j} = \frac{e_j}{kT}, \quad (6)$$

where d_j is the microscopic diffusion coefficient of a defect of type j , having a mobility μ_j , and a charge e_j . Experimentally, however, one measures macroscopic quantities. The total conductivity (σ) and the diffusion coefficient D_σ are given by

$$\sigma = n_i e_i \mu_i + n_v e_v \mu_v \quad (7)$$

and

$$D_\sigma = \frac{n_i}{N} d_i + \frac{n_v}{N} d_v; \quad (8)$$

combining the three equations above, one obtains the macroscopic

Einstein relation (see eq. 1).

As has been mentioned in the introduction, experimental results deviate appreciably from this relation. If one considers that the conductivity experiment follows the motion of vacancies and interstitials, whereas the diffusion experiment measures the displacement of the tracer ions which move by means of the vacancies and interstitials, it becomes apparent that it is the equation for the diffusion coefficient which must be corrected. A theoretical interpretation of an experimentally measured correction factor $f = \frac{D_T^*}{D_0}$ is made by analyzing the individual defect mechanisms shown in fig. 1.

C. Correlation Effect for the Vacancy Mechanism

The theory of correlation effects, as first introduced by Bardeen and Herring,¹³ proposes that successive jumps of a tracer atom moving by means of the vacancy mechanism (see fig. 1a) are directionally correlated. A numerical investigation by Compaan and Haven,¹⁴ in which diffusion was treated as a random walk problem, produced the value $f_v = 0.781$ for the correction due to this effect in the face centered cubic lattice for Ag ions in AgCl.

D. Displacement and Correlation Effects for the Interstitial Mechanisms

The displacement effect arises from the fact that the effective displacement of the tracer ion during a collinear or noncollinear jump is appreciably less than the displacement of positive charge during this jump. During a collinear or noncollinear jump, an

interstitial tracer ion displaces a neighboring Ag ion into another interstitial site, as shown in figures 1b, and 1c for the case of a plane square lattice.

It is seen that during a collinear jump, for instance, the tracer is effectively displaced only half as far as the charge. The displacement effect, neglecting correlation effects for the moment, is represented by

$$\frac{D_T^*}{d_i} = \frac{1}{2} \frac{n_i}{N} = f_i' \frac{n_i}{N}, \quad (9)$$

where f_i' is the contribution of the displacement effect to the total correction factor f_i . There is also some correlation in this case, but only one-half the time. When the tracer lands in a lattice site, the direction of its next jump depends upon the position of the displaced interstitial ion, and correlation exists. If, however, the tracer lands in an interstitial site, no preferred jump direction exists, and therefore no correlation is present. This correlation factor (f_i'') is also obtained using the random walk treatment of diffusion. The total correction factor for the collinear interstitialcy jump, including both the displacement and correlation effects, is given by

$$\frac{D_T^*}{d_i} = f_i' f_i'' \frac{n_i}{N} = f_i \frac{n_i}{N}. \quad (10)$$

A similar analysis can be done for the noncollinear interstitialcy mechanism. The result is the same general expression for $\frac{D_T^*}{d_i}$ but with different values of f_i' and f_i'' .

The direct interstitial jump would seem another obvious choice for a defect mechanism in AgCl. In this case, however, there is no displacement effect since both f_i' and f_i'' are equal to 1; moreover, this diffusion mechanism has been shown to be energetically unfavorable by (Hove).¹⁴ The correction factors arising from the correlation and displacement effects for the different defect mechanisms in AgCl have been calculated by Compaan and Haven.¹⁵ The results for the fcc lattice are given in Table 1.

The case must also be considered in which both collinear (type 1) and noncollinear (type 2) interstitial jumps occur simultaneously in the Ag half of the lattice with jump frequencies ν_1 and ν_2 respectively. The amount of the correction f_i in this case will depend on the geometry and on the relative jump frequency ($K = \nu_1 / \nu_2$) of the two types of jumps; the two extremes $K = \infty$ and 0 represent the existence of type 1 or type 2 jumps only, respectively. To determine f_i the diffusion coefficients are related to the mean square displacement of the diffusing entities. It is found that

$$\frac{D_T^*}{d_i} = \frac{[(r_{Ti})^2]_{av}}{[r_i^2]_{av}} = \frac{(r_T^2)_{av}}{(r_i^2)_{av}} \frac{(r_T^*)^2_{av}}{(r_T^2)_{av}} = f' f'' \frac{n_i}{N} = f_i \frac{n_i}{N}, \quad (11)$$

where

$$f_i' = \frac{2\nu_1 b_1^2 + \nu_2 b_2^2}{\nu_1 a_1^2 + \nu_2 a_2^2} = \frac{1}{2} \frac{K+1}{K+2/3}, \quad (12)$$

here values of a_i and b_i for the displacements of the interstitial and tracer ions respectively have been inserted already. Compaan

and Haven also found that

$$f_i'' = 1 - (\kappa + 1/3)^2 (\kappa + 1)^{-2} P, \quad (13)$$

where an interpolation formula for P is estimated by Haven as

$$P = \frac{1}{3} \left(\frac{\kappa + 1}{\kappa + 11/9} \right). \quad (14)$$

Table 1

Mechanism	f_i'	f_i''	f_i
Vacancy		0.781	0.781
Direct Interstitial	1	1	1
Collinear Interstitialcy	1/2	2/3	1/3
Noncollinear Interstitialcy	3/4	32/33	0.7273
Mixed Interstitialcy ($V_1=V_2$)	3/5	0.8782	0.5269

E. Total Tracer Diffusion

The total tracer diffusion coefficient can now be written as

$$D_T^* = f_v \frac{n_v}{N} d_v + f_i \frac{n_i}{N} d_i \quad (15)$$

and the corrected Einstein relation now reads

$$\frac{D_T^*}{\sigma} = \left(\frac{f_v + \phi f_i}{1 + \phi} \right) \frac{kT}{Ne^2}, \quad (16)$$

where $\phi = \frac{\mu_i}{\mu_v}$ is the ratio of the two mobilities.

The mobilities of the collinear and noncollinear jumps are obtained by the following considerations. The total mobility due to the interstitialcy defects is given by

$$\mu_i = \mu_1 + \mu_2. \quad (17)$$

The microscopic Einstein relation can now be utilized together with $\sigma_i = n_i e_i \mu_i$ to give

$$\mu_i = \mu_2 \left(\frac{3}{2} K + 1 \right), \quad (18)$$

so that, once the quantity K is known, μ_1 , and μ_2 can be determined from μ_i .

F. Conductivity in Doped Crystals

1. Stasiw and Teltow's Equations¹⁶

It is seen in the previous section that in order to calculate the value of f the values of the mobilities of the Ag ion vacancies and interstitial ions must be known. This knowledge can be obtained by making conductivity measurements on AgCl crystals doped with a known concentration of divalent ions. Teltow¹⁷ has investigated AgBr and AgCl in this manner by using crystals containing small concentrations of Cd^{++} ions. This treatment is given below.

First, since only dilute concentrations of Cd^{++} ions were introduced, the laws of ideal solutions were assumed to apply. The law of mass action requires that

$$n_i n_v = n_o^2, \quad (19)$$

$$n_o = C \exp \left(- \frac{1}{2} \frac{E_F}{kT} \right), \quad (20)$$

Electrical neutrality requires that

$$y + n_i = n_v, \quad (21)$$

where y is the concentration of divalent ions. By combining the above two equations, one obtains

$$n_i = -\frac{y}{2} + \sqrt{(y/2)^2 + n_o^2} \quad (22)$$

and

$$n_v = \frac{y}{2} + \sqrt{(y/2)^2 + n_o^2}. \quad (23)$$

The ratio (2) of the conductivity of a doped crystal to the conductivity of a pure crystal (σ_o) is given by

$$\begin{aligned} z = \frac{\sigma(y)}{\sigma_o} &= \frac{en_v\mu_v + en_i\mu_i}{en_o\mu_v + en_o\mu_v} = \\ &= \sqrt{(y/2n_o)^2 + 1} - \frac{y}{2n_o} \left(\frac{\phi + 1}{\phi - 1} \right). \end{aligned} \quad (24)$$

Since $\phi > 1$, an equation for a parabola is obtained if z is plotted vs. y . The desired quantities ϕ and n_o were obtained by Teltow by graphical evaluation of the two quantities

$$\left(\frac{dz}{dy} \right)_{y=0} = \left(\frac{\phi - 1}{\phi + 1} \right) \frac{1}{2n_o} \quad \& \quad \frac{2\sqrt{\phi}}{1 + \phi}. \quad (25)$$

Some scatter in the results is to be expected in the above procedure; the reason is, of course, the uncertainty of determining the slope of the curve at $y = 0$ and the minimum of the relative conductivity itself.

2. Kurnick's Analysis

It was found to be desirable to reanalyze Ebert and Teltow's data using a method devised by Kurnick.¹⁸ The same assumptions are made in this case as before; it is therefore possible to start with the expression for the relative conductivity (z), as shown in equation 24. Kurnick's method also uses a graphical analysis. The above equation can be transformed into an equation for a straight line given by:

$$\frac{X}{A} + \frac{Y}{B} = 1. \quad (26)$$

The transformation is obtained by letting

$$X = \frac{1}{y} \left(\frac{1}{z} - z \right) \quad (27a)$$

and

$$Y = \frac{y}{z}. \quad (27b)$$

Then the intercepts are then given by

$$A = \frac{1}{n_o} \left(\frac{\phi - 1}{\phi + 1} \right) \quad (28a)$$

and

$$B = n_o \left(\phi - \frac{1}{\phi} \right). \quad (28b)$$

Thus if A and B are known, the desired quantities n_o and ϕ can be found by solving the above two equations simultaneously.

The result is

$$\phi = \left(1 + \frac{AB}{2}\right) \pm \sqrt{\frac{AB}{2} \left(1 + \frac{AB}{2}\right)} \quad (29a)$$

and

$$n_o = \left(\frac{\phi - 1}{\phi + 1}\right) . \quad (29b)$$

III. EXPERIMENTAL PROCEDURE

A. Crystals

Pure silver chloride was precipitated in the laboratory using Baker's analytical reagent grade materials. Silver nitrate salt was dissolved in a 2 molar solution of nitric acid. This solution was then heated and poured through a dropping flask into a 0.5 molar solution of HCl. The precipitate was thoroughly washed with distilled de-ionized water, and then dried in an oven at 50-60° C for about 2½ days; frequent stirring kept the precipitate from caking. All work during this process was done under red-filtered light because of the sensitivity of AgCl to ultraviolet rays.

Single crystals were grown in a vacuum from the melt using Bridgman's technique. A quartz tube 0.14 cm in diameter was filled with AgCl and degased overnight at 350° C. The tube was then sealed off with a torch under a vacuum of 2×10^{-5} microns. The experimental arrangement shown in fig. 2 was now used to heat the AgCl to 500° C; (45° above T_m). By allowing the melt to remain at this temperature for approximately 8 hours, small bubbles, formed because of the granular nature of the AgCl were eliminated. A single crystal was now grown by lowering the melt through the steep temperature gradient at the bottom of the furnace at a rate of 0.63 cm/hr.

Because AgCl crystals do not cleave, cylindrical samples roughly 1 cm in all dimensions were machined on a lathe. Smooth

1. Thermocouple
2. 0.50 in. I.D. Quartz Tube
3. Furnace 1
4. Inconel Heat Sink
5. Thermocouple
6. Furnace 2
7. Asbestos
8. AgCl Melt
9. Single AgCl Crystal
10. Thermocouple
11. 1/4 in. Diam. Quartz Rod

Fig. 2 Crystal Growing Apparatus

surfaces on the faces of these cylinders were obtained by micro-toming. It was usually possible to obtain 5 of these samples from a single crystal.

B. Conductivity

Electrodes were applied to each sample by vacuum-evaporating a 2000 Å thick layer of Ag onto each cylinder face; these surfaces were then painted with Dupont Silver conducting paint (electronic grade 4817). Excess conducting paint on the cylinder sides, if there was any, was scraped off with a razor blade. The dimensions of each sample were determined to five places with a measuring microscope. An average value taken from 10 readings was found for each dimension.

Purity checks on grown crystals were made by measuring the conductivity of two samples; one taken from each end of a crystal. An average conductivity curve was then established by combining the conductivity measurements from three different crystals. The conductivity at a certain temperature was found from the equation $\sigma = 1/AR$, where l is the length of a cylindrical sample of cross-section A , and R is the measured resistance of the sample.

Difficulty arose with some of the early conductivity measurements. Starting at approximately 400° C local melting of the sample sometimes occurred next to the electrodes; the samples were also very yellow, and were sometimes only partially transparent after a σ -run. These difficulties were overcome by slightly changing the sample holder; see fig. 3. Solid silver cylinders 1 cm long were introduced next to each sample end, and the silver plate

1. Thermocouple (Chromel - Alumel)
2. Ceramic Thermocouple Insulator
3. Copper Wire (High Lead)
4. Brass Plate
5. 1/8" Cylindrical Brass Can
6. Baked Lavite Insulating Pieces
7. 1/4" Brass Nuts
8. 13/16" Diam. Brass Plate
9. 13/16" Diam. Brass Cylinder (Heat Sink)
10. 9/32" Diam. Stainless Steel Spring
11. 1/2" O.D. Quartz Tubing
12. 0.72" O.D. Brass Cylinder
13. 0.72" O.D. Silver Cylinder
14. 0.72" Diam. Silver Electrode
15. AgCl Sample
16. 1/4" S.S. Rods
17. Thermocouple Junction
18. 17/32" Diam. Silver Plate
19. Copper Wire

Fig. 3 Crystal Holder.

(item 13) was introduced loosely instead of being silver-soldered to the bottom plate. It is believed that the original trouble was caused mainly by the close proximity of the silver solder to the sample.

Conductivity measurements were made over the intrinsic temperature range from 300 to 400° C at 20° intervals. Equilibrium was insured by regulating the sample temperature with a Brown controller to $\pm 1^\circ$ C for 2 hours. The sample temperature was measured to five places with a Leeds & Northrup millivolt potentiometer.

An A-C bridge method shown in fig. 4 was used to measure the conductivity. The apparatus utilized was a General radio 716-C Capacitance Bridge, with a General Radio 1231-B amplifier and null detector. The electrical circuit also included a General Radio type 1302A beat frequency oscillator, so that resistance measurements could be made between 1 and 10 KC. A General Radio Resistance Box was used in parallel with a variable capacitor, and an oscilloscope served as the null detector of the circuit. The two upper arms of the bridge were kept in a 1:1 ratio, so that the sample resistance R_s could be read directly when a null was obtained.

C. Diffusion

The radio-isotope Ag-110 ($\frac{1}{2}$ life = 270 days) was used for the diffusion measurements. It was obtained from the Oak Ridge Lab. in the form of AgNO_3 dissolved in a 2 molar nitric acid solution. The activity at the time of the experiments was about 0.2 mc/ml.

A small amount of Ag^*Cl (0.1 mc) was precipitated in a platinum evaporating tray; crushed dry ice was added, freezing the solution,

- 1. General Radio Beat Frequency Oscillator
- 2. General Radio Decade Resistance Box
- 3. AgCl Sample

Fig. 4 Schematic Diagram of Bridge Circuit

the excess water and acid were removed with a vacuum system. All surfaces of the samples except one end were wrapped with Scotch tape and were then mounted 5 cm above the bottom of the evaporating tray. About 1 μ c of the radioactive AgCl deposited upon each sample during the vacuum evaporation that followed, which was effected by heating the tray.

Electrodes were now applied onto the samples as previously described, so that the conductivity could be checked during a diffusion run.

The crystal was now placed into the holder, its radioactive end face down, next to the thermocouple junction. The heating and cooling times amounted to about $1\frac{1}{2}$ hours from room to the diffusion temperature. During the rapid part of the heating and cooling curves, the sample temperature was read every minute; at the equilibrium temperature, it was read every hour. A Brown recorder controlled the furnace temperature to $\pm \frac{1}{2}^{\circ}$ C; the inside thermocouple drifted only $\frac{1}{2}^{\circ}$ C if the control temperature was adjusted every 3 hours.

Diffusion measurements were made in the intrinsic temperature region from 300-435 $^{\circ}$ C at 20 $^{\circ}$ intervals. The diffusion time at a specific T was estimated from the equation

$$x_{rms} = \sqrt{2Dt}, \quad (30)$$

where D is found from the Einstein relation using the measured conductivity. The diffusion times used ranged from 8 to 13 hours. They were limited at the higher temperatures especially because of the large x_{rms} distances.

D. Slicing and Counting

After a diffusion sample had cooled, its silver electrodes were removed with heated nitric acid. The crystal was next sectioned on a microtome. The radioactive end of the sample was aligned parallel to the cutting plane of the knife by means of an optical lever and the adjustment screws of the microtome. Usually, it was possible to obtain a full cut over the crystal surface with the second slice. Misalignment was estimated by the cutting pattern, and a correction by Shirn, Wajda and Huntington¹⁹ was applied. Ten micron slices were taken and brushed into a 2 cc planchet. The slices came off very nicely in the form of small rolls. Usually 15 planchets, each containing around 100μ were prepared. For an accurate determination of the amount of material, each planchet was weighed on a balance having a sensitivity of 0.01 mg.

The planchets were now prepared for counting. In order to obtain sufficient counting consistancy, it was desirable to have the AgCl material distributed uniformly in each planchet. The sliced material was dissolved in a 6M solution of NH_4OH in each planchet and dried in an oven at 50°C . Freeze drying was also attempted, but proved unsatisfactory.

The activity of each planchet was now determined with a Geiger-tube. The background was kept to a fairly constant 30 cpm by a thick lead shield. In order to keep the statistical counting error to less than 1%, a minimum of 10000 counts was counted in a

minimum time of 8 minutes. The total counting time ranged from 6 hours to about 30 hours at the high temperatures.

E. Analysis of Data

The procedure for analyzing the data can best be presented by first looking at the solution to the diffusion equation,

$$\ln n^* = \text{const.} + x^2/4Dt, \quad (31)$$

where n^* is the concentration of radioactive atoms at a penetration depth x , after a diffusion time t . A diffusion profile was obtained from the counting data by plotting the $\log_{10}$ of the concentration vs. the square of the penetration depth.

The thickness of each slice is determined from its mass by

$$x_i = m_i / \rho A, \quad (32)$$

where m_i is the mass of AgCl for the i th slice, ρ is the density of the material, and A is the cross-sectional area of a sample. A reduced thickness, which takes into account the variation of mass for successive slices, is given by

$$r_i = \frac{x_i}{x_0} = \frac{m_i}{m_0}. \quad (33)$$

Here x_0 is the mean slice thickness and m_0 is the corresponding mass. Because of the finite slice thickness, the radioactivity for each slice was considered to be concentrated at the center of that slice. The total penetration depth to the center of the i th slice is

$$W_i = \sum_{j=1}^{i-1} r_j + r_i \cdot \quad (34)$$

The diffusion profile equation now becomes

$$\ln c_i = \text{const.} + \frac{(m_o/\rho A)^2}{4Dt} \left(\frac{m_i}{m_o} \right)^2. \quad (35)$$

Here C_i is the concentration of radioactive atoms per slice and is given by

$$c_i = \left(\frac{G_o}{G_i} \frac{P_i}{t_i} - B_o \right) \frac{m_o}{m_i}. \quad (36)$$

The factor $\frac{G_o}{G_i}$, which is the ratio of a standard count rate G_o taken at the beginning of the counting process to a subsequent count rate G_i taken every third slice, eliminates any slow variation in the Geiger tube counting rate. The observed number of counts P_i in time t_i is also corrected for background B_o . The diffusion coefficient is then obtained from the slope of the diffusion profile,

$$D^* = \frac{(m_o/\rho A)^2}{(4t \text{ slope})}. \quad (37)$$

Because the temperature is not constant during the entire diffusion run, an effective diffusion time $t_{\text{eff.}}$ has to be calculated from

$$t_{\text{eff.}} = \int_0^\infty \frac{D(T)}{D(T_o)} dt, \quad (38)$$

where $D(T_o)$ is the diffusion coefficient at the equilibrium temperature. A first estimate of $D(T_o)$ is made using the activation energy

found from conductivity measurements; a second and final value of $D(T_0)$ is then obtained utilizing the activation energy found from the radioactive diffusion measurements.

Two computer programs were written by Dr. Friauf to analyze the data. A least-squares calculation is used to obtain a best straight line through the individual points of the diffusion profile. The slope and its % error are found in his calculation. The integral for t_{eff} is determined graphically by the computer by utilizing the measured variation of the temperature T with the time t during a diffusion run.

F. Errors

Two sources of error occurred in measuring the conductivity.

1. Errors in Measuring Crystal Dimensions

The error in the cross-section was less than 0.3% in all cases except one; here an error of 0.7% occurred; the reason for this was that this crystal was used for 2 different diffusion runs thus slightly changing its shape.

2. Error in the Resistance

This error was confined to the accuracy of the resistance boxes used. General Radio resistance boxes with a specification of $\pm 0.1\%$ were used.

In the measurement of the diffusion coefficient, several sources of errors are encountered.

1. Errors in T

The absolute calibration error of the Chromel alumel

thermocouple used was 0.07 mv (1.8° C). The same thermocouple was used for both σ and D^* measurements. In the comparison of these measurements then, these errors tended to cancel out.

2. Error in the Diffusion Time

These corrections to the eff time were found by taking $1/5$ of the time correction. The time correction was obtained by considering the difference in area of the approximated square curve and the actual time curve.

3. Errors in the Slope B

Errors here come from statistical errors in counting and weighing errors. The first was kept to a minimum by observing 10000 counts per slice; the second was kept low by the large amount of mass used per slice.

4. Errors in the Cross-Section of the Crystal

These errors were kept small by using crystal cross-sections of about 0.7 sq. cm; the dimensions were measured to 5 places with a measuring microscope. The errors in the cross-sections of the samples ranged from 0.1 to 0.67%; the latter error is rather high and surely occurred only because sample 3a was used for two diffusion measurements, thus slightly changing its shape.

5. Errors in Slicing

These errors stemmed from the misalignment of the microtome knife and because of the finite slice thickness. The following expression due to Shirn, Wajda, and Huntington¹⁹ was used to estimate the possible error.

$$\frac{\Delta D}{D} = \frac{1}{12} \left(\frac{s}{x_{rms}} \right)^2 + \frac{1}{12} \left(\frac{m}{x_{rms}} \right)^2, \quad (39)$$

where S is the slice thickness and m is the alignment error.

IV. EXPERIMENTAL RESULTS

A. Conductivity

The conductivity measurement results are shown in figure 5. At least one sample from each crystal, taken from the most impure end, was used to check the impurity. The curve in fig. 5 represents the mean of 5 conductivity curves taken from 3 different crystals. Samples from these same crystals were later used for the diffusion measurements. Conductivity results obtained by Ebert and Teltow²⁰ for pure AgCl are also shown for comparison purposes. The two curves show excellent agreement in the intrinsic temperature region, which is considered here.

During each conductivity experiment, a check on the change of σ with time was made. The results of this test indicated that the conductivity did not vary appreciably over the longest diffusion time used.

B. Diffusion Results

A typical diffusion profile obtained in these experiments is shown in Fig. 6. The graph represents a plot of the radioactive concentration as a function of the square of the penetration distance of the tracer atoms. A least squares calculation determined the best straight line through the experimental points. When the deviation of a point from this line was more than twice the r.m.s.

Fig. 5 Temperature Behavior of the Conductivity in Pure AgCl.

Fig. 6 Log of Activity Vs. Square of The Penetration Depth.

deviation, the point was dropped and a new least squares fit was made without this point.

In all there were eight diffusion runs made on samples taken from 3 crystals. Numerical data for each run are given in the Appendix.

Figure 7 shows the results of the diffusion of Ag^+ in AgCl as a function of temperature. A smooth curve was drawn through the data; the deviation from a straight line is attributed to the fact that 2 exponential terms contribute to the diffusion coefficient. The dotted line represents diffusion results obtained by Compton and Maurer. The agreement between the two measurements is quite good except for the points at 320 and 342° C, which exhibit a noticeable deviation from the diffusion curve. This difference is appreciably larger than the experimental errors and is believed to be due in part to a difference in experimental technique.

For comparison purposes fig. 7 also shows the diffusion coefficient D_σ , which is obtained from σ by means of the Einstein relation; D_σ , as calculated from Compton and Maurer's conductivity results on pure AgCl is also presented.

Fig. 7 Self Diffusion of Ag in AgCl.

V. ANALYSIS OF RESULTS

A. Mobility

Before any thorough analysis of the experimental results can be made, the values of the mobility ratio $\phi = \frac{\mu_i}{\mu_v}$ must be known as a function of the temperature. The results obtained by Ebert and Teltow¹⁹ are shown in fig. 8. The values of ϕ which are used in subsequent calculations, however, were obtained by analyzing Ebert and Teltow's data by Kurnick's method, which is described in the theory section.

In this method, the observed values of z and y at a given temperature are used to calculate X and Y from equations 23a and 23b; if the assumptions of an ideal, dilute solution are valid, a plot of X vs. Y should give a straight line. Figure 9 shows a typical plot of this kind. For concentrations of divalent ions greater than 0.1%, the deviation of the data points from a straight line shows that the original assumptions are no longer valid. In many of these plots, the point corresponding to the lowest concentration ($y = 0.0022$ mole %) also differs appreciably from the straight line; this is probably due to impurity effects which may occur at such a low concentration. Therefore the only points used in the analysis are the four remaining points corresponding to concentrations of $y = 0.046, 0.022, 0.01, \text{ and } 0.0046$ mole %. A least squares line through these points is then used to determine

Fig. 8 Temperature Dependence of the Mobility Ratio

Fig.9 Analysis of Conductivity Data at 350 °C

the mobility ratio ϕ and the equilibrium concentration of defects n_0 from the intercepts A and B. It is not possible to do this analysis for $T = 425^\circ \text{C}$ however, because of the wide scatter in the values of X and Y; values of ϕ at this and any higher temperature were therefore extrapolated from the least squares line.

The mobilities of the vacancy and the interstitial defects are calculated using the equation for the conductivity of the pure substance,

$$\sigma_0 = en_0\mu_i + en_0\mu_v = en_0\mu_v(1 + \phi), \quad (40)$$

from which

$$\mu_v = \frac{\sigma_0}{en_0(1 + \phi)} \quad \& \quad \mu_i = \phi\mu_v. \quad (41)$$

The mobility values are plotted as a function of $10^3/T$ in fig. 10. For comparison purposes, Ebert and Teltow's values are also shown on this graph. The smooth behavior of the results between 300 and 400°C is encouraging, and it appears that the values of ϕ , μ_i , and μ_v have some significance in this range. The mobilities at 420 and 435°C , however, must be obtained from the extrapolated values of ϕ .

B. Comparison of Conductivity and Diffusion

The results of the conductivity and diffusion measurements obtained from these experiments are compared in fig. 11, in which the total correction factor $f = D_{\text{Ag}^*}/D_\sigma$ is plotted as a function of the temperature. A smooth curve has been drawn through the data points.

Fig.10 Temperature Dependence of the Mobilities

Fig.11 Theoretical & Experimental Correction Factor Vs. Temperature

It may be informative at this point to compare the experimental f curve with other, theoretical f curves, which can be calculated separately for each proposed defect mechanism by the following procedure. First, since the effect arising from the vacancy jumps is well known, the partial correction factor $f_v = 0.781$ can be substituted into the equation for the total correction factor to give

$$f = \frac{f_i \phi + 0.781}{1 + \phi} \quad (42)$$

With the mobility ratio obtained from the preceding analysis, the theoretical f curves are found by substituting the appropriate values of f_i (see table 1) for a given interstitial mechanism into the above equation.

The direct interstitial jump is pretty well ruled out by a comparison of the theoretical and experimental f curves. It appears, furthermore, that the two interstitialcy mechanisms do occur simultaneously, as proposed, with the number of collinear interstitialcy jumps predominating over the number of noncollinear jumps.

C. Interstitialcy Mechanisms

The effect produced by the two interstitialcy mechanisms alone is found by solving equation (42) for f_i ,

$$f_i = \frac{1}{\phi} [(1 + \phi)f - 0.781] \quad (43)$$

The result of this calculation is shown in fig. 12; again the theoretical results by Compaan and Haven are introduced for comparison purposes.

Fig. 12 Interstitial Correction Factor f_i as a Function of T (°C)

The next step in the analysis is to try to find the relative jump frequency $K = \nu_1/\nu_2$ of the collinear compared to the noncollinear jumps as a function of the temperature. This is done by solving equation 11 for K in terms of f_i .

$$K = \frac{1}{2(3f_i - 1)} \left[(9 - 17f_i) \pm \sqrt{25f_i^2 - 26f_i + 17} \right]. \quad (44)$$

The expected temperature dependence of K is given by

$$K = \frac{\nu_1}{\nu_2} = \frac{\nu_{10} \exp(-U_1/kT)}{\nu_{20} \exp(-U_2/kT)} = K_0 \exp(-\Delta U/kT), \quad (45)$$

where $\Delta U = U_1 - U_2$ is the difference in activation energies.

The log of K is thus plotted as a function of $10^3/T(^{\circ}\text{K})$ at each diffusion temperature, as shown in fig. 13. It is seen that an appreciable scattering of the K values exists, and at this point one should start to wonder whether the calculations in this analysis should be carried out any further. Possible reasons for this scatter will be discussed in the next section.

Once the relative jump frequency is known as a function of the temperature, the calculations of μ_1 and μ_2 can be carried out in the manner described in the theory section; the results are graphed in fig. 14. The scatter in the points on this plot is carried over from the scatter in K .

If least squares lines are drawn through the mobility points in each case, the activation energy for each interstitialcy mechanism can be calculated from the slope of the appropriate line. The obtained values for the activation energies are $U_1 = 0.11$ ev and $U_2 = -0.08$ ev for the collinear and noncollinear jumps respectively.

Fig. 13 Relative Jump Frequency $\kappa = \nu_1/\nu_2$ Vs. T

Fig. 14 Collinear (μ_1) & Noncollinear (μ_2) Interstitialcy Mobilities.

These values check pretty well with the observed difference in activation energies, $\Delta U = 0.20$ ev obtained from K , but the occurrence of a negative activation energy indicates that something is wrong, as discussed in the next section.

IV. DISCUSSION OF RESULTS

The conductivity curve which was obtained for pure AgCl in this experiment is in excellent agreement with Teltow's measurements; this is demonstrated in fig. 7, which compares Teltow's values of D_o with those due to Compton and Maurer as well as with our values. The reason for the appreciable difference between Compton and Maurer's conductivity measurements compared to our results is not understood, but may be the result of the different surroundings of the sample. It is also seen in fig. 7 that the radioactive tracer diffusion coefficient D_T^* measured by Compton and Maurer agrees very well with our values.

The results of a theoretical investigation by Hove²⁰ of the different defect mechanisms proposed for AgCl predict activation energies of 3 ev for the direct interstitialcy jump, -0.1 to 0.4 ev for the collinear, and 0.8 ev for the noncollinear interstitialcy jumps. On the basis of these values, it is clear that the direct interstitial jump cannot compete with the two interstitialcy mechanisms because of its much higher activation energy. Furthermore, it may be expected that both the collinear and noncollinear interstitial jumps occur simultaneously in the AgCl lattice, with the number of collinear interstitialcies predominating because of their lower activation energy. In addition, as the temperature increases, more of the noncollinear interstitial jumps will be activated and will in turn produce an increase in the overall value of the correction

factor f_i .

An experimental verification of these theoretically expected results has been done by Friauf,¹⁷ who made conductivity and radioactive tracer diffusion measurements on pure AgBr crystals. These experiments yielded values of $U_1 = 0.078$ ev and $U_2 = 0.225$ ev respectively for the collinear and noncollinear jumps, which is in reasonable agreement with Hove's results for AgCl. Qualitatively speaking, at least, the results which are to be theoretically expected as described in the preceding paragraph are also verified by the experimental results of this work for AgCl. This is indicated in fig. 11, by the position of f_{exp} relative to the theoretical f curves.

Difficulty is encountered, however, in the quantitative analysis of the results. The "wrong" temperature dependence of f_i in fig. 12, (i.e. a decrease of f_i with increasing T) is obtained from the measured values of f , instead of the theoretically predicted increase. This "wrong" temperature dependence causes a wrong slope to be obtained in fig. 13; this in turn finally causes the activation energy of one of the interstitialcies to turn out negative, a physically unreasonable result.

There are two possibilities as to how the encountered difficulty arises. First, there is still some uncertainty in the mobility ratio ϕ shown in fig. 8. Secondly, the source of the trouble may be in the diffusion measurements; the good agreement between Compton's and our diffusion results should be borne in mind, however. Because of the nature of the calculations, small errors in ϕ as well as small variations in f_{exp} are blown up considerably in the calculation

of f_i , and again when the relative jump frequency (K) is found, which is a function of f_i .

In Hove's theoretical calculations, he obtained a negative activation energy for an assumed equilibrium position of a defect complex moving by the collinear interstitialcy mechanism. This result simply means that the assumed equilibrium position of the defect complex does not correspond to the lowest energy state of the system and that different equilibrium positions have to be tried. A possibility is the dumbbell model, in which the two Ag ions involved occupy sites at equal distances from a normal Ag-ion position on the diagonal of a unit cell of the Ag lattice. Unfortunately, it is not possible to distinguish between these possibilities by diffusion measurements alone since the geometry of the jump processes leads to exactly the same correlation and displacement factors for the two cases.

In order to have more confidence in the results of future experiments of the type done in this thesis, the following suggestions are made. First, a thorough investigation of the relative conductivity must be made for many different concentrations of divalent ions, especially in the region where the laws of an ideal, dilute solution apply. Secondly, it is essential to obtain more accurate diffusion measurements in order to have faith in the results of the type of investigation which has been done in this thesis.

APPENDIX I

Numerical Analysis of the Einstein Relation

The measured conductivity σ at a temperature T is to be used to calculate D_{σ} for Ag^*Cl .

The lattice parameter a_0 for AgCl was taken from: 1*

$$a_0 = 5.545 \times 10^{-10} \text{ m}$$

N = concentration of Ag or Cl atoms

$$N = \frac{4 \text{ sites}}{(5.545 \times 10^{-10})^3} = 2.360 \times 10^{28} \text{ atoms/m}^3$$

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

$$\rho = 2.3602 \times 10^{22} \times \frac{143.323}{6.025 \times 10^{23}} = 5.617 \text{ g/cm}^3$$

$$\frac{D_{\sigma} (\text{cm}^2/\text{sec})}{\sigma (\text{ohm-cm})^{-1}} = 2.279 \times 10^{-8} T(^{\circ}\text{K})$$

1*: Handbook of Physics and Chemistry,
Editor in Chief: Robt. C. Weast, 45
(The Chemical Rubber Co.) p.E76(1965).

APPENDIX II

Numerical Conductivity Data

<u>Crystal</u>	<u>Temperature</u>		σ
	<u>T(°C)</u>	<u>$10^3/T(^{\circ}\text{K})$</u>	<u>(ohm-cm)⁻¹</u>
4a	203.5	2.098	7.11×10^{-5}
	228.4	1.993	1.88×10^{-4}
	249.8	1.912	3.97×10^{-4}
	274.2	1.827	8.87×10^{-4}
	300.2	1.744	1.95×10^{-3}
	322.1	1.680	3.72×10^{-3}
	350.9	1.602	8.20×10^{-3}
4b	296.4	1.756	1.78×10^{-3}
	325.7	1.670	4.01×10^{-3}
	349.9	1.605	7.73×10^{-3}
	376.2	1.540	1.595×10^{-2}
	399.3	1.487	2.86×10^{-2}
	426.3	1.429	5.68×10^{-2}

Numerical Conductivity Data (cont)

<u>Crystal</u>	<u>Temperature</u>		$\frac{\sigma}{(\text{ohm-cm})^{-1}}$
	<u>T(°C)</u>	<u>$10^3/T(^{\circ}\text{K})$</u>	
4d	201.0	2.109	6.54×10^{-5}
	224.9	2.007	1.71×10^{-4}
	250.8	1.909	4.24×10^{-4}
	276.1	1.821	9.62×10^{-4}
	303.5	1.734	2.16×10^{-3}
	323.7	1.676	3.84×10^{-3}
	350.4	1.604	7.94×10^{-3}
	373.1	1.548	1.46×10^{-2}
	401.5	1.482	3.14×10^{-2}

Numerical Conductivity Data

<u>Crystal</u>	<u>Temperature</u>		σ
	<u>T(°C)</u>	<u>$10^3/T(^{\circ}\text{K})$</u>	<u>(ohm-cm)⁻¹</u>
2e	201.2	2.108	3.30×10^{-5}
	231.3	1.982	1.44×10^{-4}
	292.8	1.767	1.50×10^{-3}
	326.2	1.668	4.10×10^{-3}
	361.1	1.577	1.06×10^{-2}
	414.4	1.454	4.40×10^{-2}
2c	200.8	2.110	4.64×10^{-5}
	301.5	1.741	2.05×10^{-3}
	324.7	1.672	3.98×10^{-3}
	351.5	1.601	8.09×10^{-3}
	375.4	1.542	1.515×10^{-2}
3c	201.5	2.107	6.42×10^{-5}
	238.7	1.953	2.78×10^{-4}
	286.0	1.788	1.30×10^{-3}
	320.5	1.684	3.54×10^{-3}
	350.1	1.605	8.00×10^{-3}
	379.2	1.533	1.73×10^{-2}
	409.7	1.465	3.82×10^{-2}
	428.2	1.426	6.44×10^{-2}

Numerical Conductivity Data (cont)

<u>Crystal</u>	<u>Temperature</u>		<u>σ</u>
	<u>T(°C)</u>	<u>$10^3/T(^{\circ}\text{K})$</u>	<u>(ohm-cm)⁻¹</u>
2a	200.8	2.110	4.74×10^{-5}
	228.4	1.993	1.76×10^{-4}
	259.6	1.877	5.57×10^{-4}
	287.8	1.783	1.41×10^{-3}
	318.7	1.690	3.54×10^{-3}
	348.7	1.608	8.06×10^{-3}
	377.8	1.536	1.72×10^{-2}
	410.0	1.464	3.89×10^{-2}
	435.0	1.412	7.79×10^{-2}

General Numerical Data

Crystal	3E1	3B1	3A1	3D1
<u>Temperature Data</u>				
T_o ($^{\circ}\text{C}$)	300.25	320.00	342.00	358.00
$10^3/T$ ($^{\circ}\text{K}$)	1.744	1.686	1.626	1.579
V_o (mv)	12.220	13.040	13.960	14.63
W_o (ev)	0.86	1.19	0.87	0.94
H_o ($^{\circ}\text{C}/\mu\text{v}$)	0.02457	0.02454	0.02452	0.02447
G_o ($\%/ \mu\text{v}$)	0.07416	0.07234	0.06831	0.06659
<u>Diff. Coeff. Data</u>				
A (cm^2)	0.693	0.703	0.687	0.696
m_o (mg)	0.01923	0.0251	0.0354	0.0381
slope	0.010235	0.009796	0.01049	0.009374
time eff(min)	762.67	771.32	646.45	546.36
<u>Conductivity Data (during diffusion)</u>				
A (cm^2)	0.693	0.703	0.687	0.696
L (cm)	0.9545	0.9810	0.9690	0.9881
G (cm^{-1})	1.378	1.395	1.410	1.415
R (ohms)	673.0	403.3	223.0	140.7
σ (ohm-cm^{-1})	2.05×10^{-3}	3.46×10^{-3}	6.32×10^{-3}	1.005×10^{-3}
D_o (cm^2/sec)	2.677×10^{-8}	4.676×10^{-8}	8.859×10^{-8}	1.446×10^{-7}

General Numerical Data (cont)

Crystal	3E1	3B1	3A1	3D1
<u>Slicing Data</u>				
x (rms) (microns)	346	449	633	712
slice thickness (microns)	50	66	90	100
tilt error (microns)	35	21	25	35
loss of mass (mg)	1.77	2.10	—	1.27
<u>Errors</u>				
slicing (%)	0.24	0.19	0.18	0.18
cross section (%)	0.23	0.02	0.04	0.17
slope (%)	0.90	0.67	0.66	0.66
time correction (%)	0.60	0.68	0.76	0.72
loss of mass (%)	0.61	0.56	—	0.22
Total error in D^* (%)	1.13	0.97	1.02	1.01
Total error in σ (%)	1.95	0.73	0.56	0.24
Total combined error (%)	2.25	1.22	1.18	1.04
<u>Correlation factor</u>				
D^*/D_G	0.487	0.477	0.583	0.518

General Numerical Data

<u>Crystal</u>	4E1	4C1	3A2	2D1
<u>Temperature Data</u>				
$T_o(^{\circ}\text{C})$	380.00	400.00	420.00	435.00
$10^3/T(^{\circ}\text{K})$	1.531	1.486	1.443	1.412
$V_o(\text{mv})$	15.550	16.400	17.240	17.880
$W_o(\text{ev})$	1.02	1.04	1.19	1.27
$H_o(^{\circ}\text{C}/\text{v})$	0.02444	0.02439	0.02436	0.02433
$G_o(\%/ \text{v})$	0.06763	0.06488	0.06989	0.07158
<u>Diff. Coeff. Data</u>				
$A(\text{cm}^2)$	0.705	0.704	0.709	0.697
$M_o(\text{mg})$	58.62	39.00	43.10	54.40
slope	.008793	0.003430	0.002156	0.002462
time eff (min)	768.08	519.33	534.79	518.52
<u>Conductivity Data</u>				
$A(\text{cm}^2)$	0.705	0.704	0.709	0.697
$L(\text{cm})$	0.9456	1.0735	0.8208	0.8653
$G(\text{cm}^{-1})$	1.349	1.524	1.158	1.241
$R(\text{ohms})$	76.15	51.56	24.32	17.16
$\sigma(\text{ohm-cm})^{-1}$	1.77×10^{-2}	2.96×10^{-2}	4.77×10^{-2}	7.24×10^{-2}
$D_G(\text{cm}^2/\text{sec})$	2.634×10^{-7}	4.540×10^{-7}	7.533×10^{-7}	1.168×10^{-6}

General Numerical Data (cont)

<u>Crystal</u>	4E1	4C1	3A2	2D1
<u>Slicing Data</u>				
x (rms) (microns)	1115	1191	1650	1980
slice thickness (microns)	150	110	120	120
tilt error (microns)	35	35	35	35
loss of mass (mg)	4.20	0.70	0.29	1.12
<u>Errors</u>				
slicing (%)	0.16	0.08	0.04	0.03
cross-section (%)	0.14	0.17	0.66	0.06
slope (%)	0.81	0.59	0.69	1.08
time correction (%)	0.58	0.77	0.65	0.51
loss of mass (%)	0.45	0.06	0.02	0.07
Total error in D^* (%)	1.02	0.99	1.16	1.20
Total error in σ (%)	0.29	0.20	0.10	0.15
Total combined error (%)	1.08	1.01	1.35	1.22
<u>Correlation factor</u>				
D^*/D_σ	0.513	0.501	0.562	0.540

Numerical Diffusion Data

<u>Crystal</u>	<u>Temperature</u>		<u>D*(Ag)</u>	<u>Error</u>	<u>D_g</u>
	<u>T(°C)</u>	<u>10³/T(°K)</u>	<u>(cm²/sec)</u>	<u>%</u>	<u>(cm²/sec)</u>
3 E 1	300.25	1.744	1.304x10 ⁻⁸	1.13	2.677x10 ⁻⁸
3 B 1	320.00	1.686	2.228x10 ⁻⁸	0.97	4.676x10 ⁻⁸
3 A 1	342.00	1.626	5.159x10 ⁻⁸	1.02	8.858x10 ⁻⁸
3 D 1	358.00	1.579	7.481x10 ⁻⁸	1.01	1.446x10 ⁻⁷
4 E 1	380.00	1.531	1.352x10 ⁻⁷	1.02	2.634x10 ⁻⁷
4 C 1	400.00	1.486	2.276x10 ⁻⁷	0.99	4.540x10 ⁻⁷
3 A 2	420.00	1.443	4.230x10 ⁻⁷	1.16	7.533x10 ⁻⁷
2 D 1	435.00	1.412	6.302x10 ⁻⁷	1.20	1.168x10 ⁻⁶

General Numerical Information

<u>Temperature</u>		<u>mobility (cm²/V-sec)</u>					
<u>T(°C)</u>	<u>10³/T(°K)</u>	<u>$\mu_i^T \times 10^{-3}$</u>	<u>$\mu_v^T \times 10^{-3}$</u>	<u>ϕ^T</u>	<u>$\mu_i^K \times 10^{-3}$</u>	<u>$\mu_v^K \times 10^{-3}$</u>	<u>ϕ</u>
300	1.745	4.49	0.755	5.88	4.41	0.666	6.62
320	1.686	4.54	0.910	5.00	4.66	0.891	5.23
342	1.626	4.57	1.16	4.26	4.92	1.22	4.03
358	1.584	4.60	1.27	3.79	5.11	1.48	3.45
380	1.531	4.72	1.62	3.28*	5.37	1.92	2.80
400	1.486	4.90	1.97	2.90*	5.58	2.39	2.33
420	1.443	5.10	2.24	2.58*	5.81	2.96	1.96
435	1.412	5.23*	2.69*	2.37*	5.97	3.45	1.73

* = Interpolated values

μ_j^T = values obtained by Teltow

μ_j^K = values obtained from Teltow's data using Kurnick's method of evaluation; values shown were obtained using least squares calculations.

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