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EXPERIMENTAL VERIFICATION OF THE CORRELATION FACTOR
FOR VACANCY DIFFUSION IN SILVER CHLORIDE

Joseph P. Gracey

September, 1967

Department of Physics and Astronomy
The University of Kansas
Lawrence, Kansas

U. S. Atomic Energy Commission
Contract AT(11-1)-1197

Point Defects in Ionic Crystals

Robert J. Friauf
Principal Investigator

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89

TABLE OF CONTENTS

I.	Introduction and Theory	1
A.	Basic Theory and Experimental Technique	1
B.	The "Intrinsic" Region in AgCl	3
C.	Conductivity and Diffusion in the "Structure Sensitive" Region of Silver Chloride	5
D.	Correlation Effects in AgCl at Low Temperatures	7
II.	Experimental Procedure	9
A.	Starting Material and Crystal Growth	9
B.	Conductivity Measurements	11
C.	Diffusion Measurements	13
D.	Time-Temperature Correction	15
E.	Slicing, Weighing, and Counting	17
F.	Errors	20
III.	Experimental Results	23
A.	Conductivity	23
B.	Impurity Concentrations	24
C.	Diffusion Coefficients	26
D.	Effect of the Concentration Gradient	27
E.	Interpretation of Results	31
	APPENDICES	36

I. INTRODUCTION AND THEORY

A. Basic Theory and Experimental Technique

The importance of lattice imperfections in ionic crystals in the explanation of ionic conductivity and diffusion has long been recognized. The original development of the theory of lattice defects was done by Frenkel¹, Schottky^{2,3}, and Wagner³ as early as 1926.

Schottky developed a model in which simultaneous formation of positive and negative ions in the otherwise perfect crystal lattice provides a mechanism for conductivity and diffusion. In his model, positive ions often acquire enough thermal energy to jump into vacant positive ion sites, and negative ions into vacant negative ion sites. Application of an electric field, then, causes ions to drift in one direction or another, depending on their charge. This movement of charge explains the conductivity of a number of substances, notably the alkali halides. Since a mixing of ions is also involved, the Schottky theory also explains how diffusion can occur.

Frenkel's model has been successful in explaining the conductivity and diffusion of the silver halides. He pictures an ion as being transferred from a normal lattice position to an interstitial site by acquiring a certain amount of thermal energy. Then, upon further acquisition of energy, the interstitial ion might do one of two things. It might jump directly to another interstitial position, or it might displace an ion already occupying a normal lattice site to an interstitial site. If the latter happened to be the case,

the ion in the normal site may be knocked out along the line of travel of the interstitial ion (collinear interstitialcy), or it may be knocked out sideways, at certain angles to the direction of travel of the interstitial (noncollinear interstitialcy). In either case, as with the Schottky type defects, this is a possible explanation of both conductivity and diffusion.

If conductivity and diffusion occur because of the same kind of process, one would expect that a relationship should exist between the ionic conductivity and the diffusion coefficient. Such a relationship has been derived⁴, and is called the Einstein relation. It states that, when conductivity and diffusion are produced by the same mechanism,

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

where σ is the ionic conductivity, D_{σ} is the self-diffusion coefficient, N is the number of diffusing ions per unit volume, q is the charge on the ions, k is Boltzmann's constant, and T is the absolute temperature.

Experimentally, then, the quantities σ and D_{σ} are usually measured by independent methods to ascertain whether the above relation is satisfied. The conductivity is measured by finding the current passed by a crystal of known dimensions in an electric field. The diffusion coefficient is measured by placing radioactive tracers on the end of the crystal in a thin film and allowing them to diffuse into the sample. When these two independently measured quantities are substituted into the Einstein relation, it is usually found that

it is not rigorously satisfied. Therefore it is necessary to introduce a correction factor, $f^* = D^*/D_\sigma$, where D^* is the diffusion coefficient from radiotracer measurements. Then the relation reads,

$$D^* = f^* D_\sigma = f^* \frac{kT}{Nq^2} \sigma . \quad (2)$$

The value of f^* may depend upon several effects. Recall that the Einstein relation is derived by assuming that conductivity and diffusion are caused by the same mechanism. It may be, however, that several mechanisms are involved in the process (e.g., there may be both a vacancy and an interstitialcy process at the same time). There could also be migration of a complex such as a vacancy pair (positive ion vacancy joined to a negative ion vacancy), which, since it is electrically neutral, does not contribute to D_σ , but does contribute to D^* . Also, there are correlation effects between successive jumps of a tracer ion, and for interstitialcy processes there are also displacement effects. Both the correlation and displacement effects alter the relationship between D^* and D_σ . By measuring the quantity f^* experimentally, then, valuable information about the defect mechanisms which take place in a particular kind of crystal may be deduced.

B. The "Intrinsic" Region in AgCl

Experimental evidence at the present time overwhelmingly supports the view that Frenkel defects predominate in silver chloride, and that the silver ion, rather than the chlorine, is chiefly responsible for the conductivity. Transport measurements by Tubandt⁵, and

later by Kurnick⁶, have shown that the transport number of silver in silver chloride is unity. Confirming evidence by Compton and Maurer⁷ and Reade and Martin⁸ indicate that the diffusion of the chlorine ion is only about 10^{-3} that of the silver ion. We may conclude, therefore, that the much more mobile silver ion is entirely responsible for the conductivity exhibited in silver chloride.

Measurements of the electrical conductivity of both pure silver chloride and silver bromide and of these compounds doped with small amounts of divalent positive impurities by Lehfeldt⁹, Koch and Wagner¹⁰, Teltow¹¹, Ebert and Teltow¹², Kurnick⁶, and Muller¹³ have provided very strong arguments for the existence of Frenkel defects in silver chloride and silver bromide, with the silver ion interstitials being much more mobile than the silver ion vacancies.

We might conclude from the above arguments that a direct interstitial process in which the silver ions jump from one interstitial position to another is responsible for the conductivity and diffusion in silver chloride. However, an experimental investigation⁷ of the Einstein relation reveals that D^* and D_σ are not equal, but that D^* is smaller by a factor of 0.59 at 350°C. Since with a direct interstitial process successive jumps of a tracer are clearly uncorrelated, and since there can be no contribution to the conductivity from mobile anion vacancies, we have a case where the Einstein relation should be satisfied but is not. Thus the answer must lie in an incorrect assumption, namely, that the diffusion and conductivity are due to a direct interstitial jump process. Such arguments

led McCombie and Lidiard¹⁴ to suppose that a collinear interstitialcy process took place in AgCl. However, their calculations (using the data of Ebert and Teltow¹²) gave a value of $D^* = 0.40 D_G$, compared to Compton's value of 0.59. This, they reasoned, could be due to the presence of noncollinear jumps or other mechanisms in various combinations. A theoretical investigation by Hove¹⁵ supports the view that the mechanism for diffusion and conductivity in AgCl is likely to be a combination of the collinear and noncollinear interstitialcy processes. He predicts activation energies of about 3 ev for the direct interstitial process, -0.1 to 0.4 ev for the collinear interstitialcy, and 0.8 ev for the noncollinear interstitialcy. A look at these activation energies convinces one that the direct interstitial process cannot compete with the other two, and that the most likely possibility is a combination of the two interstitialcy mechanisms, with the collinear predominating because of its lower activation energy. These results are supported by the calculations of Compaan and Haven¹⁶ and Friauf^{17,18} and have been borne out experimentally, at least in a qualitative way, by the diffusion coefficient and conductivity measurements of Weber¹⁹.

C. Conductivity and Diffusion in the "Structure Sensitive" Region of Silver Chloride

The results cited up to now explain electrical conductivity and self-diffusion in AgCl in the "intrinsic" or high temperature range, in which these processes depend only upon the nature of the

substance under study. Much information can also be gathered by a study of the lower temperature regions, in which the characteristics of the substance depend markedly upon the amount of impurities present. This is the subject of the present work.

In order to illustrate the effect of impurities upon conductivity and diffusion, suppose a small amount of a divalent, positive ion such as cadmium is introduced into an otherwise pure crystal of silver chloride. The impurity ion enters the lattice substitutionally, that is, it takes a position which would normally be occupied by a silver ion. In order that electrical neutrality be preserved in the crystal, it is necessary that a positive ion vacancy also be introduced for each Cd^{++} ion present. At $T = 0^\circ\text{K}$, the divalent impurity and the vacancy will be tightly bound together. At higher temperatures, however, neighboring silver ions may acquire enough thermal energy to break the bond existing between the two and free the vacancy to migrate throughout the crystal. The number of divalent ion-vacancy bonds which can be broken should depend strongly upon the temperature. When the temperature is high enough, nearly all the complexes can presumably be broken up, resulting in an influx of free vacancies throughout the crystal lattice.

The presence of additional free positive ion vacancies in the crystal tends to suppress the interstitial silver ions. Thus the conductivity at low temperatures should depend mainly upon the number of free vacancies present, which in turn depends almost proportionally upon the amount of impurity in the crystal. By adding

controlled amounts of divalent impurities to AgCl crystals, therefore, considerable knowledge of diffusion and conductivity mechanisms which take place at low temperatures can be gained.

D. Correlation Effects in AgCl at Low Temperatures

The theory of correlation effects, first introduced by Bardeen and Herring²⁰, supposes that successive jumps of a tracer ion in a crystal lattice are directionally correlated. The magnitude of the correlation factor f^* which must be introduced to correct the Einstein relation depends upon the particular type of mechanism under consideration, and upon the structure of the lattice in which the diffusion occurs. Compaan and Haven¹⁶ have made a numerical investigation of correlation factors for various mechanisms by treating diffusion as a random walk problem. For the face-centered cubic lattice of AgCl and the free vacancy mechanism, they obtained the value $f_v^* = 0.781$.

This value of f_v^* has been approximately verified by Miller²¹ for AgBr doped with 280 ppm cadmium by making measurements of the experimental correlation factor in the "structure sensitive" region at lower temperatures. The results of his experiments are shown in Figure 1. In the high temperature portion of the curve, interstitial silver ions are the predominant defect, and the lower value of f^* reflects the presence of the collinear and noncollinear interstitialcy processes. In the middle temperature portion the values of f^* are approximately equal to the free vacancy value predicted by Compaan and Haven. At lower temperatures, f^* increases, suggesting

that silver ion-vacancy complexes (which contribute to D^* but not to D_σ) are present in increasing numbers as the temperature is lowered.

The purpose of this investigation is to repeat the verification of the free vacancy experimental correlation factor for AgCl. In the first place it should be possible to obtain a better accuracy than the 2 to 5 per cent error in Miller's results. It is also desirable to check the absolute comparison of conductivity and diffusion measurements by the techniques used in this laboratory in order to detect any possible systematic error. We propose to do this by making diffusion and conductivity measurements on silver chloride doped with small amounts of CdCl_2 in the temperature range from 125°C to 225°C .

II. EXPERIMENTAL PROCEDURE

A. Starting Material and Crystal Growth

In order to begin with the purest possible material, silver chloride was precipitated in the laboratory using the techniques described by Nail, Moser, Goddard, and Urbach²². Reagent grade hydrochloric acid was distilled in a pyrex condenser in order to remove trace amounts of heavy metals, and the resulting distillate titrated in order to determine the molarity of the HCl. Pure recrystallized silver nitrate, obtained from Eastman Kodak²³, was used as the other reactant in the precipitation. About .2 mole of the HCl and AgNO₃ was placed in each of two pyrex separatory funnels and the contents diluted with about one liter of distilled, deionized water. The solutions were then run simultaneously, drop by drop, into one liter of preheated distilled, deionized water contained in a 4000 ml precipitation beaker. The entire reaction was accomplished in about twenty minutes in a darkroom under red safelight illumination, because of the sensitivity of silver chloride to ultraviolet light. The slurry was heated throughout the reaction time, and stirred thoroughly with a teflon coated magnetic stirring bar.

Washing was accomplished by decanting as much excess water and acid as possible after the precipitate had settled, then adding a liter of water. After heating and stirring for a few minutes, the slurry was again allowed to settle, and the procedure repeated. The heating was discontinued after the third wash. In all, ten washings

of the silver chloride precipitate were usually done.

When enough material for two crystals had been precipitated (about 175 gm.), the washed silver chloride was dried. At first, an oven drying procedure was used, in which the powder was maintained at about 60°C in an oven for two days. Constant attention was necessary, however, in order to keep the AgCl from forming large, hard clumps. As an alternative, a vacuum drying technique was used successfully. The precipitate was placed under a bell jar, and a vented vacuum pump was used to remove excess water while a small heat input kept the water from freezing during most of the drying time. The process required no attention, and the silver chloride emerged as a fine, free flowing powder.

Single crystals were grown using a modification of the Bridgman method. The silver chloride powder was placed in a long quartz tube 14 mm in diameter in the arrangement of Figure 2 and degassed in a vacuum overnight at about 375°C . The tube was tapered to a point at one end and connected to a quartz rod which was fastened to the crystal pulling apparatus. The purpose of the pointed tube was to provide a single nucleation center for beginning the growth of a single crystal. A large inconel cylinder surrounding the tube provided an excellent heat sink and minimized thermal gradients across the tube to about 1°C . The furnace was heated past the melting point of the charge and the temperature lowered slowly until the tip of the charge was at about 475°C . At a position nearly $\frac{1}{2}$ " below the tip, the melting point of 455°C was observed. Below

this position, the vertical temperature gradient was observed to be about 60°C per inch. Once equilibrium had been established, the withdrawal of the tube containing the charge through the sharp temperature gradient at a rate of 0.20 inches per hour was begun. During the withdrawal the tube was rotated at about three turns per minute, and the temperature of the furnace was controlled to $\pm \frac{1}{2}^{\circ}\text{C}$ with a Brown recorder.

In all, three single crystals, ranging in length from three to five inches, were obtained using this method. One was a pure crystal; the others were doped with approximately 230 ppm CdCl_2 (0.00023 mole fraction) by mixing CdCl_2 powder thoroughly with the pure AgCl powder before the growth procedure. The pure crystal was grown in a vacuum of less than 10^{-6} mm Hg, but the doped samples were grown in a partial pressure of 23 in Hg helium to prevent volatilization of the impurity chloride. After withdrawal, the crystal ingot was removed by shattering the surrounding quartz tube. The quartz showed no tendency to stick to the crystal in either the vacuum-grown case or the helium-grown case.

From the single crystal AgCl ingots cylindrical samples roughly $3/8$ " in diameter and from 0.5 to 1.0 cm in length were machined on a lathe. All procedures were carried out under a red safelight. Eight usable samples were obtained from the pure crystal and eight from the two doped ingots.

B. Conductivity Measurements

Conductivity measurements between roughly 135°C and 440°C were

made on five samples, three from the doped ingots and, for comparison purposes, two from the pure ingot, in the apparatus shown in the cross section of Figure 3. Electrodes were applied to a sample by vacuum evaporation of a thin film of pure silver onto the cylinder faces, followed by application of a layer of DuPont silver conducting paint (electronic grade 4817). The sample was placed in position between two silver cylinders of the same diameter, to which were welded the thermocouple leads, ground wire, and high lead. A long quartz tube enclosed the high lead, insulating it from the rest of the apparatus and serving as a support, and a short slotted quartz tube of the proper size held the sample and the silver cylinders in place. Tension to hold the apparatus together and to provide good electrical contact was supplied by three stainless steel springs mounted at the top. These were connected to silver wires which ran the length of the apparatus and were attached to a quartz disc at the bottom, which served as a platform for the lower silver cylinder. The entire arrangement was enclosed in a large diameter, round-bottom quartz tube which could be evacuated or filled with an inert gas to any desired pressure. This large tube was surrounded by a thick inconel cylinder, which served as a heat sink and minimized thermal gradients over the sample. The chief advantage of the apparatus just described was that in the heated portion (around the sample) the only materials present were quartz, which is relatively easy to clean, and silver (aside from the chromel-alumel thermocouple wires). Thus there is little worry about impurities

from the surrounding material affecting the results of the measurements.

When the sample was in place in the apparatus, the chamber was evacuated, degassed for several hours, and filled with pure helium at a pressure around 15 psi. The sample chamber was then heated to the desired temperature in a Leeds and Northrup thermocouple calibration furnace, controlled to $\pm 1/2^\circ\text{C}$ with a Brown recorder.

Once temperature equilibrium was established, the conductivity was measured using a General Radio 716-C Capacitance Bridge as an equal arm a.c. bridge.²⁴ For frequencies between 270 cycles and 100 kc, the sample was considered to be a resistance (R_s) and a capacitance (C_s) in parallel, so that by varying a capacitor C_v and a decade resistance box R_v until a null was indicated, the sample resistance R_s could be read directly. Detection was obtained with a General Radio 1231-B tuned amplifier and an oscilloscope. The conductivity σ is obtained from $\sigma = L/AR_s$, where A is the cross sectional area of the cylindrical sample and L is its length. Measurements of the sample diameter and length were made with a measuring microscope, and the average of sixteen readings was used for each of the quantities in the calculations.

C. Diffusion Measurements

The differential equation governing self-diffusion is known as Fick's second law.²⁵ For the boundary conditions of diffusion into a semi-infinite cylinder in the positive x direction of ions which initially (at $t = 0$) form a thin film on the face of the

cylinder ($x = 0$), the solution to the diffusion equation is

$$n^*(x,t) = \left[Q/(Dt\pi)^{1/2} \right] \exp(-x^2/4Dt). \quad (3)$$

Here Q is the amount of diffusing material per unit area, D is the self-diffusion coefficient, and $n^*(x,t)$ is the concentration of diffusing ions at x after time t .

This solution can be used if experimentally we approximate the boundary conditions which lead to it. Accordingly, we require that the initial layer of diffusing ions be thin, and that the length of the sample be long compared to the diffusion distances involved. We can estimate a typical diffusion distance by taking the rms displacement. Thus,

$$x_{\text{rms}}^2 = \frac{\int_0^\infty x^2 n^*(x,t) dx}{\int_0^\infty n^*(x,t) dx} = 2Dt. \quad (4)$$

Hence $x_{\text{rms}} = (2Dt)^{1/2}$, and the experimental object is therefore to have $h \ll (2Dt)^{1/2} \ll L$, where h is the film thickness.

In order to make the diffusing ions distinguishable from the ions in the crystal lattice, radioactive tracers were used. The isotope used was Ag-110 ($t_{1/2}$ life = 270 days), which was obtained from the Oak Ridge National Laboratory as Ag^*NO_3 dissolved in nitric acid. Radioactive Ag^*Cl was precipitated by adding the proper amount of HCl to the Ag^*NO_3 in a small platinum boat, through which an electric current could be passed. When the Ag^*Cl precipitate had formed in the boat (usually about 0.9 mc), crushed dry ice was added to freeze the remaining water and acid. A bell jar was then placed over the arrangement and the system pumped on with a vacuum

pump until the water, acid, and dry ice were removed, leaving a thin film of Ag^*Cl in the boat. The AgCl crystals were prepared by masking all but one face with tape and mounting them four to five cm above the platinum boat. After the vacuum was restored, the Ag^*Cl was deposited on the face of the samples by passing a small current through the boat, heating it enough to evaporate the radioactive material. From geometrical considerations it was calculated that about 4.5 microcuries deposited on the face of each sample. Electrodes were applied as before, so that the conductivity could be checked during diffusion.

After a sample was in position in the sample chamber, the furnace was heated to the equilibrium diffusion temperature and there the sample temperature was controlled to $\pm 0.1^\circ\text{C}$ with a Leeds and Northrup recorder. After a suitable length of time, the furnace was cooled and the sample removed. Usually the time was chosen to give an estimated value of $x_{\text{rms}} \approx 150$ microns.

D. Time-Temperature Correction

Since the solution to the diffusion equation assumes that the sample is immediately brought to the diffusion temperature, a correction must be made for the heating and cooling times of the furnace. As long as the correction is small, this can be done by knowing $D(t)$ for all times and using the relation

$$t_{\text{eff}} = \frac{1}{D_0} \int_0^{\infty} D(t) dt. \quad (5)$$

Here t_{eff} is the effective time for diffusion at a temperature T_0 .

close to the average temperature during diffusion, and $D_0 = D(T_0)$.

In this way we equate the area under the actual D vs t curve to the area of a rectangular curve of height D_0 and length t_{eff} .

When most of the correction comes from temperatures close to T_0 , we may let $D = C \exp (-W_0/kT)$, where the activation energy W_0 is obtained from the slope of the conductivity curves at T_0 . Thus we can write

$$t_{\text{eff}} = \int_0^{\infty} \exp \frac{W_0}{k} \left(\frac{1}{T_0} - \frac{1}{T} \right) dt = \int_0^{\infty} \frac{D(T)}{D(T_0)} dt = \int_0^{\infty} F(t) dt. \quad (6)$$

In practice the integral is evaluated graphically, using a computer. During a diffusion run, the sample temperature is read automatically at different times by a digital voltmeter and digital clock linked to an IBM card punch. Readings were taken every 10 seconds during the rapid part of the heating and cooling curves, and every 10 min. at the diffusion temperature. A program has been written for the IBM 7040 computer through which the computer evaluates the integral for t_{eff} , knowing the function $T(t)$ and the constants.

It was eventually realized that some diffusion occurs at room temperature for the doped samples. In order to correct for the time between evaporation and slicing, it is necessary to go back to equation (5) and to replace $D(T)$ by $\sigma(T)$, using the Einstein relation in the form of equation (2). Thus,

$$t_{\text{eff}} = \frac{1}{D_0} \int_0^{\infty} D(T) dt = \frac{\int_0^{\infty} f^*(T) T \sigma(T) dt}{f_0^* T_0 \sigma_0} \quad (7)$$

where $\sigma_0 = \sigma(T_0)$ and $f_0^* = f^*(T_0)$. The factors $f^*(T)$ and f_0^* in

equation (7) must be cancelled for lack of more precise knowledge, but according to Miller²¹, $f^*(T)$ should lie between 0.80 and 1.00, and hence the error in the correction is probably not very large. The average room temperature where the samples were stored was found to be 23.5°C. The conductivity at this temperature was obtained by extrapolating the conductivity for each sample from about 100°C, using the slope from Abbink's²⁶ data for a sample with a comparable amount of doping.

Corrections were calculated from

$$t_{\text{eff}} = \frac{1}{T_0 \sigma_0} \int_0^{\infty} T \sigma(T) dt \quad (8)$$

and ranged from 2.48% of the total t_{eff} for the first run on sample #14-D to 11.77% for #13-B, which spent a considerable time in storage. Samples #14-C and 14-E had corrections of 8.06% and 6.99%, respectively. The second run on sample #14-D required no correction, since the crystal was stored at liquid nitrogen temperature for the time when it was not actually undergoing diffusion.

E. Slicing, Weighing, and Counting

After a diffusion run the silver electrodes were removed with heated nitric acid, and thin slices (usually about 10 microns thick) were taken from the radioactive end with a microtome. The surface to be cut was aligned parallel to the cutting edge of the knife blade by means of an optical lever and the adjustments available on the microtome. A full cut over the surface of the sample was obtained by the second or third slice. The slices were brushed into

a previously weighed planchet, with care being taken that none of the slice mass was lost. Ordinarily, from 15 to 19 planchets were prepared for each diffusion measurement, with 2 slices in each planchet. All weighing was done on a semi-micro balance with a sensitivity of 0.01 milligrams.

Once the mass in each planchet had been determined, the planchets were prepared for counting by dissolving the AgCl in a concentrated solution of NH_4OH . The solvent was then evaporated by placing the planchets in an oven at about 50°C for a short time. After the NH_4OH had been removed, the residual silver chloride was evenly deposited in a thin film over the bottom of the planchets. In this way, consistency during the counting was achieved by making the loss of counts by self absorption the same for each planchet.

The activity in each planchet was determined by placing the planchet under the window of a Geiger tube in such a way that the geometry of the arrangement was reproducible from one planchet to the next. Background was kept to a fairly consistent level of about 35 counts per minute by a thick metal shield. In order to correct for any possible slow variation in the counting rate of the Geiger tube, the count rate G_0 of a standard was taken at the beginning of the counting process, and recounted after every second planchet. The number of counts per unit time for the i th slice (P_i) was then corrected for background B_0 , and referred to an average slice volume. The resultant count rate C_i was obtained from the following equation:

$$C_i = \left[(G_0/G_i) P_i - B_0 \right] m_0/m_i \quad (9)$$

where G_i is the count rate of the standard after the i th slice has been counted, m_i is the mass of the i th slice, and m_0 is the average slice mass. Note that for a constant cross sectional area A , the volume of a slice is proportional to its thickness x_i , which is obtained from the mass of the slice by noting that $x_i = m_i / \rho A$, where ρ is the density of the material. Then the ratio of the volumes $V_0/V_i = m_0/m_i$.

In order to make the statistical counting error small, a minimum of 10,000 counts was observed for each slice. The distance from the planchet to the window of the Geiger tube was adjusted for each set of slices so that no planchet had more than about 30,000 counts per minute, considerably less than the number of counts which would require a correction for the 200 microsecond dead time of the Geiger tube. Total counting times were always less than about seven hours.

In order to calculate D from equation (3), we first observe that $n^*(x, t_{\text{eff}})$ is proportional to the number of radioactive atoms disintegrating per unit time in a unit volume of the sample at a distance x from the end. Hence by sectioning the crystal into thin slices and observing the quantity C_i for various values of x , the value of D may be obtained from the following:

$$\log C_i = \text{constant} - x^2/4Dt_{\text{eff}}. \quad (10)$$

Since the thickness x_i varies from slice to slice, a reduced thickness r_i is introduced:

$$r_i = x_i/x_0 = m_i/m_0$$

where x_0 and m_0 are the average slice thickness and mass. Therefore, the reduced distance W_i from the end of the sample to the center of the i th slice (where we assume all of the radioactivity is concentrated) is:

$$W_i = \sum_{j=1}^{i-1} r_j + \frac{1}{2}r_i,$$

and equation (10) becomes

$$\log C_i = \text{constant} - \frac{(m_0/\rho A)^2}{4Dt_{\text{eff}}} W_i^2. \quad (11)$$

From equation (11) it will be observed that if $\log C_i$ is plotted against W_i^2 , the result will be a straight line with a slope of $(m_0/\rho A)^2/4Dt_{\text{eff}}$. Such a plot is illustrated in Figure 4, using the data for sample #13-B. In order to make the final calculation of D , a program was written for the IBM 7040 computer which determined the best straight line through the set of points $(\log C_i, W_i^2)$ by making a least squares fit. From the least squares line the computer also calculated the slope and the error in the slope. Thus the values of D from the radioactive tracer method described are found from:

$$D = \frac{(m_0/\rho A)^2}{4t_{\text{eff}}(\text{slope})} \quad (12)$$

F. Errors

In measuring the diffusion coefficients, several sources of error were encountered.

1. Errors in Temperature.

The absolute calibration error of the chromel-alumel thermocouple used was not more than 1.8°C . In the Einstein relation, however, the exponential temperature dependence of D^* and D_{σ} cancels out, so that as long as the same thermocouple was used for both $\sigma(T)$ and $D^*(T)$, no error is introduced.

2. Errors in the Diffusion Time.

Correction for the heating and cooling times of the furnace was made by using equation (6), and errors due to this correction are small due to the very long diffusion times. The error was estimated by taking 1/5 of a time correction, which was calculated by considering the difference in area under the approximated rectangular F vs t curve and the actual curve. The corrections varied between 0.3% and 1.0%.

3. Errors in the Slope of the Diffusion Profile ($\log C_1$ vs W_1^2).

Errors in the slope stem from statistical errors in counting and random errors in weighing. Counting errors were kept below 1% by requiring a minimum of 10^4 counts per planchet. Weighing errors were kept small by maximizing the mass of the slices. The total error in the slope was calculated by the computer from the standard deviation of the individual points of the diffusion profile from the least squares line. It was usually less than 1%.

4. Errors from Loss of Crystal Mass.

During slicing a small fraction (0.04% to 0.45%) of the crystal mass was unavoidably lost, as was evidenced by a difference between the sample mass before slicing and the sample mass plus the mass of

the slices after slicing. This uncertainty was assumed to have occurred uniformly over all the slices and was included in the experimental error.

5. Errors in Sample Cross Sections.

The diameter of the samples was measured with a measuring microscope which could be read to five significant figures. By making the cross section about 0.7 cm^2 , the uncertainty was minimized, but the % error in D^* because of cross section errors is doubled, since A is squared in equation (12). Actual errors amounted to 0.1 to 0.2%.

In measuring the electrical conductivity, two sources of error are encountered.

1. Error in Measuring Sample Dimensions.

As stated above, crystal dimensions were measured to five places with a measuring microscope. Since the lengths used were of the order 0.5 cm, and cross sectional areas were around 0.7 cm^2 , the errors encountered were about 0.1 to 0.2%.

2. Errors in the Resistance.

Sample resistances were read directly from the General Radio resistance boxes, which are specified to have a measurement uncertainty of $\pm 0.1\%$.

The errors for each of the samples from the various sources are summarized in Table II. Overall errors in σ ranged from 0.17% to 0.51%. Errors in D^* ranged from 0.89% to 1.63%. The combination of these errors gives an uncertainty of 0.91% to 1.64% in f^* .

III. EXPERIMENTAL RESULTS

A. Conductivity

The results of the conductivity measurements are summarized in Figure 5 and Table I. The experimental conductivities for the three doped samples (#14-A, 14-F, and 13-C) and for the two pure samples (#12-A and 12-H) are plotted against $1000/T(^{\circ}\text{K})$ along with similar data obtained by Abbink²⁶.

Several observations are possible from a consideration of the conductivity curves. First, the "intrinsic" curve for the pure samples is a straight line, which the curves for the doped samples approach at the higher temperatures. As the temperature of a doped sample is lowered, the curve first drops below the "intrinsic" line, then takes a slope which is characteristic of the low temperature "structure sensitive" region. This effect has been explained^{7,12} as follows. At the higher temperatures the number of thermally created interstitial silver ions is great enough to minimize the effect of the vacancies carried into the crystal with the divalent impurity ions. As the temperature is lowered, however, fewer interstitials are available, and the extra vacancies are able to suppress them. Since the mobility of vacancies is smaller than that of interstitials, the conductivity is lower than the "intrinsic" conductivity, which comes largely from the interstitial ions. Finally, at low temperatures the interstitials are very nearly suppressed completely, and the conductivity is due almost entirely to a vacancy mechanism.

A second possible observation from the conductivity curves concerns the amount and distribution of the Cd^{++} ions throughout the crystal ingots. As noted earlier, the dopant was added by mixing the CdCl_2 powder into the pure silver chloride before beginning the crystal growth. Since it was impossible to get a completely uniform Cd distribution in this way, and since the cadmium tends to remain in that portion of the crystal which freezes first, a non-uniform distribution of the impurity over the length of the ingot should be expected. The conductivity curves show that this was actually the case. Sample #14-A was taken from that part of the crystal ingot #14 which froze first, and #14-F from that which froze last. In Figure 5, the conductivity of sample #14-A is higher than that of #14-F in the "structure sensitive" region, indicating the presence of more "free" vacancies and hence more Cd^{++} ions. When the conductivity of the diffusion samples (#14-C, 14-D, and 14-E) was checked at their equilibrium diffusion temperatures, all were found to have conductivity values which fell between the curves for #14-A and 14-F. The conductivity sample #13-C is from a more lightly doped portion of ingot #13 than the diffusion sample #13-B, as the conductivities for each sample show.

B. Impurity Concentrations

Abbink²⁶ determined the Cd concentrations in his conductivity samples by an activation analysis, in which thin analysis samples, cut from portions of the doped single crystal ingots immediately adjacent to the conductivity samples, were irradiated in a reactor

along with polycrystalline pellets of AgCl doped with a known amount of uniformly distributed impurity. When the activity present in the analysis samples was compared to that of the standards, the Cd concentrations could be determined. Abbink states that his measurements are accurate to $\pm 5\%$.

Concentrations of impurity in the doped samples of this work were determined by a comparison of the conductivity measurements with those of Abbink. The conductivity is given by

$$\sigma = e n_v \mu_v + e n_i \mu_i. \quad (13)$$

Here e is the electronic charge, n_v and n_i are the concentrations of vacancies and interstitials, and μ_i and μ_v are mobilities. In the low temperature regions under consideration here, where $n_i \ll n_v$, the conductivity is given by $\sigma = e n_v \mu_v$. If all the vacancies present are "free" (no association with divalent impurities), then $n_v = c$, the concentration of Cd^{++} ions. Then at constant temperature (and hence constant μ_v), a plot of $\log \sigma$ vs $\log c$ should be a straight line of slope 1, since

$$\log \sigma = \log (e \mu_v) + \log c.$$

Isotherms of $\log \sigma$ vs $\log c$ from Abbink's data are plotted in Figure 6. These curves can be fit by an empirical relation

$$\log \sigma = \text{constant} + b \log c, \quad (14)$$

where $b = .86$, instead of 1 as predicted by the simple theory.

There may be some complexing at the larger impurity concentrations.

To obtain the impurity concentration of a diffusion or conduc-

tivity sample, the conductivity for a particular temperature was plotted with Abbink's $\log \sigma - \log c$ isotherms. The concentration of the unknown sample could then be read directly from the graph. In the case of the conductivity samples, a concentration value was obtained for several of the isotherms shown, and the average of these values was taken as the concentration of that sample. Since only one conductivity measurement at one temperature was taken for the diffusion samples, their concentration was obtained by estimating where that point would lie between Abbink's isotherms.

C. Diffusion Coefficients

Diffusion anneals were carried out upon one pure sample at 250°C and upon five samples doped with CdCl_2 in 25°C temperature steps from 125°C to 225°C. The necessary calculations are summarized in Table III.

Figure 7 shows a plot of $f^* = D^*/D_\sigma$ versus T . The values of D_σ were calculated from the Einstein relation, using the measured conductivity at the equilibrium diffusion temperature. The experimental points in general approximate the free vacancy value of the correlation factor ($f_v^* = 0.781$) predicted by Compaan and Haven¹⁶. However, only the point for the sample #14-D at 125°C is considered to be completely reliable, for two reasons. First, it is apparent from the data that a significant cadmium concentration gradient was present over the length of the individual samples. This point will be discussed in the next section. Also, there is some question about the accuracy of the correction to t_{eff} because of room temperature

diffusion. We do not really know how much error the cancellation of the factors $f^*(T)$ and f_o^* in equation (7) introduces. Since sample #14-D was held at liquid nitrogen temperature when not actually undergoing diffusion, no room temperature diffusion correction is necessary, as was the case for the other samples.

D. Effect of the Concentration Gradient

It was apparent from the diffusion measurements not only that there was a variation in cadmium content from sample to sample, but also that a cadmium gradient existed over the length of the individual samples. The significance of this gradient can be appreciated by considering that diffusion occurs in a thin layer at one end of a sample and depends on the concentration of impurity at that end, whereas conductivity measurements are made for the whole sample, and depend upon the average concentration throughout the sample. Although the samples were made as short in length as practicable (about 0.5 cm), it was apparent that a considerable gradient still existed. Since the theoretical f_v^* is obtained by assuming that D^* and σ are measured for the same cadmium concentration, some account must be taken of the concentration gradient in the interpretation of the results.

Since specific information regarding the nature of the cadmium distribution is lacking, we assume that the gradient is linear, that is, that the concentration $c(z)$ along the length of the crystal is given by

$$c(z) = c_o (1 + qz/l), \quad (15)$$

where the average concentration c_0 is assumed to occur at $z = 0$, and q is defined as the change in concentration in going from $z = 0$ to $z = \ell$.

In order to discover the effect the concentration gradient may have on f^* , we must first compare the average measured conductivity σ_{avg} to the conductivity $\sigma(c_0) = \sigma_0$ at the average concentration. When an electric field E is applied to the crystal and steady state conditions are allowed to prevail, then Ohm's Law holds:

$$E(z) = j/\sigma(z),$$

where the current density j is constant along the length. Thus with equations (14) and (15),

$$E(z) = j/ac^b = (j/ac_0^b) (1 + qz/\ell)^{-b}$$

where a is a constant obtained from equation (14). The voltage drop V is then

$$V = \int_{-\ell}^{\ell} E(z) dz = [j/ac_0^b] [\ell/(1-b)q] [(1+q)^{1-b} - (1-q)^{1-b}] \quad (16)$$

The measured conductivity is given by

$$\sigma_{avg} = j/E_{avg} = (2\ell/V)j.$$

Using equation (16) with $\sigma_0 = ac_0^b$ we have the desired relationship

$$\frac{\sigma_{avg}}{\sigma_0} = \frac{2(1-b)q}{(1+q)^{1-b} - (1-q)^{1-b}}. \quad (17)$$

If we now assume that q is small, we can expand equation (17) and drop the higher order terms. The result is:

$$\sigma_{\text{avg}} / \sigma_0 \approx \frac{1}{1 + (1/6)b(1+b) q^2} \approx 1 - (1/6)b(1+b) q^2 . \quad (18)$$

If $b = 0.9$ and $q = 0.1$, then the error introduced by assuming that the measured conductivity σ_{avg} corresponds to the average concentration c_0 is only 0.3%.

Suppose now that the diffusion coefficient D_1^* is measured at one end of the sample where the concentration is $c_1 = (1+q) c_0$, and D_2^* is measured at the other end, where the concentration is $c_2 = (1-q) c_0$. Then f_1^* , the experimental correlation factor at end one, is

$$f_1^* = \frac{D_1^*(c_1)}{D_{\sigma}(\sigma_{\text{avg}})} = f_v^* \frac{D_{\sigma}(c_1)}{D_{\sigma}(\sigma_{\text{avg}})} = f_v^* \frac{\sigma(c_1)}{\sigma_{\text{avg}}} .$$

Thus,

$$f_1^* = f_v^* \frac{ac_1^b}{\sigma_{\text{avg}}} = f_v^* \frac{\sigma_0(1+q)^b}{\sigma_{\text{avg}}} , \quad (19)$$

and similarly,

$$f_2^* = f_v^* \frac{\sigma_0(1-q)^b}{\sigma_{\text{avg}}} . \quad (20)$$

The average value $\bar{f}^*$ of f_1^* and f_2^* is then, with the help of equation (17),

$$\bar{f}^* = f_v^* \frac{[(1+q)^b + (1-q)^b] [(1+q)^{1-b} - (1-q)^{1-b}]}{4q(1-b)} .$$

Expanding and dropping higher order terms in q , we obtain

$$\bar{f}^* / f_v^* \approx 1 + (1/3) b(2b - 1) q^2 . \quad (21)$$

The error in the average is the second term of equation (21). For the case of $b = 0.9$ and $q = 0.1$, which represents a 20% change in cadmium concentration from end to end, the error in $\bar{f}^*$ is only 0.24%.

It is possible to make a reasonable estimate of the concentration

gradient q present in the various samples from the Cd concentrations obtained by comparing conductivities with Abbink. With the exception of sample #13-B, the values of q are always less than 0.1. With these values of q and equations (19) and (20) we can calculate the corrections to f^* from the non-uniform Cd distribution, as summarized in Table 4. In Figure 7, the estimates of f_1^* and f_2^* to be expected from the concentration gradient have been plotted as open circles.⁺ The solid circles represent the observed values. With the exception of the data for sample #14-C at 175°C, all of the observed values of f^* lie remarkably close to the estimated values. The discrepancy at 175°C is not too surprising, however, considering our incomplete knowledge of the actual concentration gradients.

Sample #14-D was chosen to solve this major experimental difficulty, namely, the non-uniform distribution of Cd over the length of the sample. After making a diffusion run on this sample at 225°C, both ends of the sample were sliced with the microtome until only background activity could be detected in any twenty micron thick slice. The dimensions were remeasured, and the sample was prepared for a second evaporation. Since the sample showed no visible defects from the previous diffusion anneal, it appeared desirable to use it again for a second diffusion run in order to check on the possible effect of the cadmium gradient. The evaporation was performed in the usual way, except that radioactive silver chloride was deposited on both end faces. A diffusion run was made at 125°C as before, and the diffusion coefficient at each end of the sample was measured by

⁺ The points at the two highest temperatures have also been corrected for the influence of interstitial ions, as described in Section E and Table V.

slicing and counting. Thus, for sample #14-D, two experimental correlation factors were obtained, one for each end. The average of these two values agrees very well with $f_v^* = 0.781$ (Compaan and Haven's theoretical value), as indicated in Figure 7.

E. Interpretation of Results

We are now in a position to draw some conclusions from the results of the diffusion measurements. First we present a brief summary of the experimental procedure and results.

- (1) A diffusion run was made on a pure AgCl sample in order to test the apparatus and provide a comparison with the results of Weber¹⁹. The diffusion coefficient and experimental correlation factor measured were found to agree very well with Weber's results. Conductivity measurements were also made upon two pure samples, the results of which also agreed well with Weber's values. The conductivities of the pure samples also agreed with Abbink's pure sample conductivities from the highest temperatures to about 225°C, where the two curves began to diverge. This indicates that the "pure" AgCl of this work is considerably more impure than Abbink's "pure" material, which he states contains only 0.1 ppm polyvalent impurity.
- (2) Conductivity measurements were made upon three cadmium doped samples, one from each end of ingot #14, and one from the low impurity concentration end of ingot #13. The shapes of the conductivity curves agreed very well with the curves of Abbink, and a good estimate of the impurity concentrations in the diffusion samples was obtained.
- (3) Diffusion coefficients were measured for samples #14-C,D,E, and #13-B. Experimental correlation factors were obtained by measuring the conductivities of the samples at the diffusion temperatures and calculating D_σ . It was found that the values of f_v^* did not agree too well with the predicted value of f_v^* , because of the distribution of cadmium over the length of the samples. The average divalent impurity concentration for each sample was obtained by comparing the conductivities with Abbink's curves.
- (4) In order to check on this impurity gradient, sample #14-D was reused, and the diffusion coefficient and experimental

correlation factor were measured for both ends of the sample.

The results of the last diffusion run, described in (4) above, were as follows:

$$\begin{aligned}
 D_{\sigma} &= 2.7942 \times 10^{-10} \text{ cm}^2/\text{sec} && \text{(entire sample)} \\
 D_1^* &= 2.3107 \times 10^{-10} \text{ cm}^2/\text{sec} && \text{(previously diffused end)} \\
 D_2^* &= 2.0500 \times 10^{-10} \text{ cm}^2/\text{sec} && \text{(other end)} \\
 f_1^* &= 0.827 && \text{(previously diffused end)} \\
 f_2^* &= 0.734 && \text{(other end)} \\
 \bar{f}^* &= 0.780
 \end{aligned}$$

In calculating $\bar{f}^*$ and thus eliminating the effect of the Cd concentration gradient for this run, it was found that the value obtained deviates negligibly from the free vacancy value ($f_v^* = 0.781$). Also, the spread in the values of f^* between the two ends of #14-D is enough to make the experimental correlation factors obtained for the other samples from ingot #14 entirely plausible. Ingot #13 had a much greater Cd gradient, as is seen by comparing the concentrations of #13-B and 13-C (135 ppm and 77 ppm, respectively). Therefore, we would expect that the non-uniform distribution would have a more pronounced effect on the value of f^* for #13-B. Estimates of the effect of the non-uniform distribution of f^* for all samples have been included in Figure 7.

A somewhat disturbing factor in the interpretation of the results is the discrepancy (5.2%) in the value of f^* for the two diffusion runs on the same end of sample #14-D at 125°C and 225°C. There are two possible explanations for this: (1) association

between Cd^{++} ions and vacancies at the lower temperature could have caused an increase in the value of f^* at that temperature, similar to Miller's results²¹ for AgBr, or (2) a contribution to D^* from interstitial silver ions not completely suppressed by vacancies at the higher temperature could have caused a decrease in the value of f^* for that temperature.

In order to combine the effects of free vacancies, associated vacancies, and interstitial silver ions, we can write the total tracer diffusion coefficient as

$$D_{\text{Ag}}^* = N^{-1} \left[\underset{\substack{\text{(free} \\ \text{vacancy)}}}{f_v n_v d_v} + \underset{\substack{\text{(interstitial)}}}{f_i n_i d_i} + \underset{\substack{\text{(associated} \\ \text{vacancy)}}}{f'_v n'_v d'_v} \right],$$

where d is the microscopic diffusion coefficient. From this it can be shown that

$$f_{\text{Ag}}^* = f_v - (f_v - f_i) \frac{\phi_i y_i}{1 + \phi_i y_i} + f'_v \frac{\phi_i y_i}{1 + \phi_i y_i}, \quad (22)$$

where

$$\phi_i = \text{the mobility ratio } \mu_i / \mu_v,$$

$$\phi'_v = \text{the mobility ratio } \mu'_v / \mu_v,$$

$$y_i = n_i / n_v,$$

$$y'_v = n'_v / n_v.$$

The last term in (22) is the contribution to f_{Ag}^* from Cd ion-vacancy complexes. By extrapolating Abbink's pure crystal data from higher temperatures it is possible to calculate the values of ϕ_i , y_i , and y'_v . The value of $f'_v \phi'_v = f'_v (\mu'_v / \mu_v) = f'_v d'_v / d_v$ may be estimated by comparing the diffusion of Cd into AgCl⁸ to the diffusion of Ag into AgCl. The experimental results show that D_{Cd}^* is

always very much smaller than D_{Ag}^* , even though a large fraction of the Cd ions are already associated with silver ion vacancies. This means that at least one of the jump frequencies associated with diffusion of the complex, ν_{Cd} or ν_{Ag}^* , must be very much smaller than ν_{Ag} for a free silver ion vacancy. It is found that $f_v^* d_v^* / d_v < 10^{-3}$ for all temperatures considered, and the value of the third term in (22) is less than 10^{-4} .²⁷ Hence this term may be neglected.

The value of f_1 at each temperature may be calculated from the results of Weber and Friauf.²⁸ Then with Abbink's data in equation (22), the value of f_{Ag}^* corrected for interstitial silver ion diffusion may be obtained. These points are plotted as open diamonds in Figure 7. The results of this calculation show that the contribution from interstitials is negligible for all but the two highest temperatures considered. For these temperatures the contribution is appreciable, and the discrepancy in the results for sample #14-D is explained. The calculations are outlined in Table V.

In summary, the principal result of this research may be said to be the confirmation of the free vacancy value of the correlation factor in the "structure sensitive" region for AgCl from 225°C to 125°C, within the limits of experimental error.

Two experimental difficulties seem to be important from the point of view of future workers on this subject. These are the non-uniform cadmium distribution over the samples, and the appreciable diffusion which occurs at room temperature. The latter

problem may be solved by storing evaporated samples at liquid nitrogen temperature, as was done for the second run on #14-D. The first problem may be eliminated by annealing the diffusion samples (before evaporation) until a uniform impurity distribution is obtained, or by diffusing both ends of the sample simultaneously. Another possibility is the use of an impurity with a segregation coefficient in AgCl very close to 1. Muller¹³ used Fe^{++} in AgBr and found the segregation coefficient to be 1.05. Elimination of these difficulties will certainly make the results of this research more conclusive.

APPENDICES

	<u>Page</u>
Table I: Numerical Conductivity Data	37
Table II: Error Data	39
Table III: Diffusion Data	40
Table IV: Corrections to f^* from the Non-Uniform Cd Distribution	41
Table V: Corrections to f^* from Interstitial Ions	42
Figure 1: f^* vs T for AgBr doped with 280 ppm CdBr ₂ (after Miller ²¹)	43
Figure 2: Crystal Growth Apparatus	44
Figure 3: Sample Holder	45
Figure 4: Log of Activity vs Square of the Penetration Depth for Sample #13-B	46
Figure 5: Conductivity vs 1000/T	47
Figure 6: Isotherms of Conductivity vs Cd Concentration (from Abbink ²⁶)	48
Figure 7: Correlation factor vs Temperature	49
References	50

TABLE I

Numerical Conductivity Data

<u>Sample #</u>	<u>Temperature</u>		<u>σ (ohm cm)⁻¹</u>
	<u>T(°C)</u>	<u>10³/T(°K)</u>	
12-A (Pure)	199.75	2.1146	5.6908 x 10 ⁻⁵
	224.25	2.0106	1.5673 x 10 ⁻⁴
	250.75	1.9087	4.0693
	274.50	1.8259	8.8523
	300.90	1.7419	1.9758 x 10 ⁻³
	325.30	1.6709	3.9634
	349.90	1.6050	7.7481
	374.37	1.5443	1.4631 x 10 ⁻²
	400.50	1.4844	2.8611
	424.40	1.4336	5.0909
	441.30	1.3997	7.8225
12-H (Pure)	202.00	2.1046	6.3265 x 10 ⁻⁵
	226.30	2.0022	1.6361 x 10 ⁻⁴
	250.10	1.9110	3.8214
	273.57	1.8290	8.1944
	300.63	1.7428	1.8829 x 10 ⁻³
	324.63	1.6728	3.7918
	349.25	1.6067	7.4715
	373.60	1.5462	1.4295 x 10 ⁻²
	399.25	1.4872	2.7710
	425.15	1.4320	5.3413
	439.40	1.4034	7.6054
13-C (77 ppm Cd)	139.50	2.4230	1.8056 x 10 ⁻⁵
	163.70	2.2890	2.9270
	179.00	2.2120	3.8517
	189.28	2.1624	4.6316
	200.30	2.1121	5.7253
	214.58	2.0503	7.8146
	230.37	1.9860	1.1794 x 10 ⁻⁴
	268.25	1.8470	4.4346
	290.78	1.7732	1.0565 x 10 ⁻³
	316.05	1.6972	2.5561
	340.40	1.6298	5.4533
	364.80	1.5675	1.0873 x 10 ⁻²
	393.90	1.4991	2.3748

TABLE I (Continued)

<u>Sample #</u>	<u>Temperature</u>		<u>σ (ohm cm)⁻¹</u>
	<u>T (°C)</u>	<u>$10^3/T$ (°K)</u>	
14-A (354 ppm Cd)	135.88	2.4447	6.1642×10^{-5}
	153.88	2.3417	9.0231
	170.27	2.2551	1.2772×10^{-4}
	174.50	2.2338	1.3416
	192.35	2.1482	1.8489
	210.47	2.0677	2.4666
	230.63	1.9850	3.3235
	246.50	1.9243	4.2610
	276.00	1.8210	7.5230
	300.15	1.7443	1.4031×10^{-3}
	325.25	1.6711	3.0102
	347.88	1.6102	6.0772
	373.98	1.5453	1.3025×10^{-2}
	400.13	1.4852	2.7070
	429.14	1.4239	5.9846
14-F (175 ppm Cd)	134.35	2.4539	3.2395×10^{-5}
	155.90	2.3307	5.0914
	173.25	2.2401	7.0515
	190.70	2.1558	9.5244
	208.63	2.0756	1.2837×10^{-4}
	228.00	1.9954	1.7902
	247.75	1.9197	2.6855
	261.08	1.8718	3.8012
	280.90	1.8049	6.9959
	305.03	1.7295	1.6102×10^{-3}
	328.62	1.6617	3.5612
	352.25	1.5990	7.3435
	375.22	1.5423	1.4185×10^{-2}
	401.88	1.4814	2.9260

TABLE II

	<u>Error Data</u>				<u>14-D (125°C)</u>		
	<u>14-C</u>	<u>14-D</u>	<u>14-E</u>	<u>13-B</u>	Previously Diffused End	Other End	<u>12-C</u>
Slice Thickness (μ)	20	20	20	16	12	12	20
Loss of Mass (mg)	0.79	--	0.55	0.06	0.04	0.40	0.38
Tilt Error (μ)	15	15	25	8	30	10	15
Total Mass Sliced (mg)	180.12	--	141.37	140.81	97.97	87.91	181.37
Time Correction (min.)	37.73	44.61	45.05	66.67	137.43	137.43	27.77
x_{rms} (μ)	155	123	121	105	93	88	117

ERRORS

Slicing (%)	0.09	0.13	0.31	0.07	0.75	0.19	0.15
Cross-Section (%)	0.11	0.16	0.06	0.04	0.22	0.22	0.11
Slope (%)	0.52	0.58	1.49	0.82	0.60	0.89	1.08
Time Correction (%)	0.68	0.76	0.41	0.33	0.87	0.87	0.96
Loss of Mass (%)	0.44	--	0.39	0.04	0.04	0.45	0.21
Sample Length (%)	0.07	0.08	0.06	0.13	0.24	0.24	0.32
Resistance (%)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Room Temp. t_{eff} (%)	0.03	0.01	0.02	0.04	0	0	0
TOTAL ERROR IN σ (%)	0.25	0.34	0.17	0.18	0.51	0.51	0.41
TOTAL ERROR IN D^* (%)	0.99	1.02	1.63	0.89	1.37	1.41	1.48
TOTAL ERROR IN f^* (%)	1.02	1.07	1.64	0.91	1.46	1.50	1.54

TABLE III

Sample Number	<u>Diffusion Data</u>						
	<u>14-C</u>	<u>14-D</u>	<u>14-E</u>	<u>13-B</u>	<u>14-D (125°C)</u> Previously Diffused End	Other End	<u>12-C</u>
Cd Concentration (ppm)	232	222	190	135	216	216	"Pure"
Diffusion Temp T_o (°C)	225.03	199.92	175.32	150.00	125.24	125.24	249.77
$1000/T_o$ (°K) ⁻¹	2.0073	2.1138	2.2298	2.3632	2.5101	2.5101	1.9123
σ at T_o (ohm cm) ⁻¹ $\times 10^{-5}$	20.339	13.074	7.8149	3.6357	3.0775	3.0775	35.358
W_o (ev)	0.3117	0.3117	0.3117	0.3117	0.3144	0.3144	0.5350
G_o (%/μv)	.03607	.04027	.04522	.05033	.05651	.05651	.05441
H_o (°C/μv)	.02474	.02491	.02514	.02491	.02458	.02458	.02447
m_o (mg)	9.50	9.45	9.61	7.59	5.68	5.21	8.98
A (sq cm)	.69503	.69664	.69679	.70061	.68779	.68779	.70614
Slope of Diffusion Profile	.01254	.01984	.02090	.01720	.01249	.01185	.01930
Uncorrected t_{eff} (min)	1025.29	1099.27	2020.13	3580.35	3151.17	3151.17	575.78
Correction to t_{eff} (min)	89.93	27.90	151.74	477.54	0	0	0
Corrected t_{eff} (min)	1115.22	1127.17	2171.87	4057.89	3151.17	3151.17	575.78
D^* (cm ² /sec) $\times 10^{-10}$	18.000	11.094	5.6492	2.2658	2.3107	2.0500	19.614
D_σ (cm ² /sec) $\times 10^{-10}$	23.092	14.096	7.9875	3.5062	2.7942	2.7942	42.138
$f^* = D^*/D_\sigma$	.77949	.78703	.70726	.64623	.82696	.73366	.46547

TABLE IV

Corrections to f^* from the Non-Uniform Cd Distribution

Sample Number	<u>14-C</u>	<u>14-D</u>	<u>14-E</u>	<u>13-B</u>	<u>14-D</u>
T_o ($^{\circ}\text{C}$)	225.03	199.92	175.32	150.00	125.24
c_o (ppm)	232	222	190	135	216
Length (cm)	0.68	0.60	0.52	0.47	0.50
^a q_1 (%)	3.44	6.02	3.95	21.5	6.02
^a q_2 (%)	^b (3.44)	3.70	6.85	^b (21.5)	3.70
^c Calculated f_1^*	.757	.740	.754	.644	.740
^c Calculated f_2^*	(.805)	.807	.830	(.934)	.807
Observed f_1^*	--	--	.707	.646	.734
Observed f_2^*	.779	.787	--	--	.827

^a q_1 and q_2 are the values of q corresponding to end one and end two of the sample.

^b Values of q_2 in parentheses were taken to be the same as the corresponding values of q_1 , since q_2 could not be estimated for these samples.

^c From equations (19) and (20) with $f_v^* = 0.781$.

TABLE V

Corrections to f^* from Interstitial Ions

Sample Number	<u>14-C</u>	<u>14-D</u>	<u>14-E</u>	<u>13-B</u>	<u>14-D</u>
T_o (°C)	225.03	199.92	175.32	150.00	125.24
c_o (ppm)	232	222	190	135	216
^a ϕ_i	18.7	24.4	32.3	44.6	64
^b f_i	0.420	0.410	0.400	0.391	0.381
^a $y_i = n_i/n_v$	0.00415	0.00096	0.00023	0.00005	0.00000
$\phi_i y_i / (1 + \phi_i y_i)$	0.0720	0.0228	0.00729	0.00238	0.00025
^c Δf_{Ag}^*	-0.0261	-0.0085	-0.0028	-0.0009	-0.0001
f_{Ag}^*	0.755	0.773	0.779	0.781	0.781
^d Calculated f_1^*	0.732	0.732	0.752	0.644	0.740
^d Calculated f_2^*	(0.778)	0.798	0.828	(0.932)	0.807

^a By extrapolation of results from reference 26.

^b By extrapolation of results from reference 28.

^c From the second term of equation (22).

^d From equations (19) and (20) with f_{Ag}^* in place of f_v^* . The values of q_1 and q_2 are taken from Table IV.

Figure 1: f^* vs T for AgBr doped with 280 ppm CdBr_2 (after Miller²¹)

Figure 2: Crystal Growth Apparatus

Figure 3: Sample Holder

Figure 4: Log of Activity vs. Square of the Penetration Depth

Figure 5: Conductivity vs. 1000/T

Figure 6: Isotherms of Conductivity vs Cd Concentration (from Abbink²⁶)

Figure 7: Correlation Factor vs Temperature

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