PHYSICAL REVIEW VOLUME 105, NUMBER 3 FEBRUARY 1, 1957

Diffusion of Silver in Silver Bromide and Evidence for Interstitialcy Migration

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(Received September 4, 1956)

Experimental results are presented for the diffusion of silver in silver bromide single crystals for temperatures from 140°C to the melting point. The results are obtained by the sectioning technique, using radioactive tracers. The observed diffusion coefficients fall below the values that would normally be expected from the electrical conductivity by a factor of 0.46 to 0.66. The discrepancy is ascribed to the simultaneous occurrence of two types of interstitialcy jumps, with corrections introduced for differing displacements of interstitials and tracer atoms and for correlation effects according to Bardeen and Herring. The resulting mobilities can be represented as $\mu=\mu_0\exp(-U/kT)$ over a wide range of temperatures with $\mu_0=6.2\times10^{-3}$ and 1.57×10^{-3} cm²/volt-sec and $U=0.078$ and 0.225 ev, respectively, for collinear and noncollinear jumps. These values are in reasonable agreement with theoretical calculations for silver chloride. The diffusion coefficient is observed to fall increasingly below expected values as the temperature approaches the melting point, and as a possible explanation it is surmised that the activation energy for collinear jumps drops gradually towards zero. A comparison is made to similar results which have been reported for diffusion of silver in silver chloride.

EXPERIMENTAL PROCEDURE AND RESULTS

THE AgBr was precipitated from J. T. Baker "Analyzed Reagent" grade HBr and $AgNO_3$, and single crystals were grown by withdrawal from the melt. After cylindrical samples, roughly 1 cm in all dimensions, were machined on a lathe, a thin layer of AgBr containing radioactive Ag^{110} was deposited on one end of the sample by vacuum evaporation, followed by evaporated metallic silver electrodes on both ends. A sample was then subjected to the desired diffusion temperature for a suitable length of time, during which time the electrical conductivity was measured with an ac bridge at 1000 cps. After diffusion the sample was sectioned on a microtome, the thickness of each section being determined from the weight of the section. Each section was then dissolved in hypo, and its activity was determined with a scintillation counter.

For a thin source with diffusion in one dimension only, a plot of the natural log of the activity *vs* the distance squared should give a straight line with slope $-(4Dt)^{-1}$, and this is found to be true in all cases as shown in Fig. 1, indicating that a genuine volume diffusion process is being observed. Since the temperature is not constant throughout the diffusion anneal, the effective time to be used in obtaining D from the slope of such a plot is determined by $t_{\mathrm{eff}}=D_0^{-1}\int_0^\infty D(T)dt$, where D_0 is an assumed value at the temperature T_0 for which D is to be determined, and where the integral is evaluated graphically by using the measured variation of T with time t. The results obtained in this fashion at various temperatures are shown in Fig. 2 and listed in Table I, where all values have been corrected for the large thermal expansion of AgBr.[1] Since the interesting features in this work arise from a comparison of the diffusion coefficient to the electrical conductivity, the value of the diffusion coefficient to be expected according to the normal relation Eq. (4), which is discussed in the next section, is shown in Fig. 2, and from these values the ratios $D_{\mathrm{obs}}/D_{\mathrm{cond}}$ in Table I are calculated.

The errors listed in Table I are composed of the internal random errors of D, as determined by least-squares fitting of a straight line[2] to plots like Fig. 1, and of σ, as determined by comparing measurements at different times during diffusion; the two sets of standard deviations are approximately equal in size. The com-

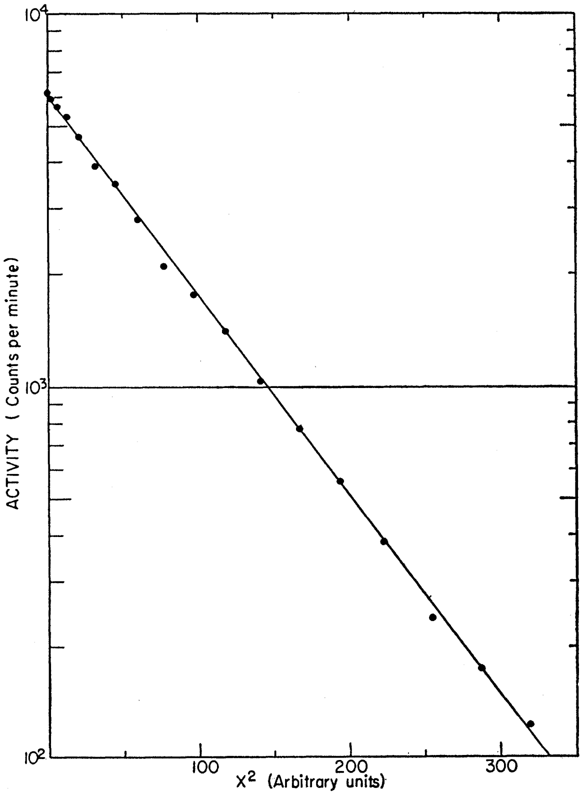

FIG. 1. Logarithm of activity *vs* square of penetration depth for 361°C. Each unit of distance equals 152 microns. The straight line is determined by a least-squares calculation.

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[1] P. G. Strelkow, Physik. Z. Sowjetunion **12**, 73 (1937).

[2] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 502.

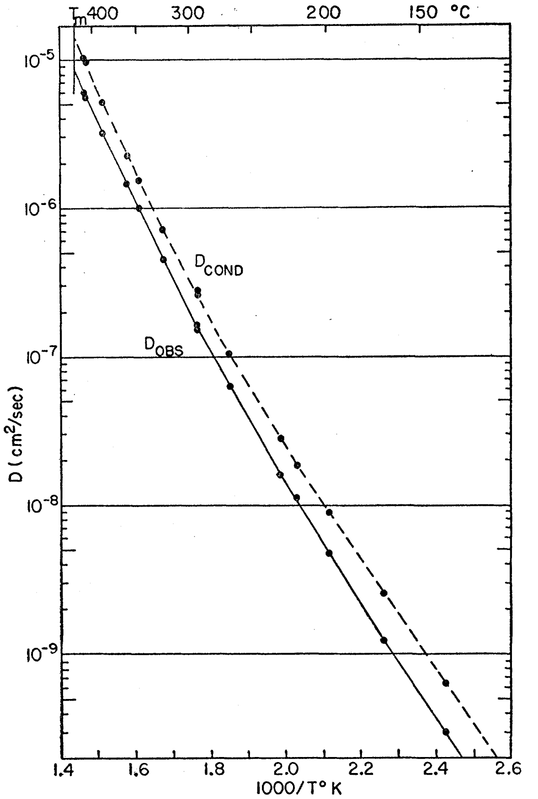

FIG. 2. Plot of $\log D$ *vs* $1/T$. D_{cond} is calculated from the observed electrical conductivity by the normal relation, Eq. (4).

parison of σ at each temperature to the average of several standard samples gives a standard deviation of 2.0%, indicating the possible extent of errors in measuring sample size or temperature. Errors caused by finite slice thickness and misalignment are certainly less than 1%,[3] as are errors caused by the finite length of the sample. The total correction for temperature changes during diffusion does not exceed 5% at the highest temperatures, and should not cause an error greater than 1%.

THEORY

The relationship between diffusion and electrical conductivity in ionic crystals arises from the Einstein relation[4]

$$D_v/\mu_v = D_i/\mu_i = kT/e, \tag{1}$$

where D_v, D_i, μ_v, and μ_i are the microscopic diffusion coefficients and mobilities for the two types of defects that occur in AgBr, silver ion vacancies and interstitial silver ions.[5,6] The observed quantities are the electrical conductivity σ and the macroscopic diffusion coefficient D_{cond}; these are normally related to the microscopic quantities by[7]

$$\sigma = en_v\mu_v + en_i\mu_i \tag{2}$$

and

$$D_{\text{cond}} = (n_v/N)D_v + (n_i/N)D_i, \tag{3}$$

where n_v, n_i, and N are the number per unit volume of vacancies, interstitials, and silver lattice sites, respectively. By combining Eqs. (1), (2), and (3) the normal form of the observed relation is expected to be

$$D_{\text{cond}}/\sigma = kT/Ne^2. \tag{4}$$

It is seen in Fig: 2 that the observed diffusion coefficient is smaller than predicted by Eq. (4), and the amount of the discrepancy is calculated in Table I. In the remainder of the paper the reasons for the existence of this discrepancy and the conclusions which can be drawn from it will be investigated.

Since Eqs. (1) and (2) appear to be irreproachable, the source of trouble must lie in Eq. (3), and this is found to be the case when it is realized that in the actual diffusion experiment the motion of tracer atoms is followed, not the motion of individual vacancies or interstitials. There are two types of effects which introduce changes in Eq. (3): (A) the tracer may not move the same distance in an elementary jump as the vacancy or interstitial does, and (B) the successive jumps of a given tracer may be directionally correlated to some extent, an effect which is not present for a vacancy or interstitial. With these effects combined into correction factors f_v and f_i, Eq. (3) must be written

$$D_T^* = f_v(n_v/N)D_v + f_i(n_i/N)D_i, \tag{5}$$

and in a pure crystal where $n_v = n_i$ and $\phi = \mu_i/\mu_v$, the

TABLE I. Observed values of diffusion coefficient and electrical conductivity.[a]

T °C	D_{obs} cm²/sec	σ_{obs} (ohm-cm)$^{-1}$	$D_{\text{obs}}/D_{\text{cond}}$
140	3.01×10^{-10}	6.03×10^{-5}	0.465 ± 0.007
170	1.24×10^{-9}	2.22×10^{-4}	0.481 ± 0.007
200	4.78×10^{-9}	7.26×10^{-4}	0.531 ± 0.005
220	1.13×10^{-8}	(1.12×10^{-3})	(0.605 ± 0.010)
230	1.62×10^{-8}	2.14×10^{-3}	0.570 ± 0.005
268	6.42×10^{-8}	7.41×10^{-3}	0.603 ± 0.006
294	1.64×10^{-7}	(1.89×10^{-2})	(0.573 ± 0.008)
294	1.54×10^{-7}	(1.76×10^{-2})	(0.576 ± 0.005)
325	4.59×10^{-7}	4.53×10^{-2}	0.635 ± 0.008
350	1.03×10^{-6}	(7.00×10^{-2})	(0.655 ± 0.010)
361	1.50×10^{-6}	1.35×10^{-1}	0.650 ± 0.006
387	3.31×10^{-6}	2.96×10^{-1}	0.620 ± 0.004
407	5.92×10^{-6}	5.41×10^{-1}	0.584 ± 0.008
409	6.29×10^{-6}	5.69×10^{-1}	0.588 ± 0.006

[a] In the last column D_{cond} is calculated from the observed conductivity according to the normal relation in Eq. (4). The values in parentheses are somewhat uncertain because of appreciable temperature gradients in the early form of sample holder.

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[3] Shirn, Wajda, and Huntington, Acta Metallurgica **1**, 513 (1953).

[4] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, p. 63.

[5] J. Teltow, Ann. Physik **5**, 63, 71 (1949).

[6] S. W. Kurnick, J. Chem. Phys. **20**, 218 (1952).

[7] Reference 4, p. 34.

over-all relation becomes

$$\frac{D_T^*}{\sigma}=\left(\frac{f_v+\phi f_i}{1+\phi}\right)\frac{kT}{Ne^2}=f\frac{kT}{Ne^2}. \tag{6}$$

The quantity f which is defined in Eq. (6) is seen by comparison to Eq. (4) to be equal to D_T^*/D_{cond}, where D_T^* should correspond to D_{obs}.

For vacancies the entire correction is due to effect (B), and $f_v=0.80$ has been calculated by Bardeen and Herring, who first proposed this effect;[8] a recalculation by the writer gives a value of $f_v=0.79$.[9] For interstitials several types of jumps as shown in Table II need to be considered. Type 0 jumps involve the passage of an interstitial through the face of a small cube and are energetically unfavorable.[10] In type 1 and type 2 jumps, an interstitial displaces a neighboring lattice ion into an interstitial site in a cell having one corner and one edge, respectively, in common with the cell occupied by the original interstitial, which occupies the vacated lattice site; jumps of this type have been called interstitialcy jumps by Seitz[11] and have been considered for silver halides by Teltow,[5] Hove,[10] and McCombie and Lidiard.[12] Also included in this table for convenience, although not strictly interstitial jumps, are type 3 jumps, which involve the initial stage of formation or the final stage of recombination of a pair of Frenkel defects, e.g., the jump of a lattice ion to one of its neighboring interstitial sites. For type 0 jumps neither effect is present and $f_i=1$. For type 1 jumps both effects are present, with (A) causing the greater correction, and $f_i=0.333$ has been calculated in reference 12. In the following, corrections will be calculated for type 2 jumps and for situations where jumps of types 1, 2, and 3 can occur simultaneously.

First consider the case where jumps of both types 1 and 2 may occur with frequencies ν_1 and ν_2 for an interstitial ion. [The probability that an interstitial will jump toward any *given* neighboring lattice ion in a short time dt is then $z^{-1}(\nu_1+\nu_2)dt$, where $z=4$ is the number of neighboring lattice ions.] The amount of the correction f_i in Eq. (5) will depend on the relative frequency of the two types of jumps, $\kappa=\nu_1/\nu_2$, attaining the values for type 1 and type 2 jumps in the limits $\kappa\rightarrow\infty$ and $\kappa\rightarrow 0$, respectively. To determine f_i, the diffusion coefficients are related to the mean square displacements of the diffusing entities;[8,13]

TABLE II. Types of interstitial jumps.[a]

Type	Description	a_i	b_i
0	Direct interstitial	a	a
1	Collinear interstitialcy	$\sqrt{3}a$	$\frac{1}{2}\sqrt{3}a$
2	Noncollinear interstitialcy	$\sqrt{2}a$	$\frac{1}{2}\sqrt{3}a$
3	Formation or recombination	$\frac{1}{2}\sqrt{3}a$	$\frac{1}{2}\sqrt{3}a$

[a] a_i is the displacement of an interstitial ion during the jump; b_i is the displacement of a tracer atom during the jump; a is the edge of the smallest cube in the NaCl type lattice.

$$\frac{D_{\text{T}i}^*}{D_i}=\frac{\langle(r_{\text{T}i}^*)^2\rangle_{\text{Av}}}{\langle r_i^2\rangle_{\text{Av}}}=\frac{\langle r_T^2\rangle_{\text{Av}}}{\langle r_i^2\rangle_{\text{Av}}}\frac{\langle(r_{\text{T}i}^*)^2\rangle_{\text{Av}}}{\langle r_T^2\rangle_{\text{Av}}}=f_i'f_i''\frac{n_i}{N}=f_i\frac{n_i}{N}, \tag{7}$$

where the total correction $f_i=f_i'f_i''$ contains separately effect (A) in f_i' and effect (B) in f_i''. Since in these jumps a tracer may move either by being in an interstitial position or by occupying a lattice site next to an interstitial ion, it follows that $\nu_{T1}/\nu_1=\nu_{T2}/\nu_2=2n_i/N$. Then

$$f_i'=2\frac{\nu_1 b_1^2+\nu_2 b_2^2}{\nu_1 a_1^2+\nu_2 a_2^2}=\frac{1}{2}\left(\frac{\kappa+1}{\kappa+\frac{2}{3}}\right), \tag{8}$$

where values for a_i and b_i have been inserted from Table II.

The calculation of f_i'' proceeds according to

$$f_i''=b_{\text{Av}}^{-2}\langle(\textstyle\sum\mathbf{b}_i)^2\rangle_{\text{Av}}=1+2b_{\text{Av}}^{-2}\textstyle\sum_j\langle\mathbf{b}_i\cdot\mathbf{b}_{i+j}\rangle_{\text{Av}}, \tag{9}$$

where $b_{\text{Av}}^2=b_1^2=b_2^2$ is the value $\langle(\sum\mathbf{b}_i)^2\rangle_{\text{Av}}$ would have if no correlation were present, since then the cross terms in Eq. (9) would average to zero. Since there will be correlation for the tracer in these jumps only for the first jump after a tracer has landed in a lattice site, all terms with $j\geq i+2$ will vanish, and only half the terms with $j=i+1$ will contribute. Hence

$$f_i''=1+b_{\text{Av}}^{-2}\langle\mathbf{b}_i\cdot\mathbf{b}_{i+1}\rangle_{\text{Av}'}, \tag{10}$$

where the prime on the average indicates that it is to be taken for jumps immediately after the tracer has jumped to a lattice site. The average in Eq. (10) may be evaluated in terms of the probability $p(s,r)$ that the interstitial which has just been displaced to site r by the tracer will first return from site s to displace the tracer. If $q(t,s)$ is the probability that the interstitial goes to site t when the tracer jumps from site s and if the tracer last jumps from site 3, then

$$\langle\mathbf{b}_i\cdot\mathbf{b}_{i+1}\rangle_{\text{Av}'}=-\mathbf{b}_3\cdot\textstyle\sum_r q(r,3)\sum_s p(s,r)\sum_t q(t,s)\mathbf{b}_t, \tag{11}$$

where $\mathbf{b}_t$ is the vector from the lattice site to the interstitial site t and where the sums over r, s, and t extend over the eight interstitial sites shown in Fig. 3. By introducing the appropriate geometry and expressing

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[8] J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952), p. 281, with the correction of a factor of two as indicated in reference 11.

[9] It has recently been brought to the writer's attention by A. B. Lidiard that a value of $f_v=0.78146$ has been calculated by K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956). Lidiard also states that Compaan and Haven have obtained values of 1/3 and 8/11 for type 1 and type 2 processes, respectively (see Table II), in excellent agreement with the values presented in this paper.

[10] J. E. Hove, Phys. Rev. **102**, 915 (1956) and thesis, Cornell University, 1953 (unpublished).

[11] F. Seitz, Acta Cryst. **3**, 355 (1950).

[12] C. W. McCombie and A. B. Lidiard, Phys. Rev. **101**, 1210 (1956).

[13] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

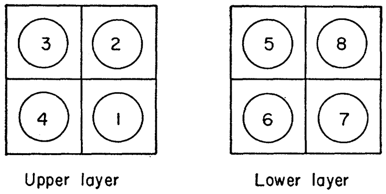

FIG. 3. Numbering of interstitial sites around a lattice site, which is midway between the two layers shown and centrally located with respect to each layer.

$q(t,s)$ in terms of ν_1 and ν_2, it is found that

$$f_i''=1-(\kappa+\tfrac{1}{3})^2(\kappa+1)^{-2}P, \tag{12}$$

with

$$P=p(1,1)+p(2,1)-p(3,1)-p(5,1).$$

The probabilities $p(s,1)$ can be obtained directly by following the motion of the interstitial step by step, using the proper probabilities for the various possible jumps at each step, counting $\frac{1}{4}$ of the probability that each neighboring site s is occupied at the end of a step towards $p(s,1)$, and using $\frac{3}{4}$ of the probability for neighboring sites and all of the probability for other sites as the starting probability distribution for the next step. This process has been carried out for the case $\kappa=\infty$ (type 1 jumps only), yielding after twelve jumps $p(1,1)=0.344$ and $p(5,1)=0.013$ (sites 2 and 3 cannot be reached in this case); combined with $f_i'=\frac{1}{2}$ these values give $f_i=0.336$, in excellent agreement with reference 11. Since such a process is tedious to repeat, however, it is convenient to estimate $p(s,1)$ for other cases from values given by McCrea and Whipple[14] for random walk of a particle on a simple cubic lattice with no restrictions such as those described above. Values are quoted for $p''(s,1)$, the total number of appearances at site s after starting at site 1; from these it follows that the probabilities of first return $p'(s,1)=[1-p'(1,1)]p''(s,1)$ are 0.35, 0.35, 0.23, and 0.18 for $s=1$, 2, 3, and 5. By inserting the factors of $\frac{1}{4}$ and $\frac{3}{4}$ as indicated above, values of $p(s,1)=\frac{1}{4}p'(s,1)\frac{3}{4}[1-\frac{3}{4}(0.35)]^{-1}$ are found to be 0.339, 0.089, 0.058, and 0.046 for $s=1$, 2, 3, and 5. The estimate agrees remarkably well with the exact value above for $p(1,1)$ and is somewhat too large for $p(5,1)$ as expected; hence the estimated values are corrected by ratios varying in equal steps between the ratios calculated for $p(1,1)$ and $p(5,1)$. The values thus obtained should be most appropriate for the case $\kappa=1$ since in this case the actual motion of the interstitial approaches most closely that of a particle on a simple cubic lattice; a value of $P=0.39$ is found from Eq. (12). Although P will in principle vary slowly as κ varies, the values of κ found in the next section are close enough to unity that no change in P is required. With this value of P, Eqs. (7), (8), and (12) then give f_i as a function of κ.

For the case where type 2 jumps predominate ($\kappa\rightarrow 0$), P is estimated to be 0.31, and $f_i'=0.750$, giving $f_i=0.725$.

At temperatures approaching the melting point it is to be expected that type 3 jumps will make a noticeable, though small, contribution to the diffusion and the conductivity. The maximum contribution of these jumps may be roughly estimated by supposing that an interstitial recombines with a vacancy whenever the two happen to occupy adjacent sites[15]; then, since only three of the four lattice sites next to an interstitial have a chance of being vacant at any one time and since the number of formation jumps must equal the number of recombination jumps, $\nu_3=2\nu_R=6(n_v/N)\nu_i$. It is found that there is a contribution to the conductivity of $\sigma_3=(e^2/kT)n_i\nu_R(\frac{1}{2}a)^2$ and to the diffusion of $D_{T3}=(6t)^{-1}\langle r_{T3}{}^2\rangle_{\text{Av}}=(n_i/N)\nu_R(\frac{1}{2}a)^2$, yielding $D_{T3}/\sigma_3=kT/Ne^2$ as expected since possible correlation effects have been neglected. Equation (6) must then be modified by adding to both numerator and denominator a term

$$\frac{\sigma_3}{\sigma_v}=\left(\frac{\sigma_i}{\sigma_v}\right)\left(\frac{\sigma_3}{\sigma_i}\right)=\phi\frac{9}{4}\left(\frac{n_v}{N}\right)\left(\frac{\kappa+1}{\frac{3}{2}\kappa+1}\right), \tag{13}$$

which is obtained by using $\nu_i=\nu_1+\nu_2$ and

$$\sigma_i=(e^2/kT)n_i(\tfrac{1}{2}\nu_1a^2+\tfrac{1}{3}\nu_2a^2). \tag{14}$$

INTERPRETATION OF RESULTS

Before discussing the results of the previous section, it may be noted that it does *not* appear to be possible to ascribe the observed deviation from the normal relation, Eq. (4), to any processes which enhance the conductivity without contributing to the diffusion of silver atoms. Both transport experiments[6] and some

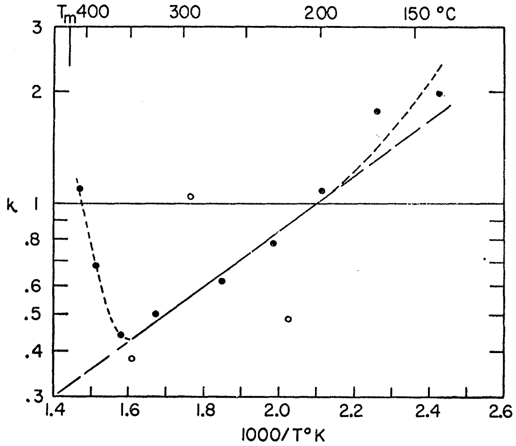

FIG. 4. Logκ *vs* $1/T$. The quantity κ is the ratio of frequencies of the two interstitialcy processes. Open circles represent less reliable data (see Table I).

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[14] W. H. McCrea and F. J. Whipple, Proc. Roy. Soc. (Edinburgh) **60**, 281 (1940).

[15] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), second printing, p. 17.

results on diffusion of bromine[16,17] indicate that bromine ion vacancies do not make any appreciable contribution to the conductivity, and the electronic conductivity has also been observed to be several orders of magnitude smaller than the conductivity actually observed.[18]

The experimental results have been analyzed in the following manner. From Teltow's[5] values of ϕ and the value of f_v obtained in the previous section, the values of f_i needed to account for the observed values of f have been calculated from Eq. (6). Then these values are used in Eqs. (7), (8), and (12) to calculate κ as a function of T; the results are shown in Fig. 4. Aside from some of the early measurements the points for intermediate temperatures follow the sort of activation curve which might be expected; explanations for the deviations at high and low temperatures are offered below. The straight line portion of the plot is represented by $\kappa=\kappa_0 \exp(U/kT)$, with $\kappa_0=0.026=1/38$ and $U=0.15$ ev. Now by using the straight line for κ at all temperatures, the process has been reversed to calculate f_i and then f, which is shown in Fig. 5 along with the experimental points. The agreement is seen to be quite satisfactory. The values of f calculated for single processes of types 0, 1, or 2 are also shown, indicating clearly that no single process gives very good agreement; it is especially evident that type 0 processes are not likely to occur, as is to be expected from energy considerations.

The mobilities for type 1 and type 2 processes may now each be calculated from κ and Teltow's values of μ_i [5]; by utilizing the Einstein relation it is possible to write

$$\mu_i=\mu_1+\mu_2=\mu_2(\tfrac{3}{2}\kappa+1),$$

as in Eq. (14). The results appear in Fig. 6, from which activation energies $U_1=0.078$ ev and $U_2=0.23$ ev are obtained. The dashed extension of μ_i is calculated from the extrapolated values of μ_1 and μ_2, indicating that the presence of two processes in the interstitial mobility would not be especially evident in the curve for μ_i even if the peculiar jog in Teltow's data were not present.

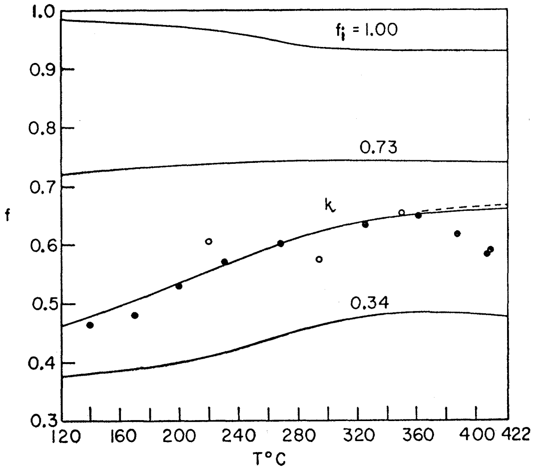

FIG. 5. Theoretical curves of $f=D_{\text{obs}}/D_{\text{cond}}$. The curves are calculated, reading from the top down, for type 0, type 2, type 1 and 2 combined, and type 1 processes (see Table II); for type 1 and 2 processes combined f_i is calculated from κ shown in Fig. 4. The dotted curve at high temperatures represents the effect of including type 3 processes. Experimental points are indicated by circles, the open circles representing less reliable data (see Table I).

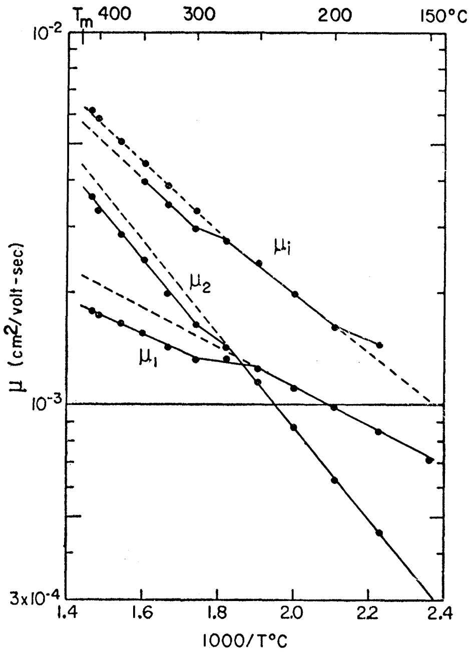

FIG. 6. Mobilities associated with jumps of interstitial ions. μ_i is experimentally observed by Teltow, reference 5; μ_1 and μ_2 are calculated from μ_i and the values of κ from Fig. 4. The dotted portion of μ_i at high temperatures is obtained by adding the extrapolated values of μ_1 and μ_2.

The values obtained here for κ_0, U_1, and U_2 appear to be in reasonable agreement with theoretical values calculated by Hove,[9] who obtains $U_2=0.8$ ev and $U_1=-0.1$ to $+0.4$ ev for AgCl. Even though Hove's value for U_2 is somewhat larger than observed, this value would be expected to be smaller in AgBr because of the larger polarizability of bromine, and an observed value of 0.15 ev has been reported for interstitial mobility in AgCl.[19] For the pre-exponential factor κ_0, the geometry of the lattice provides three type 2 jumps for each type 1 jump, leaving only a factor of thirteen to be accounted for by the entropies of activation,[20] a seemingly not unreasonable value.

The maximum possible effect of formation and recombination has been determined by calculating the term given in Eq. (13), using values of κ from Fig. 4 and

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[16] Murin, Kazakova, and Lure, Doklady Akad. Nauk S.S.S.R. **99**, 529 (1954).

[17] D. Tannhauser (private communication).

[18] J. Teltow, Z. Physik. Chem. **195**, 213 (1950).

[19] I. Ebert and J. Teltow, Ann. Physik **15**, 268 (1955).

[20] C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952), p. 289.

n_v/N from Teltow.[5] Although in principle the inclusion of this effect should alter slightly the calculation of ϕ from the conductivity data, the over-all influence on the calculated value of f, as shown by the dotted curve in Fig. 5, is so slight that no attempt has been made to perform this alteration, and in fact the total effect is negligibly small.

The lowering of the observed diffusion at the two lowest temperatures (see Fig. 5) may perhaps be due to the presence of small amounts of sulfur, which would increase the number of interstitials relative to vacancies and hence decrease D_{obs}. A simple calculation using the law of mass action indicates that 5 to 50 parts per million would be sufficient.[18] This amount is not detectable by ordinary methods and could have been introduced by the etching in sodium thiosulfate which alawys preceded a high temperature anneal.

The droop in D_{obs} at high temperatures appears to be a genuine, reproducible effect since impurities will not be effective at these temperatures. The anomalous thermal expansion offers no help whatsoever if pure Frenkel defects exist, for then the correction to N in Eq. (4) precisely cancels the corrections to D_{cond} and σ. If an appreciable number of Schottky defects coexist as suggested by Kurnick,[6] the correction to N is altered slightly, but a much larger effect is introduced by the suppression of interstitials according to the law of mass action. For Kurnick's values of n_i and n_v at 406°, this would lead to $f=0.77$, a much *larger* value than observed or expected. Since the concentration of defects approaches 1 to 2% at the melting point,[5,6] it will fairly often happen that a tracer atom will be moved by some defect other than the one which last moved it (an effect implicitly excluded both in Eq. (9) and in reference 8). Thus part of the correlation in both f_v and f_i will be destroyed, again tending to make *f larger* than expected. It is also likely that corrections of the Debye-Hückel type will be appreciable in this temperature region,[5] but since at 408°C the observed f is smaller than f_i calculated with κ from Fig. 4, this effect can offer at most only a partial explanation.

An interesting possibility for the explanation of this droop lies in the observation that U_1 may decrease rapidly as the lattice loosens up prior to melting. On this basis, values of U_1 which are necessary to yield the actual values of κ in Fig. 4 have been calculated from $\kappa=\kappa_0 \exp[(U_2-U_1)/kT]$, keeping κ_0 and U_2 constant. The results for U_1 at the four highest temperatures fall remarkably well on a straight line which extrapolates to zero at 413°, provocatively close to the melting point, which is often quoted at 422°C[21] but may lie between 416° and 420°C.[22] Of course U_2, as well as U_v, will also tend to decrease as the melting point is approached, but at least it appears likely that this effect accounts for a major portion of the observed droop.

The experimental results have been interpreted satisfactorily by considering the simultaneous occurrence of type 1 and type 2 jumps, and the values obtained for U_1, U_2, and κ_0 appear reasonable when compared to theoretical calculations. It is entirely possible, however, that other combinations of processes, perhaps involving the dumbbell model for interstitials proposed by Hove,[10] might give just as good agreement. Without more precise theoretical values, it would appear difficult to exclude completely other possibilities of this type.

Measurements of the diffusion of silver in AgCl have been reported by Compton,[23] and the general trend of the results is much the same as in AgBr. Values of $f=D_{\text{obs}}/D_{\text{cond}}$ obtained from Compton's data[24] lie between 0.4 and 0.6 except at temperatures below 150°C, where impurities are important, and there is a gradual rise of f as the temperature increases, with no evidence, however, of a droop similar to that observed in AgBr at high temperatures, even at 429°C, which is only 26°C below the melting point of AgCl. An attempt has been made to analyze the data for AgCl in the fashion described above for AgBr, but the errors of five to ten percent in the data preclude a detailed, quantitative treatment. It seems clear for both substances, however, that the motion of interstitial ions must definitely occur by some sort of interstitialcy process; furthermore the analysis in AgBr indicates that at least two such processes are present and compete with each other, and a similar type of explanation appears to be required to account for the general trend of the observed results in AgCl. As far as the author is aware, the results for these two substances represent the first unambiguous evidence for interstitialcy motion as a mechanism for diffusion in solids and may suggest the possibility of similar mechanisms in other types of solids.

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[21] Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (J. Springer, Berlin, 1931), fifth edition, Hauptwerk I, p. 355.

[22] See reference 1. This is tentatively confirmed by some experiences of the writer.

[23] W. D. Compton, Phys. Rev. **101**, 1209 (1956).

[24] W. D. Compton, thesis, University of Illinois, 1955 (unpublished).