PHYSICAL REVIEW B VOLUME 24, NUMBER 2 15 JULY 1981

Diffusion of rubidium ion in silver bromide and temperature dependence of Frenkel formation energy

P. A. Cardegna and A. L. Laskar
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29631

(Received 22 December 1980)

The diffusion of Rb^+ ion in AgBr has been measured in the temperature range 184 – 421 °C by a tracer and serial-sectioning technique. The temperature dependence of the diffusivity follows a linear Arrhenius law with parameters $D_0 = (1.04 \pm 0.30) \times 10^4$ cm²/sec and $H = 1.33 \pm 0.02$ eV. When one assumes no Coulombic binding between the monovalent solute and vacancy, the activation enthalpy for the migration of an Rb^+ ion by a vacancy mechanism, H_m, is estimated to be 0.75 eV. The curvature in the Arrhenius plot, expected on the basis of a temperature-dependent defect-formation energy, is not observed, perhaps owing to a temperature-dependent elastic binding energy between the oversized Rb^+ ion and neighboring vacancy. An important trend relating a variation in H_m to the mismatch between the sizes of the solute and host ion for all the reported impurity-diffusion studies in AgBr has been observed and discussed.

I. INTRODUCTION

A high-temperature anomaly in many of the physical properties of both AgBr and AgCl has been observed for years. Early recognition of these anomalies include elastic constants,[1,2] thermal expansion,[3,4] dielectric coefficient,[5] heat capacity,[6,7] electrical conductivity[8,9] and the cation self-diffusion.[10,11] As the melting point is approached, these crystals exhibit further anomalies[12]: loss of mechanical hardness, decrease in velocity of sound, and a greatly enhanced thermal diffuse scattering of x rays. It becomes apparent that, although the silver halides are a "simple", well-characterized ionic system with Frenkel disorder, the defect properties deviate significantly from the predictions based on Lidiard's excellent theory of ionic crystals.[13] To explore and understand the nature of this anomaly a major thrust of experimental and theoretical investigations has been focused towards the study of charge and mass transport in silver halides with more and more refined and sophisticated techniques. Friauf's[14] critical review and analysis of the excellent data acquired by a number of investigators over the last thirty years indicates the remarkable and interesting defect properties in this system.

Specifically, the electrical conductivity of AgBr and AgCl anomalously increases by more than 200% near the melting point with a corresponding increase of the self-diffusion of the cations. Four factors have been invoked to explain this and other anomalies: (1) the onset of additional defects species, (2) the effect of defect interactions on defect concentrations, (3) the possibility of alternate migration mechanisms becoming operative as the temperature increases, and finally (4) the temperature dependence of the thermodynamic parameters characterizing the Frenkel defect formation and migration. The possibility of the presence of Schottky defects (in addition to usual Frenkel defects) that had been invoked in the early explanation of thermal expansion,[15,16] the lattice expansion by x-ray diffraction,[4] and the thermal capacity[6,7] can lead to the enhanced conductivity at high temperature. Berry,[17] measuring the lattice parameter of AgBr in the temperature range 350–420 °C, concluded that the disorder was predominantly Frenkel type but because of the magnitude of the experimental uncertainties, the existence of a very small number of Schottky defects cannot be ruled out. Similar results were obtained by Lawn,[4] Fouchaux and Simmons,[3] and Nicklow and Young,[18] i.e., the dominant disorder is Frenkel type with the possible existence of a small amount of "mixed" disorder near the melting point. In his study of the defect-formation volume, determined by measuring the conductivity of AgBr under high pressure, Kurnick[9] was led to a similar conclusion. It is believed, though, that the small fraction of Schottky defects that would be expected cannot explain the major part of the anomalous behavior of the silver halides.

The second factor, that is, the defect-defect interaction due to long-range Coulombic effects, is described by the Lidiard-Debye-Hückel (LDH) theory[13] and is found at least "partly" responsible for this anomaly. However, the major part of the high-temperature anomaly still remained, even with the cluster-expansion extensions of LDH theory proposed by Allnatt and Cohen[19] and Sevenich and Kliewer.[20]

The standard transport model for the silver halides consists of migration via the cation vacancy and the collinear and noncollinear interstitialcy mechanisms. Attempts have been made to explain the high-temperature-conductivity anomaly by postulating the onset of an additional migration mechanism, for example, the back sidewards interstitialcy mechanism of Lansiart.[21]

Finally, the possible temperature dependence of the defect parameters must be considered. Müller[22] and Schmalzried[23] attributed the anomaly to a "loosening of the lattice" which caused a reduction in the defect formation energy. They treated the anomalous thermal expansion as equivalent to the application of a negative pressure which was then thermodynamically related to the defect-formation energy. Aboayge and Friauf[12] determined the defect parameters for AgCl and AgBr by fitting their conductivity data in an intermediate range of temperature where the LDH theory is expected to provide an adequate correction for defect interactions. With these parameters, they determined the increase of observed conductivity over the extrapolated values. They argued that this excess conductivity could be explained by assuming a nonlinear temperature-dependent Gibbs free energy of formation for a cationic Frenkel defect.

A striking, quantitative confirmation of this temperature-dependent formational-free-energy proposal was reported by Batra and Slifkin based on their study of the diffusion of Na^+ in AgCl (Ref. 24) and AgBr (Ref. 25). In both cases, they found a continuous positive curvature in the high-temperature region of the Arrhenius plots. For AgCl they found that by normalizing their diffusivities by the defect concentrations, as determined from the conductivity experiment of Aboayge and Friauf, the curvature was eliminated. However, using the same procedure for AgBr they found the elimination of curvature to be not as complete. Even with Kao's[26] more refined determination of the ionic conductivity of AgBr, linearity of the Arrhenius plot is not restored at the two highest-temperature points.

It should be pointed out that a nonlinear decrease in the Gibbs free energy with increasing temperature, as deduced from the conductivity studies, may be the result of changes in either the formation or migration energies of the Frenkel defects. On the other, the diffusion results of Batra and Slifkin indicate that it is only the formation energy which is responsible for the high-temperature anomaly. A support for this proposal comes from a calculation of the heat capacity based on this temperature-dependent formational-energy model.[27] The calculation agrees qualitatively with the anomalous heat capacity observed experimentally.[6,7] A quantitative agreement is precluded due to the possible role of anharmonicity at higher temperatures.

To account for this anomalous temperature dependence in the defect formation energy various theoretical approaches have been presented. Friauf[28] utilized a simplified form of a mean-field-theory approach in which he assumed the decrease in formational energy is proportional to the defect concentration. He was able to reproduce the rapid decrease in the Gibbs energy as the melting point was approached and the behavior was qualitatively similar to that deduced experimentally, although for AgBr the comparison was less satisfactory. Bauer and Leutz,[29] using a refined, classical continuum model traced the high temperature anomaly to an exceptional temperature dependence of the elastic properties of the perfect crystal. For AgBr, they report a good qualitative agreement with the observed conductivity anomaly. Varotsos and Alexopoulos,[30] accounting for both the thermal expansivity and the thermal variations of the elastic constants, proposed a model for the Gibbs energy which could successfully account for curvature in the Arrhenius plots of many systems, including the silver halides. However, the above approaches provide no detailed theoretical explanations, in that no attempts were made to specify the exact form of the interionic potentials involved. After all, it is this potential which determines the nature of the physical properties, e.g., elastic properties, "anomalous" conductivity, etc. Along this line, Catlow, Corish, and Jacobs[31] developed an interionic potential based on a quasiharmonic model. This model, characterized by large values for both the cation-cation and cation-anion attractive coefficients, was successful in reproducing the conductivity and Na^+ diffusion results in AgCl. Further, by considering the deformation of the Ag^+ ion as it passes through the saddle-point configuration, these same authors[32] were able to predict not only the temperature dependence of the cation Frenkel defect formation energy but were also able to simulate the relatively high mobility of the silver ion. The success of these calculations lend good support to the idea that it is the temperature dependence of the Frenkel formation energy that is responsible for the anomalous behavior in both AgBr and AgCl.

The above review, then, points to the general consensus that the formation energy of the Frenkel defect in AgCl and AgBr is temperature dependent. One must bear in mind, however, that in most of the comparisons (that is, conductivity with Na^+ diffusion, experimental results with various theories) the case of AgCl is excellent, whereas the case of AgBr is not so satisfactory. At this point, it would be worthy to mention the work of Corish and Jacobs.[33] In order to investigate the possible contributions due to alternate jump mechanisms, the presence of Schottky defects, and temperature-dependent defect energies, these authors subjected their earlier conductivity data[34] to an analysis based on five different models. However, because several of their models led to an equally satisfactory fitting of the experimental data, they were unable to distinguish between three of their models, for example, a temperature-dependent defect parameter model yielded as good a fit to the experimental data as the model allowing for both collinear and noncollinear interstitialcy mechanisms. Thus they found no compelling evidence to favor a temperature-dependent formation energy.

The present investigation was undertaken to generate further independent evidence on which to support the proposal of a temperature-dependent Frenkel formation energy. The choice of a monovalent diffusant was necessitated by the fact that its presence would not disturb the intrinsic concentration of thermally generated defects. Also, the use of a substitutional monovalent cationic impurity like Rb^+, which has no net charge on the AgBr lattice, would minimize the possibility of an impurity-vacancy association.

II. EXPERIMENTAL

The diffusion of Rb^+ in AgBr was performed using a standard serial-sectioning technique.[35] The single crystals of AgBr were obtained from C. Childs of the University of North Carolina—Chapel Hill Crystal Growth Facility with a stated impurity level of less than 1 ppm. Samples of approximately 1-cm^2 area and 1 cm in height were hand polished on fine-grit silicon carbide polishing paper and etched in a KCN solution. The top surface was prepared by microtoming off several 1-μm thin sections. The samples were annealed in an ultrapure-helium atmosphere at approximately 410 °C for 10 h and slowly cooled at a rate of about 9 °C/h. After annealing, approximately 1 μCi of ^{86}Rb in the form of RbCl (obtained from New England Nuclear with a specific activity of approximately 10 Ci/g) dissolved in pure HCl was deposited on the microtomed surface. After drying, the samples were encapsulated in a low-pressure helium atmosphere to insure quick thermal equilibrium and placed in the controlled diffusion furnace. A continuous record of the initial time-temperature warm-up was kept and the usual anneal time corrections were applied. Due to the high diffusivity of Rb^+ in AgBr these corrections were important, especially for the high-temperature runs where anneal times as low as one hour were used. Because the warm-up corrections were of the order of 6–9 min, the continuous time-temperature record was found essential for a meaningful estimate of the corrections. Prior to sectioning, a thickness larger than $4(Dt)^{1/2}$ was usually removed from each of the four sides to eliminate the effect of surface diffusion. The samples were then microtomed on a rotary microtome. Following the mass measurements, which were used to determine the thickness of the sections, the sections were dissolved in a sodium thiosulfate solution and the tracer activity was assayed with a conventional Geiger-Müller counter. All operations prior to the counting of the sections were carried out under safelight conditions.

Very good sample alignment prior to sectioning was achieved using a 20-m-long optical lever with a laser source making the misalignment correction negligible. This, along with the fact that the corrections due to initial warm-up were more precisely determined using the recorder, led us to estimate the overall error in the diffusivities reported here to be within ±3%.

III. RESULTS

The penetration profiles for each temperature run were constructed by plotting the natural logarithm of the specific activity against the square of the penetration depth. The resulting linearity of these plots was evidence that the experimental conditions were consistent with the one-dimensional volume diffusion from a thin source. The values of the diffusion coefficients were extracted from the slope of each profile by a least-squares fit. The diffusion coefficients along with their corresponding annealing time and temperature over the temperature range 184–421 °C are shown in Table I.

Figure 1 displays the penetration profiles for several anneal temperatures. All these profiles exhibit a slight up-turn near the surface followed

TABLE I. Diffusion of Rb^+ in pure AgBr.

Temperature (°C)	Diffusion time (sec)	Diffusion coefficient (cm^2/sec)
184.0	1.46×10^{6}	2.06×10^{-11}
221.5	3.29×10^{5}	3.58×10^{-10}
235.1	1.01×10^{5}	6.92×10^{-10}
250.5	2.50×10^{4}	1.18×10^{-9}
262.8	3.09×10^{4}	3.03×10^{-9}
274.3	7.07×10^{3}	5.55×10^{-9}
303.3	6.22×10^{4}	1.95×10^{-8}
323.6	7.86×10^{3}	5.77×10^{-8}
349.7	7.40×10^{3}	2.02×10^{-7}
362.0	4.29×10^{3}	3.00×10^{-7}
379.9	8.30×10^{3}	4.99×10^{-7}
396.8	5.44×10^{3}	9.85×10^{-7}
420.8	3.87×10^{3}	2.55×10^{-6}

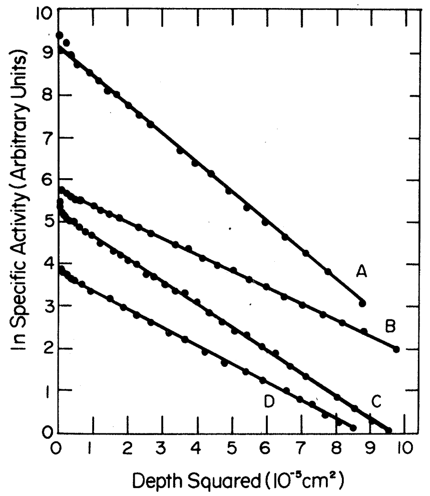

FIG. 1. Penetration profiles for the diffusion of Rb^+ into AgBr. The temperature and full-scale abscissa value for each line are (A) 323.6 °C, 120×10^{-4} cm², (B) 379.9 °C, 600×10^{-4} cm², (C) 262.8 °C, 20×10^{-4} cm², and (D) 221.5 °C, 20×10^{-4} cm².

by a long, linear penetration into the crystal. This up-turn is believed to be due to "near-surface" effects, particularly the low solubility of the tracer. The solubility problem was very evident when diffusion runs below 184 °C were attempted. However, this up-turn should have no effect on the diffusion coefficient determined from the profile since the initial points were excluded from the least-squares fit; only the long, linear portion of each profile was used to determine the diffusivity. Mitchell and Lazarus[36] showed that the effect of polyvalent impurities co-diffusing with a monovalent tracer in NaCl is such as to cause the penetration profiles to be non-Gaussian. Specifically, the profiles, rather than being linear, are concave toward the origin; the degree of curvature increasing as the divalent-impurity concentration increases. The lack of this negative curvature in our profiles leads us to believe that the tracer used in the experiment was not contaminated with any divalent impurities, although the possible existence of mitigating effects (e.g., grain boundary diffusion) could camouflage the concavity expected from a contaminated tracer.

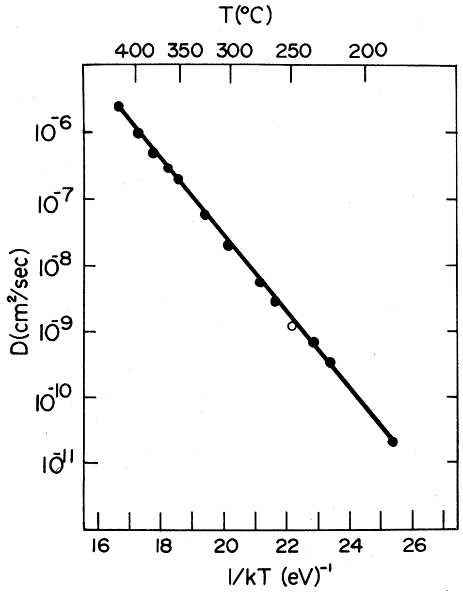

FIG. 2. Arrhenius graph for the diffusion of Rb^+ into AgBr. The solid circles refer to data characterizing intrinsic diffusion, the open circle refers to the diffusivity at 250.5 °C for a specimen with a grain boundary.

The temperature dependence of the diffusion coefficients is displayed in Fig. 2. The datum shown by an open circle in Fig. 2 corresponds to the diffusivity at 250.5 °C for a specimen which was found to have a grain boundary. The value of D was extracted from the intermediate, linear section of the non-Gaussian penetration profile. Thus the estimated diffusivity at this temperature could be somewhat uncertain. Because of the linearity of Fig. 2, the temperature dependence of the diffusion of Rb^+ in AgBr over the entire temperature range of 184–421 °C can be characterized by the normal Arrhenius relation

$$D = D_0 \exp(-H/kT)\,. \tag{1}$$

Applying a least-squares fit to the data, excluding the datum at 250.5 °C, leads to a pre-exponential factor D_0 and diffusion activation enthalpy H of

$$D_0 = (1.04 \pm 0.30) \times 10^4 \text{ cm}^2/\text{sec}$$

and (2)

$$H = 1.33 \pm 0.02 \text{ eV}\,.$$

These parameters for the diffusion of Rb^+ in AgBr are typical of a vacancy mechanism and are comparable to the parameters for the vacancy diffusion of Cd^{2+} (Ref. 37), Mn^{2+} (Ref. 38), Fe^{2+} (Ref. 39), and Na^+ (Ref. 25) in AgBr. Assuming no solute-vacancy association, the diffusion coefficient for a monovalent ion in AgBr can be expressed as

$$D = 4a^2 f\nu \exp[(\tfrac{1}{2}S_f + S_m)/k]\exp[-(\tfrac{1}{2}H_f + H_m)/kT]\,, \tag{3}$$

where a is the nearest cation-anion separation distance, f is the correlation factor, ν is the attempt frequency of the diffusant, H and S are the enthalpy and entropy, respectively, and the subscripts f and m refer to the formation of a Frenkel pair and migration of a vacancy, respectively. Assuming $f = 1$ and using $a = 2.88$ Å, $\nu = 3\times10^{12}$ sec^{-1} along with Kao's[26] most recent values $H_f = 1.16$ eV and $S_f/k = 7.28$ and the experimentally determined values of $D_0 = 1.04 \times 10^4$ cm^2/sec and $H = 1.33$ eV, the enthalpy and entropy of migration for the impurity ion Rb$^+$ in AgBr are found to be

$$H_m = 0.75 \text{ eV}$$

and (4)

$$S_m = 6.58k \, .$$

IV. DISCUSSION

A. Linearity in Arrhenius plot

The most important feature of the present investigation is that the data, within experimental error, fail to exhibit the expected curvature predicted by a temperature-dependent Frenkel formation energy. Had the anomalous curvature existed to the same degree as observed in Kao's[26] conductivity experiments, the diffusivity at the highest temperature would have been more than a factor of 4 greater than actually observed. Apart from Na$^+$, the results of the diffusion of two other alkali ions in silver halides are available. In both cases, Cs$^+$ in AgCl by Batra and Slifkin[40] and Li$^+$ in AgCl by Ptashnik and Naumov,[41] the expected curvature was not observed. In fact, if one considers the large number of impurity ions diffused in the silver halides (18 in AgCl and 8 in AgBr, by far the largest in any ionic system) this continuous curvature in the intrinsic range is "conspicuous" by its absence in most of the cases, in contrast to the observation for Na$^+$ in AgCl and AgBr. Exceptional cases are Zn^{2+} in AgCl (Ref. 42) and Cl$^-$ and I$^-$ in AgBr (Ref. 43). In the former case the curvature was speculated to be due to the Debye-Hückel effect leading to an increase of vacancy concentration with temperature. For Cl$^-$ and I$^-$ in AgBr, an additional mechanism of migration by vacancy pairs was proposed.

The question arises as to what it is about these particular ions that makes them so unique in showing the high-temperature curvature. The answer is not easy. It has been argued that a cancellation of the effect of a temperature-dependent Frenkel formation energy is plausible in the case of the diffusion of polyvalent solutes due to the extra factors involved.[39,44] These factors are: solute-vacancy association, change in the activity coefficient in LDH theory, and the tighter "gates" seen by the diffusing ions due to the electrostatic relaxation caused by the extra charge. In the case of Cs$^+$ diffusion in AgCl,[40] it was argued that due to the large size of the Cs$^+$ ion relative to the host cation a strain-induced binding energy was present. The binding energy would be expected to decrease with increasing temperature as the lattice "softens up" (and the elastic moduli decrease[2]) and this temperature dependence could wash out the effects of a temperature-dependent formation energy. Although the Rb$^+$ ion (1.47 Å) is smaller than the Cs$^+$ ion (1.67 Å), it is still oversized relative to the host Ag$^+$ ion (1.26 Å). Thus, an analogous explanation could presumably apply to the present results. However, detailed analysis will show that this explanation is not completely satisfactory in the case of Rb$^+$ in AgBr.

A most general form of the impurity diffusion activation enthalpy is

$$H = (\tfrac{1}{2}H_f + H_m - H_a) + [-\Delta H_f(T) - \Delta H_m(T) + \Delta H_a(T) - H_{\mathrm{cf}}(T) + H_\gamma(T)] \, , \quad (5)$$

where the terms in the first parentheses represent the temperature-independent enthalpies of defect formation (H_f), impurity migration (H_m), and impurity-vacancy association (H_a). The square brackets contain terms which may be temperature dependent; they include the possible temperature dependence of the formation (ΔH_f), migration (ΔH_m), and association (ΔH_a) enthalpies as well as contributions from a temperature-dependent correlation factor (H_{cf}) and a temperature-dependent activity coefficient (H_γ). The activity coefficient is a measure of the amount the association energy increases due to the Coulombic interactions between defects.[13] It is possible that the temperature dependence of H can indeed be negligible due to compensation arising out of the terms in the square brackets. A quantitative estimate, however, is precluded as many of the parameters are not independently known. It can be shown (see, for example, Ref. 39) that, in general, for impurity diffusion the correlation factor (f) is temperature independent and equal to unity. Any anomalous temperature variation in the diffusion activation enthalpy due to a temperature dependent activity coefficient must arise from a temperature dependence in the average potential energy of the defect in its surrounding Debye-Hückel charge cloud, but this variation is expected to be small. It appears then, that any decrease in the defect formation energy (H_f) as the temperature increases is compensated for by a corresponding decrease in the enthalpy of solute-vacancy association. The increase of solute migration enthalpy with temperature should not be entirely ruled out. The argument of the decrease of binding energy with the softening of the lattice[40] may also lead to a decrease in the migration enthalpy.

The first parentheses in Eq. (5) refer to the contribution to the temperature-independent activation enthalpy of the diffusion of Rb$^+$ in AgBr. If solute-vacancy association is present then, from Eq. (2)

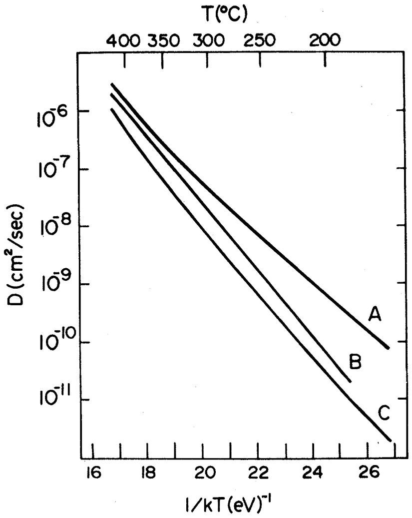

FIG. 3. The temperature dependence of (A) the vacancy component of the self-diffusion coefficient of Ag^+ (Ref. 11) and the impurity-diffusion coefficients of (B) Rb^+ and (C) Na^+ (Ref. 25) in AgBr.

one obtains $H_m - H_a = 0.75$ eV. A monovalent ion like Rb^+ is not expected to have any Coulombic binding with a cation vacancy in AgBr. It appears that the strain-induced binding energy of the solute should not be much greater than 0.1 eV. Otherwise, for Rb^+ one obtains $H_m = 0.75 + H_a \geq 0.85$ eV, which is an unusually high value when compared to the corresponding values of 0.60 and 0.32 eV for the vacancy diffusion of Na^+ (Ref. 25) and Ag^+ (Ref. 26) in AgBr. This is unlikely in view of the trend of the ionic size effect on mass transport as discussed in a later section.

It should be pointed out that this conclusion is in contrast to the result of Batra and Slifkin,[40] namely, an unusually large strain-induced binding energy is present for Cs^+ (an alkali ion like Rb^+, though slightly larger) in AgCl. If no binding is assumed, the small diffusion activation enthalpy of 0.83 eV in their case leads to a motion enthalpy $H_m \simeq 0.1$ eV. The fast diffusion of Cs^+ in AgCl with so little migration energy is comparable to the interstitial migration of noble metal ions in silver halides.[45,46] In our case the strain-induced binding energy for the solute-vacancy association, if present, could be quite small but it is the temperature dependence of the binding energy which may be appreciable, so that this, with other factors (as discussed before), leads to the compensation for $\Delta H_f(T)$. This essential difference between the Rb^+ in AgBr and Cs^+ in AgCl can not be explained.

B. Ionic size effect

Figure 3 shows a comparison of the diffusivities of Na^+ and Rb^+ in AgBr along with the vacancy component of the self-duffusion coefficient of silver in AgBr. It is of interest to note that the diffusivity of Rb^+ is larger than that of Na^+ at all temperatures considered even though the rubidium ion is larger than the sodium ion. This is contrary to the intuitive notion that a smaller ion should be transported more easily. Additionally, the diffusivity of the vacancy component of the self-diffusion coefficient of silver is larger than both that of Na^+ and Rb^+. In fact, a trend observed is that the motional enthalpies are related, not to the size of the solute, but to the amount of mismatch between the impurity and host cation. Table II is a current compilation of the cationic tracer diffusion studies in AgBr. Absent from the list is the result for the diffusion of the monovalent noble-metal ion Cu^+ which Süptitz[45] showed diffuses via a direct interstitial mechanism. All others have been shown to proceed via a vacancy mechanism.

Before proceeding further, certain qualifications regarding Table II must be considered. The values of the ionic radii are taken from Ahrens[47] who revised those of Pauling by using more refined values for the alkali ions. Nevertheless, since the "size" of an ion is a rather nebulous quantity, being dependent on its local environment, these values should not be considered absolute but should be used only for comparative purposes. The fourth column contains just the motional energy H_m and certain comments need

TABLE II. Size effect on diffusion in AgBr.

Tracer	Ionic radius (Å)	$H_m - H_a$ (eV)	H_m (eV)	Mismatch (Å)	Reference
Fe^{2+}	0.74	0.85	1.05	−0.52	40
Mn^{2+}	0.80	0.52	0.74	−0.46	39
Na^+	0.97		0.60	−0.29	25,26
Cd^{2+}	0.97		0.55	−0.29	38
Ag^+	1.26		0.32	0	26
Rb^+	1.47		0.75	+0.21	present work

be made here. For Fe^{2+}, Mealing and Laskar[39] had to assume a value for H_a equal to 0.2 eV since no independent determination of the association enthalpy for an Fe^{2+}-vacancy complex has ever been carried out in AgBr. However, this is a valid assumption since the association enthalpies for divalent cationic impurity-vacancy complexes are all of the order of 0.2 eV.[48] For both Mn^{2+} (Ref. 38) and Cd^{2+} (Ref. 37), the authors determined the motional enthalpies from Arrhenius plots for heavily doped AgBr single crystals (2.1 mol% Mn and 3.3 mol% Cd, respectively). In both cases, however, since the diffusion coefficient versus dopant concentration isotherms failed to saturate, equating the diffusion activation enthalpy (for the doped samples) to the motional enthalpy becomes questionable. Because of the very high concentration of thermally generated defects, this procedure for determining H_m could underestimate the true value. Finally, the value of H_m listed for Na^+ is not the value quoted by Batra and Slifkin,[25] whose result involved the use of the conductivity data of Aboagye and Friauf,[12] but is the value determined by Kao[26] using his more refined conductivity data. The fifth column of Table II lists the mismatch between the impurity diffusant and host cation. This mismatch is defined as the difference in radii between the tracer ion and the silver ion.

Table II shows that as the amount of mismatch increases, whether the tracer be smaller or larger, the migrational enthalpy increases. Admittedly, the table includes both divalent as well as monovalent ions and no attempt has been made to subtract out the effect different valence has on the motional enthalpy. That electronic configuration does effect the motional energy has been quantitatively shown by Batra, Hernandez, and Slifkin.[44] They showed that the difference in the migrational enthalpies of the six adjacent, first-row transition-metal ions V^{2+} through Ni^{2+} could be accounted for by considering the work done by the crystalline electric field on the d-shell electrons during the jumping process. Nevertheless, Table II does suggest that size can make a significant contribution to the activation energy. For example, compare the results for Mn^{2+} and Cd^{2+}. For both ions, the electronic configuration is spherical (d^5 for Mn^{2+} and d^{10} for Cd^{2+}) and thus the effect of the crystal field to a first approximation should be zero. One could argue that the difference observed in the motion energy for these two ions could be due to the difference in their effective nuclear charge, but this charge difference is related to their relative sizes; referring to Table II, the Mn^{2+} suffers a greater mismatch than the Cd^{2+} and has a correspondingly higher motional enthalpy. The conclusion that one reaches is that both size and electronic configuration influence the transport properties in AgBr. For ions very similar in size, e.g., Na^+ and Cd^{2+}, valence-shell configuration will be the dominant factor while for ions of similar electronic configuration, e.g. Na^+ and Rb^+, size will be the dominant factor.

Indeed, it is difficult to separate the "size effect" from "charge effect" because whenever charge effects occur, size effects in principle accompany them. Also, the role of the size of a diffusing ion squeezing through a "gate" is certainly complicated and there has been very little theoretical study in this direction. However, Mullen's[49] theory of diffusion on the basis of the Einstein model of ionic solids does predict a dependence of the activation enthalpy of motion on the mismatch between the solute and the host ion. A similar "size effect" is noticed, in general, for the impurity diffusion in AgCl also.

V. CONCLUSION

This study shows that the temperature dependence of the diffusivity of Rb^+ in AgBr, like most other impurity diffusion in the silver halides, obeys a linear Arrhenius law. This indeed can be the case if the temperature dependence of the defect formation energy is linear. However, this is unlikely in the face of the other overwhelming evidence which has been reviewed. It is more probable that the decrease of H_f with increasing temperature is compensated by (along with other factors) a strain-induced association energy of the solute with a vacancy which decreases as the lattice "softens" with increasing temperature. Unlike the case of Cs^+ in AgCl, this binding energy could be quite small. It is also evident that the interesting observation of a "size effect" on the transport properties of AgBr could be real. To get a better understanding of this effect we have undertaken a program to study the diffusion of some other alkali ions in AgBr. These ions have the advantage of having the noble-gas configuration (spherical), therefore, they will not be affected to a first approximation by the crystal field nor will their tendency to bond covalently with a neighboring halide ion vary significantly from one to another. Also, being monovalent, their presence will not perturb the intrinsic defect concentration and will therefore be an accurate probe of the vacancy concentration. This will enable us to study the high-temperature anomalous behavior in the system and provide new evidence on which to judge the idea of a temperature-dependent defect-formation enthalpy.

ACKNOWLEDGMENTS

The authors wish to thank Charles Childs, University of North Carolina, Chapel Hill for kindly supplying the high-purity AgBr crystals and John Isbell for assisting us with some of the experiments. We are also grateful to Dr. L.M. Slifkin both for valuable discussions and providing us with the unpublished data on the association energy of a number of solutes in the silver halides.

---

[1] B. Dorner, J. W. Windschief, and W. von der Osten, in *Proceedings of the International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1978).

[2] D. S. Tannhauser, L. J. Bruner, and A. W. Lawson, Phys. Rev. 102, 1276 (1956).

[3] R. D. Fouchaux and R. O. Simmons, Phys. Rev. A 136, 1664 (1964).

[4] B. R. Lawn, Acta Crystallogr. 16, 1163 (1963).

[5] G. C. Smith, Report # 51, Material Science Center, Cornell University (unpublished).

[6] H. Kanzaki, Phys. Rev. 81, 884 (1951).

[7] K. Kobayashi, Phys. Rev. 85, 150 (1952).

[8] J. Teltow, Ann. Phys. (Leipzig) 5, 63, 71 (1949).

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

[10] W. D. Compton and R. J. Maurer, J. Phys. Chem. Solids 1, 191 (1956).

[11] A. S. Miller and R. J. Maurer, J. Phys. Chem. Solids 4, 196 (1958).

[12] J. K. Aboayge and R. J. Friauf, Phys. Rev. B 11, 1654 (1975).

[13] A. B. Lidiard, in *Handbuch der Physik*, Vol. 20, edited by S. Flügge (Springer, Berlin, 1957), pp. 246–349.

[14] R. J. Friauf, J. Phys. (Paris) 38, 1077 (1977).

[15] A. W. Lawson, Phys. Rev. 78, 185 (1950).

[16] W. Zieten, Z. Phys. 145, 125 (1956).

[17] C. H. Berry, Phys. Rev. 82, 422 (1951).

[18] R. M. Nicklow and R. A. Young, Phys. Rev. 129, 1936 (1963).

[19] A. R. Allnatt and M. H. Cohen, J. Chem. Phys. 40, 1860, 1871 (1964).

[20] R. A. Sevenich and K. L. Kliewer, J. Chem. Phys. 48, 3045 (1968).

[21] S. Lansiart, J. Phys. Chem. Solids 36, 543 (1975).

[22] P. Müller, Phys. Status Solidi 21, 693 (1967).

[23] H. Schmalzried, Z. Phys. Chem. (Leipzig) 22, 199 (1959).

[24] A. P. Batra and L. M. Slifkin, Phys. Rev. B 12, 3473 (1975).

[25] A. P. Batra and L. M. Slifkin, J. Phys. Chem. Solids 38, 687 (1977).

[26] K. J. Kao, Ph.D. thesis, University of Kansas, 1978 (unpublished).

[27] W. L. Freeman and A. L. Laskar, Bull. Am. Phys. Soc. 23, 605 (1978).

[28] R. J. Friauf, J. Phys. (Paris) Colloq. 41, C6-97 (1980).

[29] R. Bauer and R. K. Leutz, J. Phys. (Paris) Colloq. 41, C6-516 (1980).

[30] P. A. Varotsos and K. Alexopoulos, J. Phys. Chem. Solids 39, 759 (1978).

[31] C. R. A. Catlow, J. Corish, and P. W. M. Jacobs, J. Phys. C 12, 3433 (1979).

[32] P. W. M. Jacobs, J. Corish, and C. R. A. Catlow, J. Phys. C 13, 1977 (1980).

[33] J. Corish and P. W. M. Jacobs, Phys. Status Solidi B 67, 263 (1975).

[34] J. Corish and P. W. M. Jacobs, J. Phys. Chem. Solids 33, 1799 (1972).

[35] E. W. Sawyer and A. L. Laskar, J. Phys. Chem. Solids 33, 1149 (1972).

[36] J. L. Mitchell and D. Lazarus, Phys. Rev. B 12, 734 (1975).

[37] J. E. Hanlon, J. Chem. Phys. 32, 1492 (1960).

[38] P. Süptitz and R. Weidmann, Phys. Status Solidi 27, 631 (1968).

[39] W. J. Mealing and A. L. Laskar, Phys. Rev. B 17, 860 (1978).

[40] A. P. Batra and L. M. Slifkin, J. Phys. Chem. Solids 37, 967 (1976).

[41] V. B. Ptashnik and A. N. Naumov, Fiz. Tverd. Tela (Leningrad) 12, 1496 (1970) [Sov. Phys.—Solid State 12, 1174 (1970)].

[42] A. P. Batra and L. M. Slifkin, Phys. Status Solidi A 19, 171 (1973).

[43] A. P. Batra and L. M. Slifkin, J. Phys. Chem. Solids 30, 1315 (1969).

[44] A. P. Batra, J. P. Hernandez, and L. M. Slifkin, Phys. Rev. B 22, 734 (1980).

[45] P. Süptitz, Phys. Status Solidi 7, 653 (1964).

[46] A. L. Laskar, A. P. Batra, and L. M. Slifkin, J. Phys. Chem. Solids 30, 2061 (1969).

[47] L. H. Ahrens, Geochim. Cosmochim. Acta 2, 155 (1952).

[48] R. Lieb, J. Gerlach, and L. M. Slifkin (unpublished).

[49] J. G. Mullen, Phys. Rev. 143, 658 (1966).