

## Diffusion of divalent calcium in silver bromide

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(Received 15 May 1989; revised manuscript received 20 February 1990)

Using a radiotracer-sectioning method, the diffusion coefficients of calcium tracer in single crystals of pure AgBr in the temperature range 325–416 °C have been determined. The diffusion Arrhenius plot is found to consist of two linear branches with a break occurring around 380 °C. The diffusion parameters determined from this plot for the region below 380 °C are typical of a vacancy mechanism. The diffusion coefficients in AgBr are consistently higher than in AgCl because of the relatively larger concentrations of intrinsic cation vacancies in AgBr. Treating the diffusion to take place by means of impurity-vacancy complexes, the low-temperature data give the activation enthalpy and entropy for impurity migration to be 0.92 eV and  $4.2k_B$ , respectively. The significant deviations encountered at the higher temperatures from the extrapolated values show that simple ideas of mass action are inadequate at high defect concentrations.

### I. INTRODUCTION

Atomic diffusion is of major importance in many physical and metallurgical processes. Our knowledge and understanding of point defects, often responsible for the elementary diffusion step, has vastly increased over the years from copious research in phenomena related to mass transport in solids. New concepts of ionic transport have evolved as a result of the many studies of alkali and silver halides which are considered to be prototypic ionic substances.

It is well known that many physical properties, e.g., dielectric constant,<sup>1</sup> elastic moduli,<sup>2,3</sup> thermal expansion,<sup>4,5</sup> and ionic conduction,<sup>6–10</sup> exhibit large anomalous changes in silver halides at high temperatures. Of these, the most extensively and thoroughly investigated phenomenon has been the ionic conductivity which results from the charge transport by the cation Frenkel defects.<sup>6–10</sup>

The rapid anomalous increases in the conductivity of silver chloride and silver bromide occurring at high temperatures<sup>6–10</sup> can only be partially accounted for by the contribution to ionic conduction resulting from the long-range Coulomb interactions between the isolated charge defects. The remaining conductivity has been ascribed to additional defects which are generated from a substantial nonlinear decrease with increasing temperatures of the Gibbs free energy of formation of the Frenkel defects.<sup>6</sup> This nonlinearity is thought to be triggered by a general softening of the silver halide crystal lattice at high temperature, which is reflected in the large increase in the lattice constant and the rapid decrease of elastic constants. Friauf *et al.*<sup>6,7,11</sup> expanded this interpretation and carefully determined the numerical values for the temperature-dependent decreases in defect formation energy which brought the calculated conductivities into agreement with the observed values.

This explanation of anomalous ionic conductivity in

the silver halides has been proved to be essentially correct by the corroborating evidence from tracer diffusion measurements<sup>12–14</sup> as well as from theoretical calculations using computer simulation techniques.<sup>15–17</sup> The continuously curved Arrhenius plots of the diffusion coefficient as a function of temperature for substitutional monovalent sodium<sup>12,13</sup> and potassium<sup>14</sup> in both silver chloride and silver bromide reflected the anomalous rise of cation vacancy concentration with temperature, and has the same origin as the anomalous ionic conductivity. Recent calculations based on reliable interionic potentials<sup>15,18</sup> have confirmed the existence of the nonlinear temperature dependence of the Gibbs free energy for the formation of Frenkel defects in the silver halides.

The diffusion coefficients of the other impurity ions in the silver halides have yielded both linear and nonlinear Arrhenius plots.<sup>19</sup> The quantitative understanding of these, based on the simple ideas of mass action relating to crystal defects and the well established nonlinear temperature-dependent Gibbs free energy of Frenkel defect formation, is far from satisfactory. The likelihood of nonlinear temperature dependence in the Gibbs free energies of defect association, electrostatic or elastic in origin, and of defect migration has additionally been invoked to qualitatively understand these data. Though the argument seems plausible, the realization of a quantitative explanation remains a formidable and challenging task.

In this paper, the results of diffusion of calcium tracer in single crystals of pure silver bromide in the temperature range 325–416 °C are presented. The intrinsic concentrations of cationic vacancies encountered at these temperatures are rather large. However, the data are examined in light of the theories which are based on simple ideas of mass action, presumably valid only at much lower defect concentrations. Further, some information on the role of defects is obtained from comparison of the present results with those available in silver chloride,<sup>20</sup> which has relatively lower concentrations of intrinsic cation vacancies at all temperatures.

## II. EXPERIMENT

We used a radiotracer-sectioning method for the determination of the diffusion coefficients, which is generally considered to give the most accurate results.<sup>21</sup> Very pure single-crystal silver bromide, with less than two parts per million of total heavy impurities, was used in this study. Specimens, in the shape of rectangular parallelepiped, were carefully polished, and one surface of each specimen, to which the tracer was later applied, was flattened with a microtome blade.<sup>22</sup> The specimens were then preannealed in an inert atmosphere to reduce the strain introduced in their preparation.

An extremely small amount, three to six microcuries, of high-specific-activity <sup>45</sup>Ca as the chloride (obtained from the New England Nuclear Corporation) was placed on the microtomed-flat surface of the specimen. It was then diffusion annealed in ultrapure nitrogen for a specified time during which the temperature was carefully and frequently monitored by a chromel-alumel thermocouple made from NBS-calibrated wires placed in the furnace cavity-just outside the encapsulated specimen. Subsequent to the diffusion anneal, a thickness of 6–8 times the distance  $(Dt)^{1/2}$  was microtomed off each of the four sides of the specimen to avoid the effects arising from surface diffusion. Several sections parallel to the tracer-plated surface, 5–10  $\mu\text{m}$  in thickness, were then cut off with the microtome blade. The alignment was accomplished by the usual optical arrangement, and the first cut almost always cleared the entire crystal surface.

The section thickness was determined from its mass, which was measured using a Perkin-Elmer ultrabalance. Its specific activity was determined from its count rate. Since <sup>45</sup>Ca emits beta particles of energy 0.258 MeV, a large fraction of these gets absorbed in the section itself, and therefore it is imperative to have the same reproducible counting geometry for each of the sections. This was accomplished by dissolving each section in ammonium hydroxide and allowing it to dry at room temperature so as to settle the residue as a layer at the bottom of the planchet. The planchets were then counted with a low-background, thin-window Geiger-Müller counter. At least  $10^4$  counts above the background counts were taken to give a counting statistics of better than 1%.

## III. RESULTS

Ideally, diffusion into a semi-infinite medium from an infinitely thin planar source gives rise to a Gaussian penetration profile. Consequently, a diffusion coefficient can be calculated from the slope of  $\ln(a_i)$  versus  $x^2$ , where  $a_i$  is the activity of the tracer and  $x$  is the penetration distance from the active specimen surface. The initial conditions chosen for our diffusion measurements closely approximated this situation.

Six successful runs at diffusion temperatures in the temperature range 325–416 °C were made. The diffusion profiles for three of the measurement temperatures, selected to illustrate low, medium, and high temperatures, are shown in Fig. 1. Each of the six plots accurately represents the expected Gaussian behavior. There are,

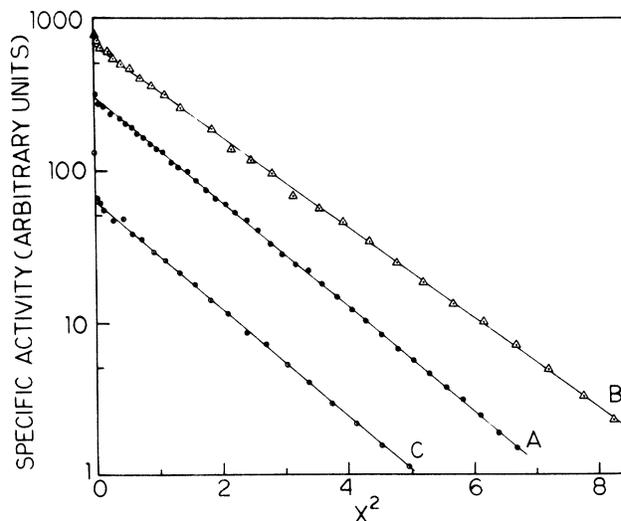


FIG. 1. Penetration plots for diffusion of calcium tracer in pure AgBr. For plot A, the annealing temperature is 415.5 °C and the  $x^2$  scale (abscissa) is in units of  $6 \times 10^{-4} \text{ cm}^2$ ; the corresponding values for plot B are 379.0 °C and  $1.0 \times 10^{-4} \text{ cm}^2$ , and for plot C they are 325.2 °C and  $1.0 \times 10^{-4} \text{ cm}^2$ , respectively.

however, a few points in the initial region near the specimen surface for some of the plots which have slightly higher activity than expected. The depth from the specimen surface to which this non-Gaussian behavior extends is in the worst case only about 50  $\mu\text{m}$  whereas the total measured penetration is of the order of 300  $\mu\text{m}$ . These deviations may be due to an oxide-induced trapping of some tracer and then its gradual release into the bulk. They are so small that the diffusion coefficients determined from the long deep linear tails of the penetration profiles are considered to be reliable and accurate.

Table I shows the values of the diffusion coefficients calculated from the penetration profiles together with the annealing temperatures and times. Figure 2 shows the same data as a semilogarithmic plot of the diffusion coefficients versus reciprocal temperatures, and includes the results of tracer diffusion of the divalent calcium ion in AgCl as reported by Brébec and Slifkin for comparison.<sup>20</sup>

The nominal anneal time for each of the four runs at the highest temperatures was 2 h. This short time, neces-

TABLE I. Diffusion of  $\text{Ca}^{2+}$  in pure AgBr.

Temperature (°C)	Diffusion anneal time (s)	Diffusion coefficient ( $\text{cm}^2/\text{s}$ )
415.5	$6.93 \times 10^3$	$2.73 \times 10^{-8}$
397.0	$6.91 \times 10^3$	$1.22 \times 10^{-8}$
379.0	$6.85 \times 10^3$	$5.32 \times 10^{-9}$
352.5	$6.82 \times 10^3$	$1.90 \times 10^{-9}$
334.0	$2.50 \times 10^4$	$8.82 \times 10^{-10}$
325.2	$4.93 \times 10^4$	$6.26 \times 10^{-10}$

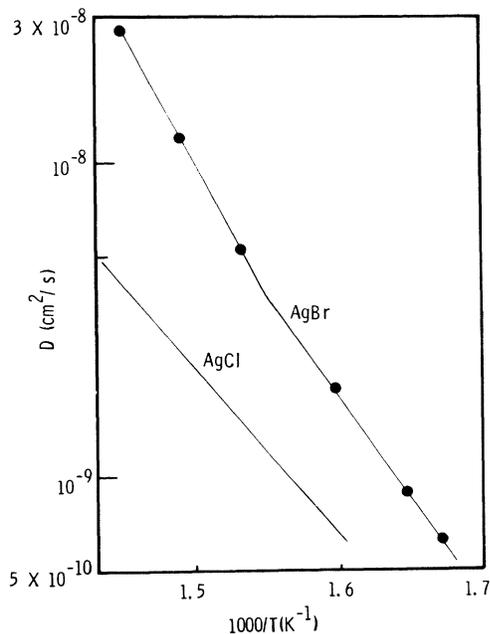


FIG. 2. Diffusion coefficient of  $\text{Ca}^{2+}$  in pure AgBr as a function of temperature, shown as solid circles. For comparison, the earlier results of Brébec and Slifkin in AgCl are included.

sitated by the relatively high tracer diffusivities, was corrected for the initial heating period, during which the specimen was brought to the desired annealing temperature. Such corrections have been found to be quite reliable, as earlier experimental evidence indicates.<sup>13</sup>

The single major contribution to the uncertainty in the diffusion coefficients comes from the anneal temperature, which could only be specified to within 0.5°C. All our diffusion runs were carried out in the same diffusion furnace and used the same thermocouple. The quality of the data displayed in Fig. 1 shows that fairly uniform and similar geometries were obtained for all sections when they were dissolved in ammonium hydroxide prior to counting. The overall uncertainty in the diffusion coefficient is estimated to be no more than 4%.

#### IV. DISCUSSION

The Arrhenius plot, displayed in Fig. 3, for diffusion of the calcium ion in AgBr single crystals is not linear over the entire temperature range, but shows two linear branches with a break around 380°C. An activation energy of 1.89 eV and a preexponential factor of  $1.9 \times 10^6 \text{ cm}^2/\text{s}$  are obtained from the high-temperature data and they are substantially larger than the corresponding values of 1.33 eV and  $77 \text{ cm}^2/\text{s}$  found from the low-temperature data. The observed nonlinearity in the Arrhenius plot is not surprising or unexpected. Similar two-segmented plots have earlier been reported for diffusion of cadmium<sup>23</sup> and manganese,<sup>24</sup> and more recently for cobalt<sup>22</sup> in AgBr. Only in the case of divalent iron diffusing in AgBr has a linear Arrhenius plot been found.<sup>25</sup>

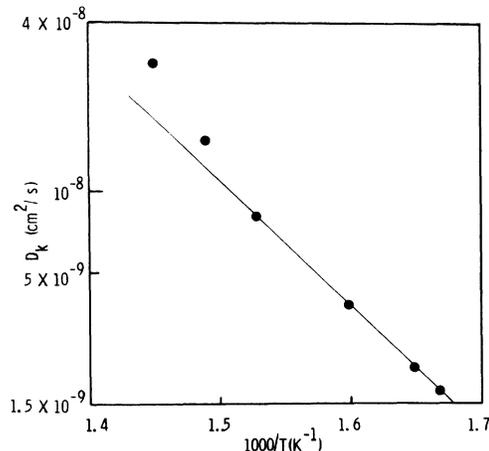


FIG. 3. Diffusion coefficient of  $\text{Ca}^{2+}$ -vacancy complex in AgBr as a function of temperature.

It is known that  $\text{Ca}^{2+}$  substitutes for  $\text{Ag}^+$  in the silver halides, and is compensated by a silver vacancy. This is supported by the ionic conductivity measurements in  $\text{AgCl}:\text{Ca}^{2+}$  and  $\text{AgBr}:\text{Ca}^{2+}$ , which have been successfully interpreted in terms of a model that includes cation vacancies created by the divalent calcium ions in order to preserve electrical neutrality in the crystal.<sup>26,27</sup> The ionic thermocurrent experiments in  $\text{AgCl}:\text{Ca}^{2+}$ , which use the relaxation of low-temperature dielectric polarization by dipolar impurity-vacancy complexes, also lend credence to the fact that calcium dissolves substitutionally in the silver halides.<sup>28</sup> The diffusion parameters obtained in the present investigation for the region below 380°C are typical of diffusion by a vacancy mechanism, and are comparable to those reported earlier for the other divalent cation impurities in AgBr.<sup>22-25</sup>

In the silver halides, as higher temperatures are approached, two important considerations enter the data analysis. Firstly, a general softening of the crystal occurs, as is evidenced from the drastic changes observed in the physical properties which include elastic constants, ionic conductivity, dielectric constant, and thermal expansion.<sup>1-10</sup> Secondly, since the defect concentrations are relatively large, the Coulomb interactions between the charged defects become increasingly significant. These interactions are usually treated by the Lidiard-Debye-Hückel theory, which adapts the Debye-Hückel treatment of aqueous ionic solutions to ionic crystals containing charged defects.<sup>29</sup> These two factors give rise to a substantial temperature-dependent nonlinear decrease in the Gibbs free energy of formation of Frenkel defects, with major contributions at higher temperatures presumably coming from the phenomena concomitant with lattice softening. Since the solute diffusion depends on the concentration of vacancies, the diffusion coefficient is expected to show departure from an Arrhenius relation for a constant activation enthalpy and entropy.

For impurity diffusion in the silver halides, the situation becomes more complicated. It is suspected that the

thermodynamic parameters for defect mobility and association, in addition to those for defect formation, will also show some variation with temperature.<sup>19</sup>

The substitutional divalent impurity ion can only diffuse if it becomes associated with a cation vacancy at the nearest-neighbor lattice site. Thus the diffusion may be thought of as occurring by the migration of the impurity-vacancy complex, which is regarded as the diffusing entity. Lidiard<sup>29</sup> has shown that the diffusion coefficient  $D_k$  of the impurity-vacancy complex, for tracer experiments involving pure crystals with negligible impurity concentration such as those reported here, is given by

$$D_k = D/p, \quad (1)$$

where  $D$  is the measured impurity tracer diffusion coefficient, and the degree of association  $p$  is the fraction of the divalent cations which are associated with the cation vacancies. Further illuminating discussion and examples of the diffusion of divalent ions in ionic crystals have been provided by Friauf.<sup>30</sup>

The basic condition for the use of Eq. (1) is that the concentration of the intrinsic defects must be larger than the total divalent impurity concentration in the crystal. In the temperature range of our measurements, the intrinsic defect concentration ranges from  $1.6 \times 10^3$  ppm at 325°C to  $1.6 \times 10^4$  ppm at 416°C. On the other hand, in addition to the 2-ppm concentration of residual impurities, the average concentration of divalent ions introduced into the crystal by the tracer at its surface is estimated not to exceed 8 ppm.<sup>30</sup> It is therefore obvious, from the comparison of the concentrations of intrinsic defects and divalent impurity ions, that Eq. (1) is indeed appropriate for the situation described in this paper.

The value of  $p$ , the degree of association, is calculated from the following equations:

$$X_i X_c = 2 \exp(-g_f/k_B T) \exp(\Delta g_f/k_B T), \quad (2)$$

which governs the Frenkel-defect equilibrium in the silver halides,

$$p/\gamma^2 X_c (1-p) = 12 \exp(g_k/k_B T), \quad (3)$$

which describes the equilibrium of the formation of impurity-vacancy complexes, and

$$X_c = X_i + c(1-p), \quad (4)$$

which expresses the condition of electrical neutrality in the bulk of the crystal. In these equations,  $X_i$ ,  $X_c$ , and  $c$  are the fractional concentrations of interstitial cations, cation vacancies, and divalent cations, respectively;  $g_f$  and  $g_k$ , assumed to have the usual linear temperature dependence, are the Gibbs free energies for the formation of a Frenkel defect and for the dissociation of an impurity-vacancy complex;  $\Delta g_f$  is the total reduction in  $g_f$  both due to long-range Coulomb interactions between the isolated charged defects and the general softening of the crystal;  $\gamma$  is the activity coefficient of an isolated defect;  $k_B$  is the Boltzmann constant; and  $T$  is the absolute temperature. Since the long-range Debye-Hückel correc-

tion is included in  $\Delta g_f$ , the activity coefficient  $\gamma$  does not appear explicitly in Eq. (2) for the Frenkel-defect equilibrium.

The correct calculation of the degree of association  $p$  using Eqs. (2)–(4) is crucial for the interpretation of the results. We have used Kao and Friauf's values of  $g_f$  for the Frenkel-defect formation in AgBr and their nonlinear temperature-dependent correction,  $\Delta g_f$ , to this energy,<sup>31</sup> and Lieb's value of 0.222 eV for the enthalpy of dissociation of  $\text{Ca}^{2+}$ -vacancy complex,  $h_k$ , determined from the temperature dependence of the ionic conductivity in doped AgBr crystals.<sup>27</sup> We have assumed the entropy of dissociation of the complex  $s_k$  to be about equal to zero.

For the concentration  $c$  of the total divalent impurity ions, a value of 10 ppm is assumed. As indicated earlier, this value is much smaller than the intrinsic vacancy concentration at all temperatures in our measurements. For this reason, the degree of association is found to be rather insensitive to small variations in  $c$ .

The degree of impurity-vacancy association  $p$  is calculated to range from 0.37 at 325°C to 0.79 at 416°C. These values of  $p$  are rather large, which means that a large fraction of the calcium ions has a silver ion vacancy on a nearest-neighbor site. The increasing complex concentration with increasing temperature is a consequence of the fact that the tendency for the complex to dissociate at higher temperatures is overshadowed by the presence of larger concentration of cation vacancies which become available for complex formation.

For diffusion of a divalent impurity cation in a monovalent ionic crystal, the jump frequency  $\omega_2$  of the impurity cation into the vacancy is much less than the jump frequency  $\omega_1$  for a host cation into the vacancy that leaves the complex bound.<sup>29,30</sup> The diffusion for this case is therefore limited by the impurity-vacancy exchange. Since the diffusion is presumed to occur by means of impurity-vacancy complexes, the activation energy for the migration of the complex is thus expected to equal that for the impurity-vacancy exchange. The diffusion coefficient  $D_k$  of the complex may then be written in terms of an attempt frequency  $\nu$  of the diffusing impurity ion and the Gibbs free energy  $g_m$  for the migration of the impurity ion into a nearest-neighbor cation vacancy:

$$D_k = \frac{1}{3} a^2 \nu \exp(-g_m/k_B T), \quad (5)$$

where  $a$  is the smallest cation-anion separation distance.

If the free energy  $g_m$  is decomposed into enthalpy of migration  $h_m$  and entropy of migration  $s_m$ , then a plot of the logarithm of  $D_k$  versus the reciprocal temperature will yield values for these motional parameters. Figure 3 displays the temperature dependence of  $D_k$ , calculated from Eq. (1), for the  $\text{Ca}^{2+}$ -vacancy complex. From the slope and the intercept of the straight line drawn through the four low-temperature points, which appear to follow the Arrhenius relation of Eq. (5), values of 0.92 eV for  $h_m$  and  $4.2k_B$  for  $s_m$  for the jumping of the calcium ion into a nearest-neighbor cation vacancy are determined. These values seem to be reasonable when compared to those for other divalent impurities in AgBr (Ref. 22) obtained by similar analysis (cobalt, 0.79 eV and  $4.4k_B$ ; cadmium,

0.93 eV and  $6.5k_B$ ; iron, 0.97 eV and  $6.2k_B$ ; manganese, 0.78 eV and  $2.7k_B$ ).

The value of 0.92 eV for the  $\text{Ca}^{2+}$ -vacancy exchange is about 3 times larger than the 0.325 eV required for the jump of  $\text{Ag}^+$  ion into a vacancy.<sup>31</sup> For an ion to interchange with a vacancy, it must surmount a potential energy barrier, the height of which is usually defined as the activation energy for migration. Due to the double charge on the calcium ion, the barrier height is expected to increase and so is the migration energy.

The two points at the highest temperatures, 397.0°C and 415.5°C, do not follow the Arrhenius relation of Eq. (5), as seen in Fig. 3. Similar deviations have been reported for diffusion of  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  in  $\text{AgCl}$ ,<sup>32</sup> and of  $\text{Co}^{2+}$  in  $\text{AgBr}$ .<sup>22</sup> These deviations may have resulted from the failure of the law of mass action to accurately describe the defect equilibria at large defect concentrations encountered in  $\text{AgBr}$  at high temperatures. In fact, the concept of a simple nearest-neighbor impurity-vacancy complex may be inadequate to describe the diffusion phenomenon at such high defect concentrations. Some complexes may perhaps very well involve the presence of more than a single vacancy because of an attraction between a dipole (impurity-vacancy complex) and a monopole (cation vacancy). Because of this, the degree of association may in reality be larger than we have calculated. In any event, this observed discrepancy between theory and experiment strongly suggests the breakdown of the simple ideas of mass action at high defect concentrations, a conclusion not entirely unexpected.

As Fig. 2 shows, the diffusion coefficients of  $\text{Ca}^{2+}$  in  $\text{AgBr}$  are consistently larger than those in  $\text{AgCl}$ . Several important factors need to be considered here. The intrinsic vacancy concentrations in  $\text{AgBr}$  are much larger than in  $\text{AgCl}$ . The migration energy of  $\text{Ca}^{2+}$  in  $\text{AgBr}$  (0.92 eV), on the other hand, is much higher than that in  $\text{AgCl}$  (0.7 eV). This difference might be related to the widely

differing radii of the anions ( $\text{Cl}^-$ , 1.81 Å;  $\text{Br}^-$ , 1.95 Å) which reflect in a relatively tighter gate in  $\text{AgBr}$ . In addition, the association enthalpy for the  $\text{Ca}^{2+}$ -vacancy complex is also somewhat different in the two materials, 0.33 eV for  $\text{AgCl}$  (Ref. 26) as compared to 0.22 eV for  $\text{AgBr}$ .<sup>27</sup> Our results thus indicate that the large diffusivities in  $\text{AgBr}$  are due to the dominant effect of larger vacancy concentrations.

## V. CONCLUSIONS

The present studies have provided additional data for divalent impurity diffusion in  $\text{AgBr}$ . The diffusion of  $\text{Ca}^{2+}$  in  $\text{AgBr}$  proceeds by a vacancy mechanism. The activation enthalpy and entropy for the  $\text{Ca}^{2+}$ -vacancy exchange are determined to be 0.92 eV and  $4.2k_B$ . The calculated values of the diffusion coefficient of the impurity-vacancy complex at the highest two temperatures exhibit deviations from the extrapolation of the data from lower temperatures. These deviations strongly indicate the inability of the simple ideas of mass action to accurately describe the mass-transport properties in ionic crystals at high defect concentrations. The diffusion coefficient of  $\text{Ca}^{2+}$  in  $\text{AgBr}$  is found to be consistently larger than in  $\text{AgCl}$ —a consequence of the dominant effect of the relatively larger concentrations of intrinsic cation vacancies in  $\text{AgBr}$ .

## ACKNOWLEDGMENTS

The authors are pleased to acknowledge the interest of Professor A. B. Gardner in this work and are grateful to Professor L. M. Slifkin, Dr. R. J. Borg, and Dr. C. E. Violet for their helpful comments. They also wish to express their appreciation to C. B. Childs for providing crystals of very pure silver bromide. This work was supported in part by the Howard University Faculty Research Grant Program.

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