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Diffusion of cesium in silver bromide: A surprising observation of the strain effect due to an oversize solute

P. A. Cardegna[*] and A. L. Laskar

Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29631

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The diffusion of Cs^+ in AgBr has been measured in the temperature range 300–420 °C by a tracer and serial-sectioning technique. The diffusion of Cs^+ proceeds by a vacancy mechanism. Cs^+, oversized in comparison to the host Ag^+, produces local strain in the AgBr lattice, causing diffusivities larger than those of substitutional Ag^+ and compensating partially the intrinsic curvature in the Arrhenius plot expected from the nonlinear decrease in g_f with increasing temperature. Surprisingly, the diffusivity of Cs^+ in AgBr is lower than that in AgCl, presumably due to the larger size effect in a more compact lattice.

Like alkali halides, silver halides are simple ionic solids, but they are regarded as "anomalous" due to abnormally large increases in some physical properties at high temperatures. In particular, the onset of a steep increase in the electrical conductivity and Ag^+ diffusion at about 100 °C below the melting temperature has been a subject of investigation for the last 30 years. Recently Friauf[1] has presented an excellent critical review of the various works and has shown how a number of experimental and theoretical investigations have converged to establish a unique set of values for the defect parameters in AgBr and AgCl. It is now believed that the Gibbs free energy for Frenkel-defect formation (g_f) decreases nonlinearly with the increase of temperature, thus creating an anomalously large number of vacancies and interstitials, which in turn lead to a steep increase in the electrical conductivity and Ag^+ diffusion by a vacancy exchange mechanism.

The study of the diffusion of some alkali ions in both AgCl and AgBr was crucial in providing independent verification of the above conjecture. One effect of the anomalously large increase of the cation vacancy concentration with increasing temperature (due to decrease of g_f) is that cations which diffuse via a vacancy exchange will also exhibit an anomalous increase in diffusivity. This was indeed observed as a positive curvature in the diffusion Arrhenius plots for the diffusion of Na^+ by Batra and Slifkin[2,3] and of K^+ by Cardegna[4] in both AgCl and AgBr. The "intrinsic curvature" in the diffusion Arrhenius plots was accurately accounted for by the nonlinear decrease of g_f with temperature. Being homovalent with Ag^+, alkali ions do not perturb the thermal defect concentration and thus accurately probe the properties of intrinsic defects.

In the case of alkali ions, oversized compared to the host Ag^+, the size mismatch introduces a strain-induced association between the solute ion and the vacancy which influences the activation enthalpy of diffusion. Further, the elastic moduli of silver halides decrease sharply with increase of temperature and thus lower the association enthalpy. The overall effect is to compensate for the effect due to g_f. Exactly this behavior has been observed in the linear Arrhenius diffusion plots for Rb^+ in AgCl (Ref. 5) and AgBr (Ref. 6) and for Cs^+ in AgCl.[7]

In this paper we present the results of the study of the diffusion of Cs^+ in AgBr, which verify the above conclusions in general. However, the observation that the diffusivity of Cs^+ in AgBr is much lower than that in AgCl is surprising and is an extreme example of strain effects on diffusivity due to size mismatch between the solute and host ions.

A tracer and serial sectioning by microtome technique was used to determine the diffusivity of Cs^+ in AgBr. The details of the experimental technique are described elsewhere.[5] The AgBr crystals, pure to less than 1 ppm, were kindly supplied by C. Childs, of the University of North Carolina. Approximately 1 μCi or less of carrier-free ^{137}Cs was used to minimize the perturbation of the intrinsic vacancy concentration by any divalent impurities which might accompany the cesium tracer. For runs at the highest temperatures where the diffusivity of cesium is large, it was necessary to use short diffusion anneal times. However, the anneal time in no case was less than 1 h, and warm-up corrections, calculated from the continuous record of temperature with time, never exceeded 3%.

Figure 1 displays the penetration profiles for Cs^+ diffusion in AgBr at several temperatures. All the plots are judged to be good Gaussians, as is expected for the diffusion from a thin film of solute into a semi-infinite solid. It is to be noted that the penetration profiles for some lower-temperature runs show upward concavity near the surface. This effect may be caused by the holdup of the solute at the surface due to the lower solubility of CsCl in AgBr at low temperatures. This suspicion is further supported by the fact that in several diffusion runs at temperatures lower than 300 °C there was large surface holdup and very little penetration in spite of long diffusion anneal times. These runs had to be abondoned due to the consequent uncertainty in the determination of diffusion coefficients. The diffusion coefficients exhibited in Table I were extracted from diffusion profiles which are linear through two to three orders of magnitude and the overall error is well within 4%.

The Arrhenius plot of the diffusivity of Cs^+ in AgBr (Fig. 2) is found to be nonlinear. Excluding the data points at the two highest temperatures, the diffusivity of Cs^+ in AgBr may be represented by the following Arrhenius relation over the temperature range 300–396 °C:

$$D=(9.30\pm 0.08)\exp[-(1.05\pm 0.02\ \mathrm{eV})/kT]\ \mathrm{cm^2/sec}\ .$$

The diffusion parameters indicate that the Cs^+ migrates by a vacancy exchange mechanism. The diffusion activation enthalpy (h) may be expressed as $h=h_f/2+h_m-h_a$, where

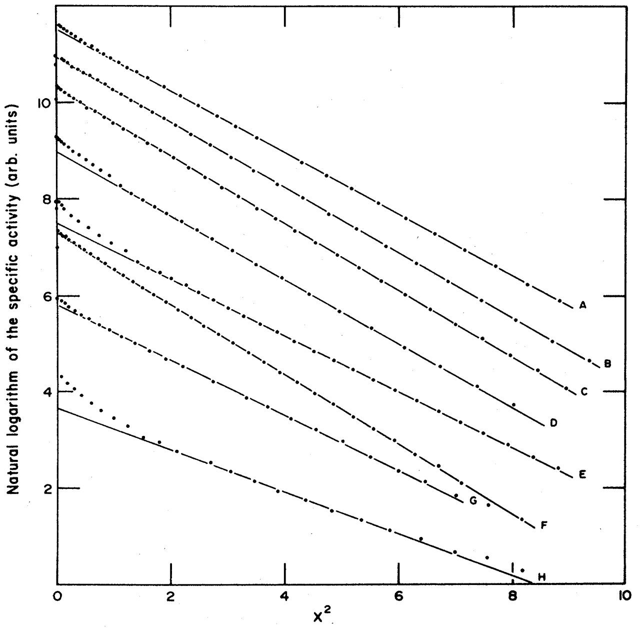

FIG. 1. Penetration profiles for the diffusion of ^{137}Ca in AgBr at several temperatures. Temperature (°C) and the full-scale values of the depth squared (x^2 in cm^2) for the graphs are indicated as follows. For A 419.49, 2.03×10^{-2}; B 396.43, 7.42×10^{-3}; C 387.73, 5.33×10^{-3}; D 366.10, 3.08×10^{-3}; E 352.37, 1.59×10^{-3}; F 382.87, 7.33×10^{-3}; G 329.95, 8.93×10^{-4}; H 300.21, 4.57×10^{-3}.

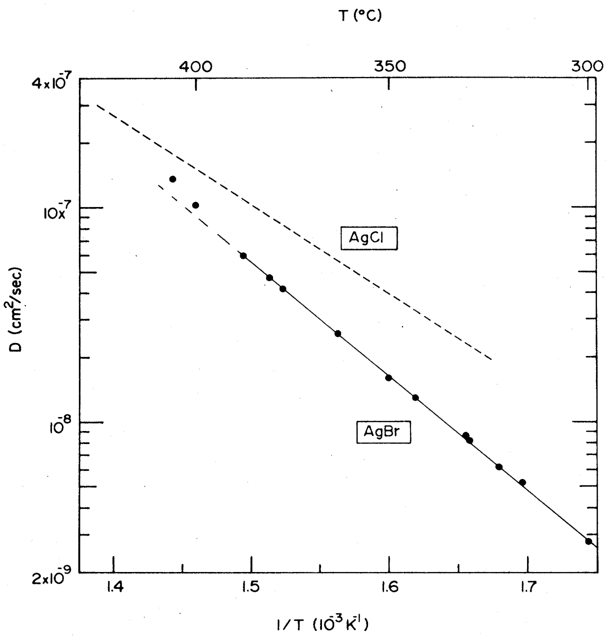

FIG. 2. Temperature dependence of the diffusivity of Cs$^+$ in AgBr is shown by the solid line. The same for AgCl (Refs. 7 and 9) is shown by dashed line for comparison. For AgBr, the two data points show an upturn when compared with the extrapolated line passing through the lower temperature data.

subscripts f, m, and a correspond to formation, migration, and strain-induced association of the solute ion with a vacancy. Taking Friauf's[1] value of $h_f = 1.16$ eV and the usual enthalpy of migration of an impurity via vacancy as ~ 0.6 eV, the association energy of ~ 0.1 eV is not unreasonable, since Coulombic binding is not expected between the homovalent Cs$^+$ and a vacancy.

The two most puzzling observations of the present investigations when compared to the results of Cs$^+$ diffusion in AgCl (Ref. 7) (shown by dashed lines in Fig. 2) are (1) the diffusivity of Cs$^+$ in AgBr is much lower than that in AgCl at all temperatures and (2) the diffusion Arrhenius plot for AgBr exhibits an upturn at the highest temperature in contrast to the linear behavior for AgCl. A survey[8] of all the results for solute diffusion in silver halides (22 in AgCl and 12 in AgBr) indicates that the diffusivity in AgBr is always much larger than that in AgCl. This prompted us to measure the Cs$^+$ diffusion in AgCl at several temperatures. Our results[9] are in excellent agreement with the earlier results of Batra and Slifkin.[7]

TABLE I. Diffusion of Cs$^+$ in AgBr.

Temperature (°C)	Diffusion anneal time (sec)	D (cm^2/sec)
419.49	3.78×10^3	1.38×10^{-7}
411.57	3.80×10^3	1.032×10^{-7}
396.43	3.23×10^2	5.92×10^{-8}
387.73	3.38×10^3	4.72×10^{-8}
382.87	3.26×10^3	4.23×10^{-8}
366.10	3.15×10^3	2.62×10^{-8}
352.37	3.46×10^3	1.58×10^{-8}
344.26	3.39×10^3	1.29×10^{-8}
330.79	3.36×10^3	8.78×10^{-9}
329.95	3.20×10^3	8.20×10^{-9}
322.20	4.29×10^3	6.15×10^{-9}
315.99	3.16×10^3	5.34×10^{-9}
300.21	3.22×10^3	2.79×10^{-9}

We do not fully understand these unexpected results. Only a tentative explanation is attempted. AgCl ($\lambda = 5.51$ Å) in contrast to AgBr ($\lambda = 5.79$ Å) has less open space for the migration of solutes. A large oversize Cs$^+$ (1.67 Å), compared to the host Ag$^+$ (1.26 Å) thus introduces a larger strain in AgCl. This results in strain-induced binding of the Cs$^+$ with a vacancy in both AgCl and AgBr. However, the binding energy in case of AgCl is ~ 0.5 eV, whereas for AgBr it is ~ 0.1 eV. Qualitatively, it is plausible that the strain-induced binding and its temperature dependence, in the case of AgCl, compensates for the "inherent curvature" in the diffusion Arrhenius plot due to the nonlinear temperature dependence of g_f as discussed earlier. Since the strain-induced binding is lower in the case of AgBr, the upturn in the diffusion Arrhenius plot still persists.

This large difference in strain-induced binding also makes Cs$^+$ more insoluble in AgCl than in AgBr. One indication of this is that for AgCl (melting point 454 °C) the diffusion experiments below 350 °C had to be abandoned due to very little penetration resulting from poor solubility of Cs$^+$ in AgCl.[7] In contrast, for AgBr (melting point 432 °C) Cs$^+$ is soluble down to 300 °C, below which diffusion runs had to be abandoned for similar reasons. It is generally expected that solutes with lower solubility also diffuse at a faster rate.[10,11] Thus the diffusion of Cs^+ in AgCl should be higher than that in AgBr, as observed. Nevertheless, the fact that the present results indicate a complete reversal of all the earlier results, establishing that the charge and mass transport is higher in AgBr than in AgCl, needs to be critically examined in the light of some theoretical investigations.

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[*] Permanent address: Department of Physics, Rochester Institute of Technology, Rochester, NY 14623.

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