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Temperature dependence of Frenkel-defect formation energy deduced from diffusion of sodium in silver chloride*

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The anomalously large excess ionic conductivity displayed by AgCl at high temperatures has been variously interpreted in terms of the onset of a second type of cation interstitialcy mechanism, or alternatively as due to a decrease in the Frenkel-defect formation energy with increasing temperature. A detailed measurement of the temperature dependence of the diffusivity of substitutional sodium-ion tracer in AgCl is here shown quantitatively to confirm the latter of these possibilities.

Two yet unsolved problems in the understanding of point defects in ionic crystals involve the extent to which such thermodynamic parameters as enthalpies of formation may depend upon temperature, and the effects of interactions between defects when their concentrations are high—of the order of 1%. For the study of each of these questions, crystals of the silver halides, especially AgCl and AgBr, represent excellent research media. First, the anomalously large change at high temperatures, within about 100 deg of the melting point, of such physical properties as the thermal expansion¹ and the dielectric coefficient² make it not unlikely that such parameters as the Frenkel-defect formation enthalpy may decrease measurably with increasing temperature. Second, at high temperatures the intrinsic Frenkel-defect concentration rises to unusually large values, 0.4% in AgCl and 2% in AgBr, so that defect-defect interactions may no longer be adequately described by the Lidiard-Debye-Hückel (LDH) theory of electrostatic interactions,³ even with the cluster-expansion extensions proposed by Allnatt and Cohen⁴ and by Sevenich and Kliewer.⁵

Among the physical properties of the silver halides which behave anomalously at high temperatures are cation transport phenomena such as the ionic conductivity,^{6,7} which increases more rapidly than the normal LDH-corrected Arrhenius-type behavior. The ionic conductivity of AgCl has been investigated extensively and with great care recent-

ly by Corish and Jacobs⁶ and by Aboagye and Friauf.⁷ In the analysis of Corish and Jacobs, the extra ionic conductivity at high temperatures is associated with the onset of a second type of cation interstitialcy migration, involving a noncollinear displacement. Aboagye and Friauf, on the other hand, deduce the various defect parameters from an analysis of data only in the intermediate range of temperature, where the LDH theory is expected to provide an adequate correction for defect-defect Coulombic interactions. The excess conductivity at high temperatures, excess relative to that calculated from the parameters determined in the intermediate temperature range, is then attributed to a decrease, with increasing temperature, of the free energy of formation of the Frenkel defect, as earlier suggested by Müller.¹ Their results show that just below the melting point, this decrease amounts to as much as 0.12 eV (almost 10% of the low-temperature value of the enthalpy of formation), of which the LDH correction can only account for about half. Very recently, Corish and Jacobs⁶ have subjected their earlier data to analysis under a number of possible models, and have concluded that there is no compelling evidence for a substantial temperature dependence of the formation enthalpy.

The present work attempts to remove this ambiguity in interpretation by providing a reliable measurement of the temperature dependence of the

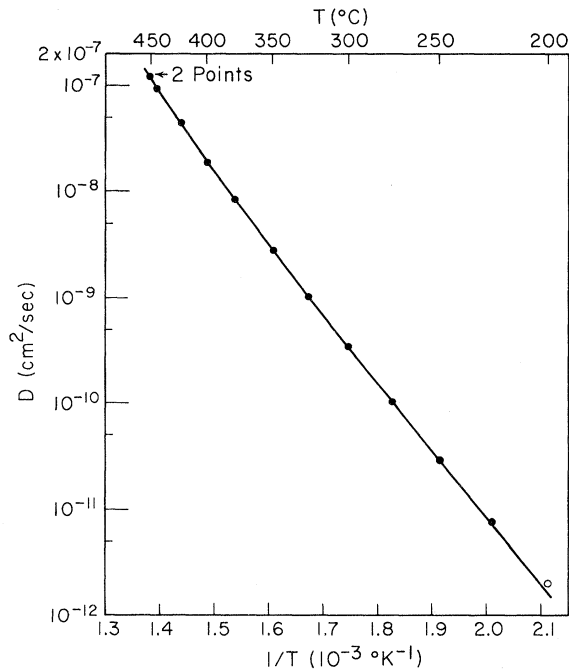


FIG. 1. Diffusion coefficient of Na^+ in pure AgCl as a function of temperature. The diffusion coefficient at the lowest temperature (open circle) is somewhat uncertain because of the background impurity in the specimen and possible contamination accompanying the tracer.

diffusivity of a substitutional monovalent cation tracer. The diffusivity of such a tracer would be insensitive to the onset of a second silver-ion interstitialcy mechanism. Moreover, because a monovalent substitutional ion has no net charge in the AgCl lattice, its rate of diffusion by the vacancy mechanism would thus represent a probe for the intrinsic concentration of cation vacancies. If, as proposed by Aboagye and Friauf, the vacancy concentration at high temperature increases faster than $\gamma^{-1} \exp(-g_f/2kT)$, where γ is the LDH activity coefficient and g_f is the formation free energy obtained from the data at intermediate temperatures, then the diffusivity of the substitutional solute tracer should show an anomaly similar to that exhibited by the conductivity.

For the solute tracer probe we have used carrier-free ^{22}Na , which had previously been demonstrated by Süptitz,⁹ on the basis of doping experiments, to diffuse substitutionally. Süptitz's data on diffusivity versus T are not adequate, however, for the proposed comparison with ionic conductivity; they show a sharp break at 300°C , at which point the slope of the Arrhenius plot increases abruptly by 25%.

The standard tracer-sectioning technique¹⁰ was here employed. The AgCl crystals, pure to approximately 1 ppm, were kindly supplied by Childs

of the University of North Carolina. For the runs at lower temperatures, a minimal amount of carrier-free tracer, only $0.01 \mu\text{Ci}$ per specimen, and long diffusion times were used, in order to minimize perturbation of the intrinsic vacancy concentration by any divalent impurities which might accompany the sodium tracer.^{11,12} For runs at the highest temperatures, where both the intrinsic vacancy concentration and the sodium diffusivity are very large, it was necessary to use rather short diffusion times, but the warmup corrections never exceeded 5%, and the resulting errors were negligible.¹³ For all runs, over the entire range of temperature, excellent Gaussian penetration plots were obtained.

The present results are shown as $\ln D$ vs $1/T$ in Fig. 1. Unlike the earlier data of Süptitz, our Arrhenius plot curves smoothly, rather than showing a sharp break. It is most probable that Süptitz's low-temperature data were perturbed by residual background impurities and by the effects of codiffusion of divalent cations introduced with the larger amount of tracer which he used. In fact, our run at the lowest temperature (designated in the figure by an open circle) is seen to yield too high a diffusivity, but the deviation of this point from the curve in Fig. 1 is completely accounted for by the known residual background impurity in these specimens. The present data therefore appear to be of adequate quality to provide a test of the two models described above for the high-temperature

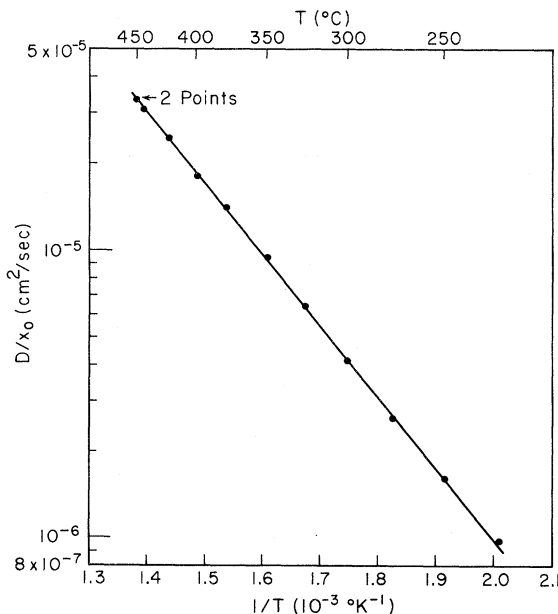


FIG. 2. Plot of $\ln(D/x_0)$ vs $1/T$; values of x_0 are calculated from the data of Aboagye and Friauf on ionic conductivity in AgCl . The solid curve is a straight line.

anomaly in the ionic conductivity.

The central result of the present work is that the curvature of Fig. 1 is exactly accounted for by the free energy decreases Δg_f reported by Aboagye and Friauf.⁷ The diffusion coefficient is given by¹⁴

$$D = 4a^2 \nu f x_0 e^{-g_m/kT}, \quad (1)$$

where a is the cation-anion separation distance, ν is an attempt frequency, f is the correlation factor (which, on the basis of Süptitz's isotope-effect measurements,⁹ may be taken to be unity), x_0 is the fractional concentration of cation vacancies, and g_m is the Gibbs free energy for migration. We have ignored the very small decrease in defect mobility that results from the LDH atmosphere.^{3,15} Now, according to Aboagye and Friauf, x_0 varies as $\exp[-(g_f - \Delta g_f)/2kT]$, where Δg_f increases with increasing temperature, and is presumably the origin of both the high-temperature anomaly in ionic conductivity and the curvature of Fig. 1. A quantitative test of this presumption is therefore to check the linearity of the dependence of $\ln(D/x_0)$ with respect to the inverse temperature; i. e., to see whether normalization of the diffusivity by x_0 eliminates the curvature in the Arrhenius plot. We have used values of $x_0(T)$ from Aboagye and Friauf; the results are displayed in Fig. 2.

The excellent linearity of the data of Fig. 2 indicates that the values of $\Delta_f(T)$ obtained by Aboagye and Friauf do indeed quantitatively account for the sodium tracer diffusivities. This agreement thus represents strong evidence for the validity of their analysis, in terms of a temperature-dependent activation energy. It also corroborates the assignment of the anomaly almost entirely to Δg_f , rather than to both Δg_f and Δg_m .

Using Eq. (1), we may also determine from Fig. 2 the enthalpy H_m and entropy S_m of activation for the jump of a sodium ion into a neighboring cation vacancy. Taking $\nu = 5.8 \times 10^{12}$ Hz,¹⁶ one finds $H_m = 0.490 \pm 0.003$ eV and $S_m/k = 1.6 \pm 0.6$. These values may be compared with those for the jump of a free vacancy in AgCl, for which $H_m = 0.275$ eV and $S_m/k = -0.64$.⁷ Of particular interest is the fact that migration enthalpy for Na^+ is so much larger than that for Ag^+ , even though both ions are monovalent and the radius of Na^+ (0.95 Å) is much smaller than that of Ag^+ (1.26 Å).¹⁷ This increase in the migration barrier perhaps results from the absence, in the case of Na^+ , of covalent interactions with the halide ions at the saddle point, interactions which presumably are present for Ag^+ , a d -electron ion. The possible role of such d -electron interactions in cation diffusion in AgCl will be discussed further elsewhere.¹⁸

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