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DIFFUSION OF VACANCIES AND VACANCY PAIRS IN NaCl*

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It is clear that cation and anion vacancies give rise to both ionic conductivity and diffusion in alkali halides. The results reported here indicate that bound vacancy pairs also make appreciable contributions to diffusion of both cations and anions.

$$D^*(\text{Na}) = D_{\text{vac}}(\text{Na}) + D_{\text{pair}}(\text{Na})$$

$$D^*(\text{Cl}) = D_{\text{vac}}(\text{Cl}) + D_{\text{pair}}(\text{Cl})$$

By means of the Einstein relation the total conductivity may be written as

$$\begin{aligned}\sigma &= \sigma_{\text{vac}}(\text{Na}) + \sigma_{\text{vac}}(\text{Cl}) \\ &= f_v^{-1} (Ne^2/kT) [D_{\text{vac}}(\text{Na}) + D_{\text{vac}}(\text{Cl})],\end{aligned}$$

where $f_v = 0.781$ is the correlation factor for diffusion by vacancies on a fcc lattice.

In order to determine the four defect contributions on the right-hand side of these equations the following experiments have been performed on single crystals of NaCl. (a) The ionic conductivity was measured in the extrinsic and intrinsic ranges (275°-797°C) with an AC bridge at 1000 Hz. (b) The diffusion of Na was measured (640°-790°C) with radioactive tracers and the sectioning method. The diffusion of Cl is taken from other work.^{1,2} (c) The drift mobility of Na tracers was measured (600°-772°C) by applying an electric field during diffusion, and two check points (692°, 773°C) were obtained with Cl tracers. The average electric field was obtained from the amount of charge passing through the sample measured with a silver coulometer, and the drift mobility $M_v(\text{Na}) = f_v^{-1} (e/kT) D_{\text{vac}}(\text{Na})$ was determined from the displacement of the diffusion profile.

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The sum of $D_{\text{vac}}(\text{Na}) + D_{\text{vac}}(\text{Cl})$ at the two check points is approximately 15% lower than the value calculated from the conductivity. This discrepancy is probably a fair indication of the experimental uncertainties, which are caused largely by poor contact at the interface between the two crystals. An attempt was made to fit the intrinsic conductivity (600°-800°C) with a sum of two Arrhenius terms, but systematic discrepancies of 4 to 6% remain. Thus there is a possibility that other contributions to the conductivity, such as vacancy triplets, need to be taken into account, as also suggested in other recent work.^{3,4}

The two measurements of $D_{\text{vac}}(\text{Cl})$ agree rather well with the results of Laurance but are considerably above those of Barr *et. al.* The results for $D_{\text{vac}}(\text{Na})$ obtained from the drift mobility are shown in the figure, along with measured values of $D^*(\text{Na})$ and values of $D_{\text{pair}}(\text{Na})$ obtained by subtraction. The lines in the figure are represented by $D = D_0 \exp(-W/kT)$ with:

$D^*(\text{Na})$	$D_0 = 620 \text{ cm}^2/\text{sec}$	$W = 2.21 \pm 0.08 \text{ eV}$
$D_{\text{vac}}(\text{Na})$	32	2.00 ± 0.05
$D_{\text{pair}}(\text{Na})$	1.1×10^5	2.75 ± 0.14

The activation energies agree quite well with theoretical values for cation vacancies of $W = \frac{1}{2} h_s + \Delta h_c = 1.93 \text{ eV}$ and for vacancy pairs of $W = h_{\text{pair}} + \Delta h_c' = 2.73 \text{ eV}$.⁵ In combination with the conductivity these results yield a cation transport number of approximately 70% throughout the intrinsic range, and the figure shows that $D_{\text{pair}}(\text{Na}) \sim D_{\text{vac}}(\text{Na})$ at the melting point.

Our results show that $D_{\text{pair}}(\text{Na})$ is 4 to 7 times larger than $D_{\text{pair}}(\text{Cl})$ given by Laurance. This seems surprising (the theoretical activation energies are $\Delta h_c' = 1.46$ and $\Delta h_a' = 1.27 \text{ eV}$) but is required to account for all of $D^*(\text{Na})$. Since the cation and anion jumps are coupled in the motion of a vacancy pair, the theory of the correlation factors shows that the maximum value of $D_{\text{pair}}(\text{Na})/D_{\text{pair}}(\text{Cl})$ is 5.6 when $v_{\text{pair}}(\text{Na})/v_{\text{pair}}(\text{Cl}) \gg 1$.⁶ Our

values at the highest temperatures are slightly outside this limit, but experimental uncertainties could easily be the cause. It is also possible to estimate the total vacancy pair diffusion from dielectric loss measurements, which purportedly give the mole fraction x_{pair} and the sum $v_{\text{pair}}(\text{Na}) + v_{\text{pair}}(\text{Cl}) = 1/\tau$.⁷ Although the concentrations from the loss measurements already appear unreasonably large, the diffusion coefficients calculated from them are too small even to account for $D_{\text{pair}}(\text{Cl})$, to say nothing of the larger $D_{\text{pair}}(\text{Na})$; it would be necessary to have jump frequencies at least 10 times larger in order to obtain agreement with reasonable values of x_{pair} . Thus a further enigma is added to the dielectric loss problem.

In conclusion the technique of measuring tracer drift mobilities in an electric field shows promise as a tool for delineating the contributions of single vacancies. The overall picture for conductivity and diffusion in NaCl confirms the importance of conduction by anion as well as cation vacancies, and there is an appreciable contribution of vacancy pairs to diffusion of both anions and cations.

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