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IMPURITY — POINT DEFECT EQUILIBRIA.

Energy parameters for the migration of anion vacancies in alkali halides

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Résumé. — On a déterminé les paramètres d'énergie pour la migration des lacunes anioniques dans le KCl, le NaCl et le NaF en utilisant les mesures de basse fréquence de l'absorption diélectrique.

Abstract. — The energy parameters for the migration of anion vacancies have been determined in KCl, NaCl and NaF from low-frequency dielectric absorption measurements.

1. Introduction. — The energy parameters connected with the motion of cation vacancies in the alkali halides have been well established [1-4]. This is not the case for anion vacancies.

We have recently reported [5] what we believe to be the first reliable determination of the enthalpy of motion of anion vacancies in NaCl using crystals doped with S²⁻ ions. In this paper we report on similar measurements in KCl and NaF. In NaCl : S²⁻ and KCl : S²⁻ we have been able to measure the concentration of the bivalent anions and therefore to calculate the migration entropy.

2. Experimental. — The methods used (i) to purify the starting materials, (ii) to grow the single crystals, and (iii) to measure the electric conductivity were essentially the same as those described in our recent publication [5].

Sulphide ion concentrations were determined using a sulphide specific ion electrode (1).

3. Results and discussion. — The d.c. electric conductivity (σ) of the crystals was obtained by measurement of the dielectric loss factor (ε″) at low frequencies (f = 0.05 Hz to 10 Hz). As in the case of NaCl [5], the main contribution to ε″ is from the bulk d.c. electric conductivity of the crystal which varies as f⁻¹. The variation of ε″ with frequency was fitted by non-linear least squares to the expression

ε″ = Af⁻¹ + Bf⁻ⁿ.  (1)

In most cases the best fit is with n = 0.5, as was the case with NaCl [5]. A is equated to σ/2πε₀. Only measurements in which the first term contributed 90% or more to ε″ at the two lowest frequencies were used in the determinations of energy parameters.

4. Decay in the conductivity. — When crystals doped with bivalent anions are heated to above 600 °C, quenched to room temperature, and aged at a temperature about 100 °C, the electric conductivity decreases with time at an appreciable rate. We believe this decrease occurs because free anion vacancies diffuse through the lattice and are trapped by bivalent anions, in which case the decrease should be second order. The decay with time of the electric conductivity of a KCl : S²⁻ sample is an excellent fit to a second order curve (Fig. 1). (We have also included the first and third order curves which are the closest fits to the experimental points.) By measuring the decay at different temperatures we obtain an activation energy.

5. Conductivity as a function of temperature. — The electric conductivity has been measured as a function of temperature over a range which is limited at the upper end by the requirement that no significant pairing occurs during the measurement, and at the lower by interference from the background absorption. The migration enthalpies of the anion vacancies are equated with the activation energies determined from Arrhenius plots (σT = C exp(- E/kT)). These enthalpies, listed in table I, agree with the activation energies determined from conductivity decay.

6. Determination of entropies of migration. — The equation for the conductivity $\sigma$ of an alkali halide when the only mobile defects are anion vacancies is

$$\sigma T = 2 e^2 c w/k a k = 2 e^2 c a k D \exp(-h_m/kT) \tag{2}$$

where $c$ is the anion vacancy concentration in mole fractions, $w$ the probability per second of an anion jumping into an adjacent vacancy, $a$ the anion-cation distance, and $e$, $k$ and $T$ have their usual significance. Provided $c$ is known, $w$ can be determined. In Table I we list values of $D$ in those cases where we have been able to determine $c$. $D$ is equal to $v \exp(s_m/k)$, where $v$ is the number of times per second that an ion approaches the energy barrier. We take $v$ to be the frequency at very long wavelengths of the transverse optic mode. The entropy values are listed in Table I.

7. Debye-Hückel correction. — Equation (2) is only true for vanishing small concentration of vacancies. At high concentrations there is a decrease in the conductivity because of the reduction in mobility from the drag of the defects of opposite sign, in this case the bivalent anions. We have estimated this drag using the Debye-Hückel corrections as given by Lidiard [6] although these corrections apply to the case where the defects of opposite sign are mobile. When applied to our KCl results we obtain 1.21 eV for $h_m$ and 9.4 K for $s_m$.

8. Comparison with literature values and with energy parameters for cation vacancies. — 8.1 KCl. — Literature values for the enthalpy of migration of anion vacancies determined from d.c. electric conductivity vary from 0.67 to 1.30 eV. In only two cases have the experiments included measurements on crystals in which the anion vacancy concentration has been varied by doping with the bivalent anions, CO$_2^-$ [7] and even less soluble SO$_4^{2-}$ [8]. We place greater reliance on these two sets of measurements than on others; their results are 0.99 eV and 4.14 eV and 0.85 eV and 3.2 K [8] for $h_m$ and $s_m$ respectively. It can be seen that the agreement with our values is not good. However, when we compare values of $w$, the jump probabilities, rather than the enthalpies and entropies, the disagreement is not so marked (Fig. 2). This comparison of values of $w$ requires a large extrapolation but we are encouraged to make this extrapolation by the excellent agreement (Fig. 2) between values of $w$ for cation vacancies extrapolated from our low temperature (dielectric relaxation) values for $w$ with those obtained from electric conductivity at high temperatures. Of course, in the anion case our determination extends over a smaller range of $1/T$ than for the cation and therefore the extrapolation is less accurate.

8.2 NaF. — The only published value is 1.46 eV [9] for crystals without any anion doping. It can also be seen that the extrapolated $w$ for the anion vacancies crosses the $w$ for the cation vacancies below the melting point, implying that the major contribution to the electric conductivity just below the melting point is from anion vacancies, which is contrary to experimental evidence. However a small error in $s_m$ or $h_m$ or both would remove this discrepancy.

A comparison of the enthalpies of migration for cation and anion motion in these three halides shows that the anion enthalpy is higher than the cation (Table I), confirming the conclusion [5] about disagreement between experiment and recent calculations which predict much closer values [10, 11].

9. Comparison between diffusion and electric conductivity. — The decrease in the concentration of anion vacancies after quenching is given by

$$\frac{dp}{dt} = -Fw e_0 p^2 \tag{3}$$
where \( c_0 \) is the mole fraction at the beginning of the ageing experiment, \( p \) is the ratio of the concentration of vacancies at the time \( t \) to that at time \( t = 0 \), and \( F \) is made up of (i) a term which depends on the number of ways a bivalent ion may form a pair with a vacancy, and (ii) a term allowing for Coulomb interactions between bivalent ions and vacancies. The time \( (t_{1/2}) \) to reach \( p = 0.5 \) is \( 1/F_{wc_0} \), and using equation (2)

\[
F = \frac{2e^2}{ak} \frac{1}{\sigma T \cdot t_{1/2}}.
\]

Taking our measurements on NaCl at \( 1/T = 0.0027 \) where

\[
t_{1/2} = 3.2 \times 10^4 \text{s}
\]

and

\[
\sigma T = 7 \times 10^{-10} \Omega^{-1} \text{m}^{-1} \text{K}^{-1}
\]

we calculate \( F \) to be 0.6. A similar value is obtained for KCl : S\(^{2-}\). If the pair forms on nearest neighbour sites we believe the first term in \( F \) will be 24, in which case the second has a magnitude of 1/40.

10. Optical absorption. — We refer briefly to absorption and emission measurements to be reported fully elsewhere.

10.1 \( \alpha \) BAND. — The absorption, at liquid air temperature, in the vacuum ultraviolet of a pure KCl crystal and of a freshly quenched KCl crystal containing about \( 4.5 \times 10^{-5} \) mole fraction of S\(^{2-}\) ions is shown in figure 3. Subtraction gives a band with a peak at 172 nm which should be the band due to a localized exciton produced in the vicinity of an anion vacancy (\( \alpha \) band). It is usually assumed that there are two bands, \( \beta \) and \( \alpha \) bands, due to the perturbation of the exciton by an \( F \) centre or an ionized \( F \) centre (anion vacancy) respectively. The maximum in our absorption occurs at a wavelength midway between those of the \( \alpha \) and \( \beta \) bands given by Onaka and Fujita [12]. The situation is similar in NaF.

11. Emission spectra. — When bivalent anion doped crystals are heat-treated so as to produce pairing of the bivalent anions and vacancies, both the absorption and emission spectra change from those of the quenched crystals. With NaF : O\(^{2-}\) before pairing there is a single broad emission with a large Stokes shift. After pairing there are two emissions, one close to the exciting wavelength and another close to the \( F \) centre emission in pure NaF. In the S\(^{2-}\)-doped NaCl and KCl the isolated S\(^{2-}\) ion has a similar emission to the isolated O\(^{2-}\) in NaF. However on pairing the emission moves closer to the exciting radiation but no emission similar to that from an \( F \) centre appears, indicating that in the ground state the electron may be shared between the anion and the vacancy.

**DISCUSSION**

Comment. — R. J. Friauf.

Nelson and I have looked at ionic transport in NaCl at high temperatures (600-780 °C). By combining information from ionic conductivity, Na diffusion (our work) and Cl diffusion (other workers), we conclude that \( \Delta n_{an} \) is almost the same for both cation and anion vacancies. (Transport number \( t \approx 0.3 \), practically independent of temperature.) These results are quite different from yours, but there is a very long extrapolation over temperature.

Question. — P. W. M. Jacobs.

I have a brief comment and a question. Although the calculated value for the migration of anion vacancies communicated at Berlin was probably a little low, I think that the discrepancy between your values and those from diffusion and ion activity analysis requires some further consideration. Did you consider the possibility that the concentration of S\(^{2-}\) might be changing during your measurements?

Reply. — J. S. Dryden.

The agreement between the activation energies determined (i) from the isothermal decrease in conductivity and (ii) from the measurement of conductivity as a function of temperature makes it unlikely that there is any process affecting S\(^{2-}\)-concentration (other than pairing) which will invalidate our interpretation of the measurements. In our experiments on the conductivity as a function of temperature we change the sequence of temperatures. This does not change the electric conductivity/\( 1/T \) plot.
Comment. — P. VAROTSOS.

We have recently carried out ITC measurements in KCl doped with SO₂⁻. The prominent peak has a migration enthalpy between 1.05 eV and 1.1 eV and the entropy between 9 and 10 k. The smaller peak, which was very weak and close to the central peak, has an enthalpy close to 0.85 eV and an entropy to close to $4k \sim 3k$. The parameters of the central peak are close to the values of Professor Dryden. The others are close to that reported by F. Bénère for the free anion motion. But in any case we agree with Professor Dryden that the anion migration enthalpies obtained from our experiments are appreciably larger than those reported by Catlow et al. in the previous conference.

References