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Arrhenius law for self-diffusion and ionic conductivity in NaI

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Résumé. — Les coefficients de diffusion du cation et de l'anion ont été mesurés dans NaI en relation avec une étude détaillée de la conductivité.

Une forte courbure vers le haut des représentations d'Arrhenius a été observée à haute température (environ 30 degrés avant le point de fusion). L'analyse des résultats expérimentaux montre que la contribution des paires de lacunes à la diffusion est très faible. La courbure peut être expliquée en considérant les hypothèses récentes de Varotsos et Alexopoulos qui disent que les effets anharmoniques ont une forte influence sur les paramètres des défauts. Ils indiquent que les énergies de Gibbs pour la formation et la migration diminuent plus vite que linéairement.

Abstract. — The diffusion coefficient for the cation and anion motion have been measured in NaI in conjunction to a detailed measurement of the conductivity.

A strong upwards curvature of the Arrhenius plots have been found at high temperatures (i.e. about 30 degrees below the melting point). An analysis of the experimental data shows that the contribution of the vacancy pairs (to the diffusion process) is appreciably small. The curvature observed can be explained if one considers recent proposals by Varotsos and Alexopoulos that the anharmonic effects have a strong influence on the defect parameters. The later indicate that the Gibbs energies for the formation and migration processes decrease faster than linearly.

One of the most interesting facts during the past several years is the detection and the explanation of the deviation observed from the Arrhenius plots in alkali halides.

We have performed an exact measurement of : 1) the diffusion coefficient for the cation and anion motion (Fig. 1) and 2) the d.c. conductivity of NaI (Fig. 2). The results of these measurements showed that the Arrhenius law is well obeyed from low temperatures up to 630 °C (we remind that the melting point for NaI is 661 °C); about 30 °C below the melting point a strong upwards curvature appear in all the plots $\ln D^+$ vs. $1/T$, $\ln D^-$ vs. $1/T$ and $\ln(\sigma T)$ vs. $1/T$. The contribution of vacancy pairs to the diffusion process, was found to be negligible [1, 2] and the correlation factor was close to 0.78 [1].

This later value of correlation factor shows that the migration mechanism takes place mainly through monovacancies.

The experimental results of the linear parts of the plots $\ln D^+$ vs. $1/T$, $\ln D^-$ vs. $1/T$, in conjunction to the conductivity values of this region have been analysed in a similar way as indicated by Benièr

et al. [3]. The results are given in table I. In the same table we have inserted the experimental values obtained by Kostopoulos, Varotsos and Mourikis [4], by Wylde [5, 6], by Schmidt and Staude [26], and by Pershits and Veisman [24]. In the same table we have inserted the migration enthalpy for the cation motion of the bound vacancy, reported by Dryden and Heydon [25], and by Kostopoulos, Varotsos and Mourikis [27].

We see that our value [2] of h_{m+} is in fine agreement with the value 0.57 eV of Kostopoulos, Varotsos and Mourikis obtained by d.c. conductivity technique, but it is smaller than that of Schmidt and Staude, and Pershits and Veisman, and it is appreciably larger than that obtained by Wylde. Also our h_{m+} value is in fine agreement with the value 0.59 eV of Kostopoulos, Varotsos and Mourikis obtained by Ionic Thermocurrent (I.T.C.) measurements and is compatible with the value 0.54 eV obtained by Dryden and Heydon obtained by dielectric loss measurements.

Our h_s value is compatible with the value of Kostopoulos, Varotsos and Mourikis, and Wylde, but it is appreciably smaller than that obtained by Schmidt and Staude, and Pershits and Veisman.

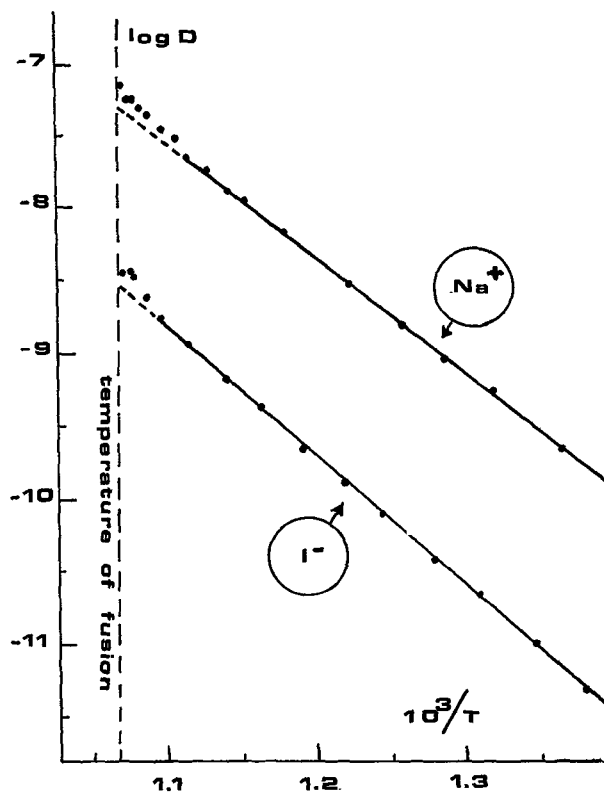


Fig. 1. — Temperature dependence on the self-diffusion coefficient of $^{22}\text{Na}^+$ (upper curve) and of $^{125}\text{I}^-$ (lower curve) in NaI pure single crystals. Full lines are the calculated values in the temperature range considered in the present study.

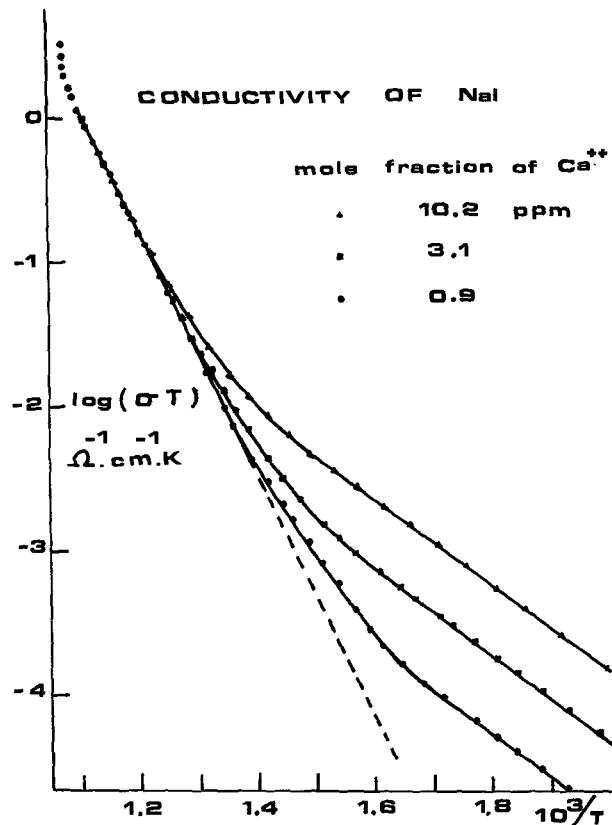


Fig. 2. — Temperature dependence of the ionic conductivity of pure and Ca^{++} doped NaI single crystals. Full lines are the calculated values in the temperature range considered in the present study.

Table I. — Entropy and enthalpy of formation and migration of vacancies in NaI. Comparison with other experimental results.

| | $\underline{s_s/k}$ | $\underline{h_s \text{ eV}}$ | $\underline{s_{m+}/k}$ | $\underline{h_{m+} \text{ eV}}$ | $\underline{s_{m-}/k}$ | $\underline{h_{m-} \text{ eV}}$ |
|--|---------------------|------------------------------|------------------------|---------------------------------|------------------------|---------------------------------|
| 1) Schmidt-Staude (1968) Ionic conductivity | | 1.58 | | 0.65 | | |
| 2) Pershitz-Veisman (1971) Ionic conductivity | | 1.46 | | 0.78 | | 1.35 |
| 3) Wylde (1972) Ionic conductivity | 15.05 | 2.27 | 1.28 | 0.47 | 12.6 | 1.55 |
| Cation diffusion | | | | | | |
| 4) Kostopoulos-Varotsos-Mourikis (1975) D.C. Technique conductivity | | 1.84 | | 0.57 | | |
| 5) Kostopoulos (Thesis) (1977) Ionic conductivity | 9.33 | 2.02 | 3.02 | 0.60 | 1.68 | 0.75 |
| Cation diffusion | | | | | | |
| Anion diffusion | | | | | | |
| 6) Dryden-Heydon (1978) Dielectric loss measurements | | | | 0.54 | | |
| 7) Kostopoulos-Varotsos-Mourikis Ionic thermocurrent (I.T.C.) | | | | 0.59 | | |
| 8) Benière-Kostopoulos-Reddy [2] The same as 5) after corrections | 7.64 | 2.00 | 3.23 | 0.58 | 2.91 | 0.77 |

As for our value h_{m-} it is much smaller than the values reported by Wylde, and Pershitz and Veisman. Possibly these large discrepancies are due to the fact that the last values are obtained only from conductivity measurements.

An important point arising from our results is that the cation migration enthalpy is appreciably lower than the anion's enthalpy : this large difference of h_{m+} and h_{m-} has not been observed in NaCl and KCl (see Table II).

Table II. — Entropy and enthalpy of formation and migration of vacancies in some alkali halides.

| Crystal | s_s/k | h_s eV | s_{m+}/k | h_{m+} eV | s_{m-}/k | h_{m-} eV |
|---------|---------|----------|------------|-------------|------------|-------------|
| NaCl | 9.8 | 2.44 | 1.64 | 0.69 | 1.38 | 0.77 |
| KCl | 8.99 | 2.54 | 2.40 | 0.73 | 3.20 | 0.85 |
| NaI | 7.64 | 2.00 | 3.23 | 0.58 | 2.91 | 0.77 |

A comparison of our experimental results with the recent theoretical values are given in table III. The experimental value of h_{m+} is close to that calculated by Catlow *et al.* [7] and by Varotsos and Alexopoulos [8] whereas our h_{m-} value is about 13% higher than that predicted by Catlow *et al.* [7].

Our formation entropy h_s is slightly lower than the theoretical value given by Catlow *et al.* [7]; also it is slightly lower the value 2.08 eV obtained from the recent formula :

$$h_{s0} = \frac{2}{\left. \frac{dB}{dP} \right|_{T=0}} \cdot B_0 \cdot \Omega_0 \quad (1)$$

proposed by Varotsos [9]. In eq. (1) B denotes the isothermal bulk modulus and Ω the mean volume per atom. The subscript 0 denotes the corresponding values at absolute zero.

In this relation we have used the following values [10, 11]

$$\left. \frac{dB}{dP} \right|_{T=0} = 5.58$$

$$B_0 = 0.18 \times 10^{12} \text{ erg/cm}^3$$

$$\Omega_0 = 33.147 \times 10^{-24} \text{ cm}^3$$

The formation entropy s_s is 7.64 k and it is slightly

lower than the corresponding values found in NaCl [12] and KCl [12] (see Table II).

When one applies the relation :

$$s_s = 3.2 s_f$$

(s_f is the fusion entropy) proposed by Benière [13], one finds 9.7 k .

Our value is close to the theoretical value of 8.64 k obtained from the relation :

$$s_s = -\frac{h_0}{B_0} \left(\beta B + \frac{\partial B}{\partial T} \right) \exp \int_0^T \beta dT \quad (2)$$

proposed by Varotsos and Alexopoulos [14] (β denotes the volume thermal expansion coefficient). In this relation we have used the following values [2, 11, 22] :

$$h_0 = 2.00 \text{ eV}$$

$$B_0 = 0.18 \times 10^{12} \text{ erg/cm}^3$$

$$\beta_{570K} = 1.7886 \times 10^{-4} \text{ grad}^{-1}$$

$$B_{570K} = 0.143 \times 10^{12} \text{ erg/cm}^3$$

$$\frac{\partial B}{\partial T} = 6.35 \times 10^7 \text{ erg/cm}^3 \cdot \text{grad}$$

$$\exp \int_0^T \beta dT = 1.1$$

For the cation migration entropy s_{m+} one gets the theoretical value 2.5 k which is comparable to the experimental value 3.23 k .

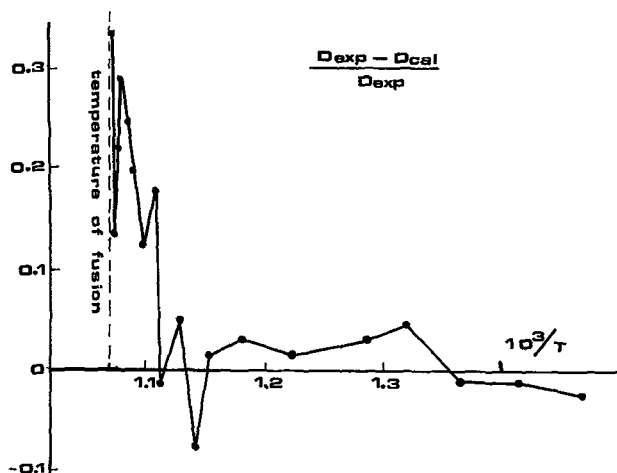


Fig. 3. — Deviation from the Arrhenius law for self-diffusion of cation.

Table III. — Entropy and enthalpy of formation and migration of the vacancies in NaI. Comparison with theoretical values.

| | s_s/k | h_s eV | s_{m+}/k | h_{m+} eV | s_{m-}/k | h_{m-} eV |
|---|---------|----------|------------|-------------|------------|-------------|
| 1) Benière (1975) | 9.7 | | | | | |
| 2) Catlow <i>et al.</i> (1977) | | 2.14 | | 0.57 | | 0.68 |
| 3) Varotsos-Alexopoulos (1977) | 8.64 | 2.08 | 2.5 | 0.59 | | |
| 4) Benière-Kostopoulos-Reddy [2] (experimental) | 7.64 | 2.00 | 3.23 | 0.58 | 2.91 | 0.77 |

We turn now our attention to the strong curvature observed in the diffusion and conductivity plots (see Figs. 3, 4 and 5). It is obvious that the vacancy pairs cannot explain the effect, due to the fact, that they do not contribute to the conductivity. Furthermore the strong curvature of conductivity plot cannot be explained by the contribution of free anion vacancies, because (as it is obtained from the diffusion study) the cation vacancies are appreciably more mobile than the anions [1, 2].

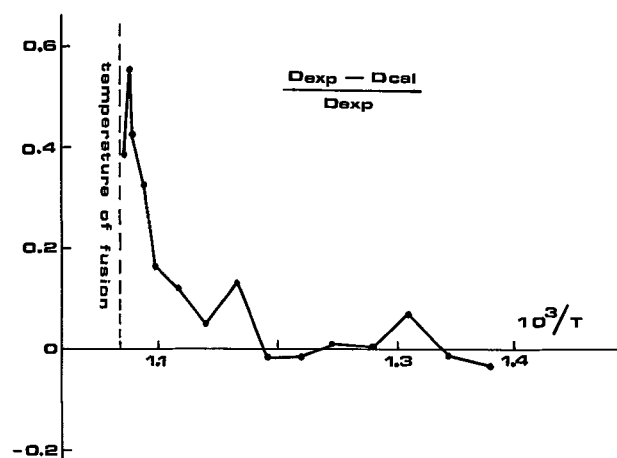


Fig. 4. — Deviation from the Arrhenius law for self-diffusion of anion.

Alternative suggestion for the explanation of these curvatures should be: the interstitialcy mechanism proposed by Catlow *et al.* [15], Frenkel defects [15], or trivacancies [17]. However it is very easy to see that these suggestions cannot explain the effect [18].

A plausible explanation of these curvatures can be reached by the proposals of Slifkin and Varotsos and Alexopoulos [14, 19] expressed in the previous conference. According to them, anharmonic effects play a very important role in the calculation of defects parameters, especially close to the melting point. According to their model, the formation and migration enthalpies and entropies increase significantly at temperatures close to the melting point. This increase

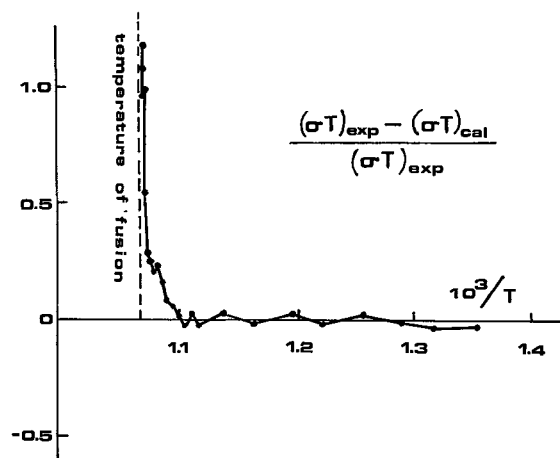


Fig. 5. — Deviation from the Arrhenius law for conductivity.

implies a decrease of the Gibbs formation energy g_s and the Gibbs cation migration energy g_{m+} , faster than linearly. Obviously this strong decrease of the Gibbs energies, leads to an upwards curvature of both, the diffusion and conductivity plots.

Varotsos and Alexopoulos [19] have indicated that even if the bulk modulus of an alkali halide crystal decrease linearly with the temperature, then the expansivity could create a deviation of the conductivity plots, from the linearity, about 12%. However the bulk modulus of alkali halides at temperatures close to the melting point are expected to decrease faster than linearly [20]. Then the formation Gibbs energy shows an excessive decrease which can finally lead to the simultaneous upward curvature of the three plots: $\ln D^+$ vs. $1/T$, $\ln D^-$ vs. $1/T$ and $\ln(\sigma T)$ vs. $1/T$. As an example, Varotsos and Alexopoulos [19] have indicated that a decrease of the bulk modulus by 5% (from its linear extrapolation) gives a deviation (from the linearity) of about 215% in the diffusion and conductivity plots in alkali halides.

The explanation of our results in the frame of the anharmonic effects proposed as above, is further strengthened by the fact that this model [21] have already quantitatively explained the strong curvature observed in silver halides where the elastic constants have been measured up to melting point.

DISCUSSION

Question. — A. S. NOWICK.

Why should these anharmonic effects occur only in certain crystals? There certainly are numerous examples of physical property measurements right up to the melting point which indicate no such deviations. Furthermore, on thermodynamic grounds, there is no reason for a solid to anticipate the melting phenomenon.

Reply. — D. KOSTOPOULOS.

I agree that from thermodynamics there is no reason for a solid to anticipate the melting phenomenon; but in some solids, as measurements show [21], the elastic constants fall faster than linearly at temperatures close to the melting point.

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