Self-Diffusion, Conductivity and Transport Numbers in Alkali Halide Single Crystals *

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The self-diffusion coefficients of the anions and cations have been measured in pure and doped NaCl and KCl crystals, together with the ionic conductivity. The experimental results give evidence for migration mechanisms via free cation and anion vacancies and vacancy pairs. Analysis of the complete set of diffusion data leads to the determination of the entropy and enthalpy of formation and migration of these defects.

In a second part, the diffusion coefficients via free vacancies are compared with the conductivity data in order to investigate the validity of the Nernst-Einstein relation. This relation is found to be verified within 2%, in NaCl as well as in KCl, no appreciable correlation effect being detected.

I. Introduction

In a theoretical description of the point defects in ionic crystals such as NaCl and KCl, it is generally assumed that the predominating defects responsible for the transport processes are of Schottky type [1], with a possible contribution of associated defects: vacancy pairs [2] and aliovalent-impurity-vacancy-pairs [3].

Evidence for Schottky defects in NaCl has been given by the experimental verification [4] of the existence of a solubility product relation between the mole fractions (x_+ and x_-) of positive and negative vacancies, as follows from thermodynamic calculations expressed by LIDIARD [3]. Furthermore, a contribution of vacancy pairs to the diffusion of the anions has been shown by LAURANCE [5] and other workers [4, 6–9], while the influence of vacancy-impurity-pairs has been extensively studied in a number of works [10].

Adopting this description, the purpose of this study is (a) to get measurements as accurate as possible of all transport properties in single crystals of NaCl and KCl, (b) to obtain reliable values for the thermodynamic parameters involved in the formation and migration of each defect, and (c) to compare the diffusion (D^*) and conductivity (σ) data in order to examine the validity of the Nernst-Einstein relation.

II. Survey of Requirements in Experimental Procedure

1. *High Accuracy in Both Diffusion and Conductivity Measurements*

Comparison of earlier data given by different workers for these systems shows [4] a rather large scatter which makes impossible any thorough investigation of the Nernst-Einstein relation with the object of making a reliable evaluation of correlation effects. The experimental methods we have recently developed [11] have allowed us to measure the tracer-diffusion coefficients with an accuracy of 1%, which is comparable to that obtained in the conductivity measurements.

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[*] This paper is published both in Z. Naturforsch. and in the Proceedings of the Marstrand Conference on Atomic Transport in Solids and Liquids, Verlag der Zeitschrift für Naturforschung, Tübingen 1971.

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[11] F. BENIERE, M. BENIERE, and M. CHEMLA, J. Phys. Chem. Solids **31,** 1205 [1970].

2. *Influence of Temperature*

Great care must be taken in measuring temperature, since an error of 1 °C would lead to an error of about 3% upon the conductivity and diffusion coefficients. In our experiments, temperature is stabilized within 0.05 °C with electronic regulators. Moreover, for a better comparison of the values of D^* and σ, we have performed all the measurements in the same apparatus and under the same conditions of temperature control (same quartz vessel, thermocouple and regulator), which insures no deviation of this parameter higher than 0.1 °C between the different kinds of experiments.

3. *Quality of the Doped Crystals*

When prepared by crystal growth methods, the doped crystals contain concentration gradients of the added impurity, the concentration of which is somewhat uncertain. On the contrary, our method of doping by diffusion[12] allows us to achieve complete homogeneity of the doped crystals and does not alter the structural quality of the initially pure single crystals (Harshaw). Moreover, a small amount of radioisotope (^{90}Sr and ^{45}Ca respectively for the $\text{Sr}^{\times\times}$ and $\text{Ca}^{\times\times}$ doped crystals) is added to the dopant in a known ratio. Specific activity of the radio-indicator then gives the doping agent concentration at each point of the crystal and with a high accuracy, even for low concentrations, while activity of the diffusing tracer leads to the determination of the diffusion coefficient (Fig. 1).

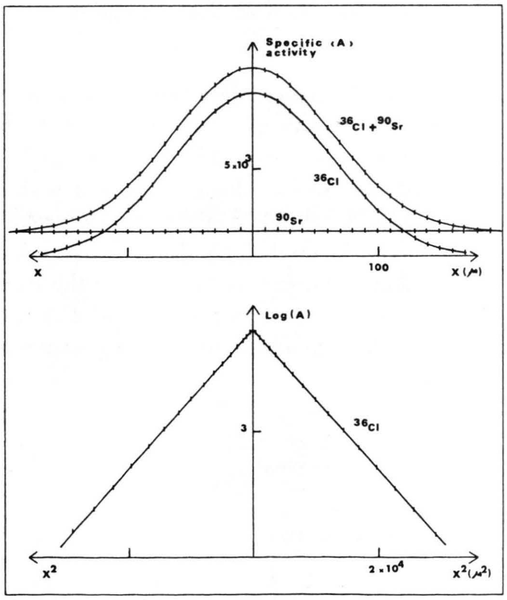

Fig. 1. Diffusion profile of ^{36}Cl in SrCl_2-doped NaCl ($C=65\times10^{-6}$, $\theta=709{,}1$ °C, $t=69\,000$ s).

4. *Interpretation of Data*

Direct comparison between D^* and σ is possible only if both self-diffusion and conductivity occur by the same mechanism. The existence of other mechanisms will lead to departures from the Nernst-Einstein relation, e. g., occurence of electronic conductivity or diffusion via associated vacancies. Concerning alkali halides, one has to consider the influence of the free cation and anion vacancies and the associated defects: cation vacancy + anion vacancy (vacancy pair) and cation vacancy + bivalent cation (complex). Only free vacancy contributions to self-diffusion and conductivity can be compared by the use of the Einstein relation.

III. Experimental Results

The experimental measurements have been reported earlier[8, 11, 13] and resulted in the determination of

- Na^+ and K^+ self-diffusion coefficients in NaCl and KCl in the intrinsic range;
- Cl^- self-diffusion coefficients in NaCl and KCl pure crystals;
- Na^+ self-diffusion coefficients in the extrinsic range of high purity crystals and in Sr^{++}-doped crystals (mole fraction $C=27\times10^{-6}$);
- K^+ self-diffusion coefficients in $\text{Sr}^{++}-\text{KCl}$ doped crystals ($C=61\times10^{-6}$);
- Cl^- self-diffusion coefficients in $\text{Sr}^{++}-\text{NaCl}$ doped crystals ($C=27$; 65 and 360×10^{-6});
- Cl^- self-diffusion in $\text{Sr}^{++}-\text{KCl}$ doped crystals ($C=61\times10^{-6}$);
- Conductivity of all above crystals and in $\text{Ca}^{++}-\text{NaCl}$ doped crystals ($C=38\times10^{-6}$) in both intrinsic and extrinsic ranges;
- Transport numbers in NaCl pure crystals.

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[12] F. Beniere and M. Chemla, C. R. Acad. Sci. Paris C **266**, 660 [1968].

[13] F. Beniere, M. Beniere, and M. Chemla, C. R. Acad. Sci. Paris C **267**, 633 [1968].

Figs. 2 and 3 show the temperature and impurity content dependence of the self-diffusion coefficients in NaCl and KCl, respectively.

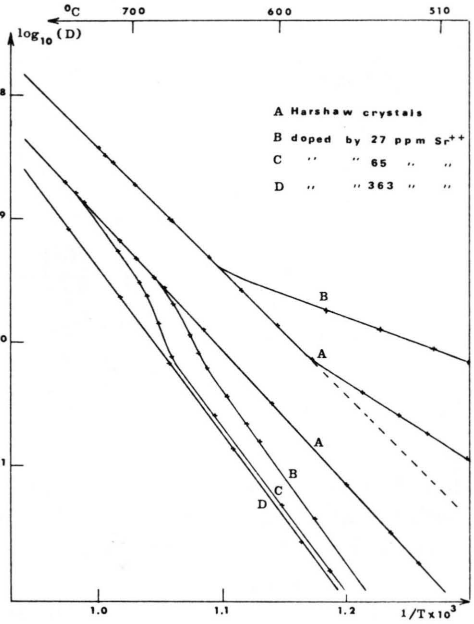

Fig. 2. Temperature dependence of the self-diffusion coefficients of Na^+ and Cl^- in pure and doped NaCl.

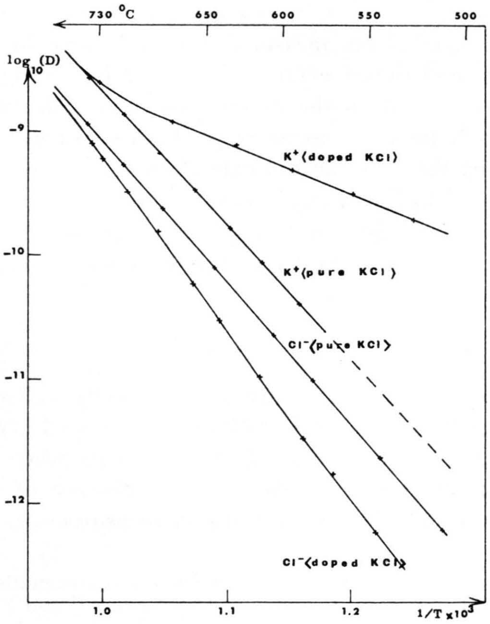

Fig. 3. Temperature dependence of the self-diffusion coefficients of K^+ and Cl^- in pure and doped KCl (61×10^{-6} Sr^{++}).

IV. Calculation of Defect Parameters in NaCl and KCl

1. General Outlines

Extrinsic Range

In the extrinsic range the predominating defects are the cation vacancies introduced by aliovalent ions. In the case of high purity crystals, the Nernst-Einstein relation is not verified (Fig. 4). It is supposed that, among the background impurities, highly associative ions give complexes which contribute to cation diffusion.

However, for lightly doped crystals ($C = 10^{-5}$ to 10^{-4}), when the concentration of added ions is much larger than the background impurity content but sufficiently low to obtain a negligible degree of association, then cation diffusion and conductivity occur with the same activation energy, which is identical for Sr^{++}- and Ca^{++}-doped crystals. Then the simple equality holds:

$$x_+ \approx C \tag{1}$$

x_+ being the mole fraction of cation vacancies.

The equations for the cation diffusion coefficient ($D_2{}^+$) and conductivity ($\sigma_2{}^+$) can be written as:

$$D_2{}^+ = 4\,a^2\,f\,\nu_0\,C\,\exp\left(\frac{S_m{}^+}{k}\right)\exp\left(-\frac{H_m{}^+}{k\,T}\right), \tag{2}$$

$$\sigma_2{}^+\,T = \frac{N\,e^2}{k}\,4\,a^2\,\nu_0\,C\,\exp\left(\frac{S_m{}^+}{k}\right)\exp\left(-\frac{H_m{}^+}{k\,T}\right) \tag{3}$$

where f is the expected correlation factor ($f = 0.78$)[14], a the anion-cation separation distance, ν_0 the vibrational frequency, generally assumed equal to the Debye frequency, and $S_m{}^+$ and $H_m{}^+$ the entropy and enthalpy of motion of the cation.

In this range of temperature and impurity content, the contributions of free anion vacancies and of vacancy pairs to D^* and σ are negligible. Actually, the activation energy is found to be the same for both conductivity and cation diffusion, which will allow a reliable determination of $H_m{}^+$ and $S_m{}^+$.

Intrinsic Range

In the intrinsic range, one has to account for the simultaneous participations of cation free vacancies, anion free vacancies and vacancy pairs. Both cation and anion free vacancies give contributions to the electrical conductivity, while both anion or cation free vacancies and vacancy pairs contribute to self-diffusion of each ion.

The contribution of vacancy pairs to anion self-diffusion, denoted by D_p^-, may be deduced from measurements of the anion diffusion coefficient in doped crystals. The contribution of the pairs to the cation self-diffusion, D_p^+, may be different from D_p^- if the individual frequencies of the cation and anion jumps into the pair are not equal. We shall be mostly interested in the ratio $D_p^-/(D^+ + D^-)$, which, to give an order of magnitude, is equal to 0.05 at 650 °C in NaCl. The term D_p^+ could be calculated from D_p^- making use of the calculation of the jump frequencies of THARMALINGAM and LIDIARD[15] connected with the corresponding theoretical correlation factors[14, 16]; this would give

$$D_p^+/(D^+ + D^-) \approx 0.03 .$$

Examination of the experimental transference number

$$t^+ = (D^+ - D_p^+)/(D^+ + D^-) - (D_p^+ + D_p^-)$$

shows that the ratios

$$D_p^-/(D^+ + D^-) \quad \text{and} \quad D_p^+/(D^+ + D^-)$$

are small in the temperature range we are interested in ($\approx 600 - 700$ °C), and, of same order of magnitude. So, in the following, D_p^+ and D_p^- will be taken to be equal, this assumption entailing no noticeable effect upon the determination of the free vacancy diffusion coefficients **.

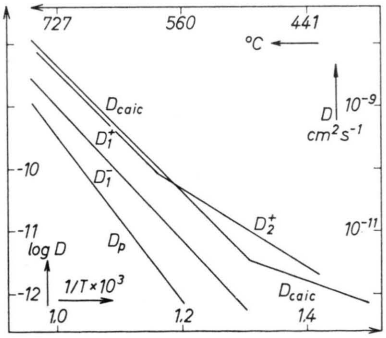

Fig. 4. Comparison of the tracer-diffusion coefficients (D_1^+ and D_2^+: diffusion coefficients of Na$^+$ in the intrinsic and extrinsic ranges, respectively; D_1^-: diffusion coefficient of Cl$^-$; D_p: contribution of the vacancy pairs to self-diffusion) to the self-diffusion coefficient calculated from the conductivity measurements making use of the Nernst-Einstein relation (D_{calc}).

At high temperature and for pure crystals, the measured self-diffusion coefficients of the cation (D_1^+) and anion (D_1^-) and electrical conductivity (σ_1) may then be represented by the following equations:

$$D_1^+ = 4\, a^2 f \nu_0 \exp\left\{\frac{S_d/2 + S_m^+}{k}\right\} \exp\left\{-\frac{H_d/2 + H_m^+}{k\,T}\right\} + D_{0p} \exp\left\{-\frac{H_p}{k\,T}\right\}, \tag{4}$$

$$D_1^- = 4\, a^2 f \nu_0 \exp\left\{\frac{S_d/2 + S_m^-}{k}\right\} \exp\left\{-\frac{H_d/2 + H_m^-}{k\,T}\right\} + D_{0p} \exp\left\{-\frac{H_p}{k\,T}\right\}, \tag{5}$$

$$\sigma_1 T = \frac{N e^2}{k}\, 4\, a^2 \nu_0 \exp\left\{-\frac{H_d - T S_d}{2\,k\,T}\right\} \cdot \left[\exp\left\{-\frac{H_m^+ - T S_m^+}{k\,T}\right\} + \exp\left\{-\frac{H_m^- - T S_m^-}{k\,T}\right\}\right]. \tag{6}$$

where S_d and H_d are the entropy and enthalpy of Schottky defect formation, S_m^- and H_m^- the entropy and enthalpy of anion migration, and D_{0p} and H_p the composite constants of diffusion by vacancy pairs. We give now a method of calculation of the involved thermodynamic parameters from the whole body of diffusion data.

2. *Fitting Method*

We calculate the following parameters S_d, H_d, S_m^+, H_m^+, S_m^-, H_m^-, D_{0p} and H_p, from the diffusion coefficients measured for both ions in both pure and doped crystals. The iterative fitting method consists in the decomposition of calculations in individual successive steps. Each step consists of fitting the experimental data Y by the least-squares method to linear expressions of the form $A\,X + B$, X being the inverse of absolute temperature and A and B being respectively proportional to enthalpy and entropy terms.

a) S_m^+ *and* H_m^+

These parameters are more directly calculated from the values of D_2^+ obtained in doped crystals of accurately known impurity contents when conductivity measurements show the absence of complexes and agree with diffusion measurements (the

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[15] K. THARMALINGAM and A. B. LIDIARD, Phil. Mag. **6**, 1157 [1961].

[16] R. E. HOWARD, Phys. Rev. **144**, 650 [1966].

** It must be mentioned that results of electromigration experiments carried out in NaCl by NELSON[17] and FRIAUF do not agree with this assumption, the discrepancy between the two sets of results being unexplained.

[17] V. N. NELSON, Thesis, University of Kansas, Lawrence 1967.

same entropy and activation energy independent of the nature of the doping agent, i. e. Sr^{++} or Ca^{++}).

b) S_d *and* H_d

During the first iterative cycle D_p is neglected in the expression of D_1^+ and comparison of D_1^+ and D_2^+ gives an approximate value for S_d and H_d.

c) S_m^- *and* H_m^-

In the general case of a crystal containing a molar fraction C of divalent cations, the concentration of anion free vacancies is equal to:

$$x_- = \tfrac{1}{2}\left[-C+\sqrt{C^2+4\exp\{-G_d/kT\}}\right]$$

and the anion self-diffusion coefficient D^- is equal to:

$$D^- = 2a^2 f \nu_0 \exp\left\{\frac{S_m^-}{k}\right\} \exp\left\{-\frac{H_m^-}{kT}\right\} \cdot \left[-C+\sqrt{C^2+4\exp\{-G_d/kT\}}\right] + D_{0p}\exp\left\{-\frac{H_p}{kT}\right\}. \qquad (7)$$

This relation shows that the difference between the coefficients D^- and D'^-, obtained in crystals of contents C and C', respectively, does not depend of D_p. Substituting the above S_d and H_d values into the expression $(D^- - D'^-)$, one gets an approximate determination of S_m^- and H_m^-.

d) D_{0p} *and* H_p

These values are then deduced from (7) where S_d, H_d, S_m^- and H_m^- are substituted by the preceding values.

The value of D_p obtained in this way is then introduced into Eq. (4). Then, a new comparison of (2) and (4) (repeated step b) leads to slightly modified values for S_d and H_d, which are in turn introduced into (7). This process is repeated until changes in the parameters become less than 10^{-3}, which occurs after about five iterations.

3. Thermodynamical Parameters for Diffusion in NaCl and KCl

The entropy and enthalpy of formation and motion of defects and the parameters of diffusion by vacancy pairs are shown in Tables 1 and 2.

It is to be noticed that the migration entropies reported in this table are calculated according to the usual, but rather arbitrary expression of the frequency jump, where ν_0 is supposed to be equal to the Debye frequency. This has been done in order to obtain values comparable with those in the literature. However, the reliable quantity is obviously the original experimental product $\nu_0 \exp\{S_m/k\}$.

Table 1. Entropy parameters for self-diffusion in NaCl and KCl.

	$S_d/2k$	S_m^+/k	S_m^-/k	D_{0p} (cm²/s)
NaCl	5.55	2.07	2.27	5200
KCl	5.45	2.94	2.47	990

Table 2. Enthalpy parameters for self-diffusion in NaCl and KCl (in eV).

	$H_d/2$	H_m^+	H_m^-	H_p
NaCl	1.25	0.72	0.86	2.63
KCl	1.32	0.79	0.85	2.49

V. Discussion

1. Comparison of Experimental and Theoretical Thermodynamical Parameters

Table 3 collects the present determinations of H_d in NaCl and KCl and the recent values of the same parameter obtained in KCl by FULLER et al. [7] and in KBr by BARR and DAWSON [9].

Table 3. Comparison of experimental and theoretical values of H_d.

	NaCl	KCl	KCl Ref. [10]	KBr Ref. [11]
H_d exper. (eV)	2.50	2.64	2.60	2.54
H_d theor. (eV) (Ref. [18])	1.84	2.05	2.05	1.92
H_d theor. (eV) (Ref. [19])	2.23	2.34	2.34	2.25

One may observe from this table that the classical vacancy model was leading to values for the defect formation energy (BOSWARVA and LIDIARD's values [18]) which were systematically about 30% lower than the experimental determinations. However, in a quite recent development, FAUX and LIDIARD [19] have calculated new values which are in better agreement with experiment.

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[18] L. M. BOSWARVA and A. B. LIDIARD, Phil. Mag. **16**, 805 [1967].

[19] I. D. FAUX and A. B. LIDIARD, this conference.

Tables 4 and 5 show the experimental values of H_m^+ and H_m^- compared to the theoretical calculations of Tosi and Doyama [20].

Table 4. Comparison of experimental and theoretical values of H_m^+.

	NaCl	KCl	KCl (Ref. [7])
H_m^+ exper. (eV)	0.72	0.79	0.79
H_m theor. (eV)	0.85	0.85	0.85

Table 5. Comparison of experimental and theoretical values of H_m^-.

	NaCl	KCl	KCl (Ref. [7])	KBr (Ref. [9])
H_m^- exper. (eV)	0.86	0.85	0.82	0.83
H_m^- theor. (eV)	0.90	0.83	0.83	

The main feature of the comparison between experimental values of H_m^+ and H_m^- is that the migration enthalpy is in all crystals higher for the anion than for the cation, which does not appear in the theoretical values. In this connection it is relevant also to mention the migration enthalpies of monovalent impurity ions of the same kind, e. g., halide ions in AgCl [21] and alkali ions in NaCl [22] where no noticeable influence of the ion size on the migration enthalpy has been found, while the theoretical calculations give far higher values when ionic radius of the diffusing impurity is let to increase [20].

2. *Comparison of Diffusion Coefficients with Transport Numbers*

The early measurements of Tubandt [23] gave erroneously high cation transference numbers in alkali halides, which has often led to neglect of the anion contribution to ionic conductivity, while our measurements of self-diffusion coefficients give a ratio of about 1/4 for the respective mobilities of anions and cations at 650 °C. We have then performed new measurements of the transport numbers in NaCl by a method using single crystals without use of $BaCl_2$ "protective electrolytes" [11]. The accuracy obtained (3%) is rather poor compared to the D^* measurements but the results agree within a few percent with the ratio of the ionic mobilities deduced from diffusion, excluding the contributions of pairs, as is shown in Table 6. This agreement shows that the assumption $D_p^+ \approx D_p^-$ is verified within the limits of error.

Table 6. Transport number of Na^+ in NaCl compared with the ratio of the diffusion coefficient of the anions and cations via free vacancies.

Temperature (°C)	580	600	650
t^+ meas.	0.81 ± 0.03	0.83 ± 0.03	0.84 ± 0.03
t^+ calc.	$0.84_5 \pm 0.01$	0.84 ± 0.01	$0.82_5 \pm 0.01$

3. *Nernst-Einstein Relation*

Let D^* denote the self-diffusion coefficient measured with tracers, and D_σ the self-diffusion coefficient calculated from the conductivity measurements, defined as:

$$D_\sigma = \sigma (k T / N e^2) .$$

In the extrinsic range, D^* will be taken as equal to the cation diffusion coefficient, while in the intrinsic range, it will be the sum of the diffusion coefficients of the anions and cations, via free vacancies only.

a) Extrinsic Range

Comparison of cation diffusion and conductivity data may directly be studied only when formation of complexes is negligible, i. e. in doped crystals of a Sr^{++} or Ca^{++} content higher than the background impurity concentrations and in the range of linear variation of σ with C. We have carried out measurements in NaCl crystals doped by 27 ppm and in KCl doped by 61 ppm Sr^{++}, where D^* and D_σ can be compared. A small correction for the isotope effects due to the use of ^{22}Na and ^{42}K tracers has been made.

For both NaCl and KCl crystals the ratio D^*/D_σ is nearly equal to 1 within the experimental range of errors. In other words, the Nernst-Einstein relation is verified, without involving noticeable correlation effects in the extrinsic range of NaCl and KCl. A more crucial test of the theory may be obtained from a similar study of the intrinsic range, where only the thermodynamically created defects have to be considered.

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[20] M. P. Tosi and M. Doyama, Phys. Rev. **151**, 642 [1966].

[21] A. P. Batra and L. Slifkin, J. Phys. Chem. Solids **30**, 1315 [1969].

[22] F. Beniere, M. Beniere, and M. Chemla, J. Chim. Phys. **66**, 898 [1969].

[23] C. Tubandt, H. Reinhold, and G. Liebold, Z. Anorg. Allg. Chem. **197**, 225 [1931].

b) Intrinsic Range

Direct examination of the ratio $(D_1^+ + D_1^-)/D_\sigma$ gives values which are temperature dependent and slightly higher than 1. The obvious reason of this small discrepancy is the influence of pairs in Eqs. (4) and (5). The contribution of pairs has been independently determined from the anion diffusion data and so it is possible to compare the influence of free vacancies only. D^* is then given by the expression:

$$D^* = D_1^+ + D_1^- - 2\,D_\mathrm{p}\,.$$

A detailed account of the experimental data has been reported earlier[8, 11] and we shall give here only the mean ratio D^*/D_σ for both NaCl and KCl in the intrinsic range, corrected for the isotope effects.

	NaCl	KCl
D^*/D_σ	1.02 ± 0.02	$0.98_5 \pm 0.02$

It is interesting to note that the temperature dependence of the ratio D^*/D_σ is lower than 2% in the temperature ranges 600 – 720 °C for NaCl and 610 – 710 °C for KCl, where the above mean values have been obtained, showing the good agreement between diffusion and conductivity data.

VI. General Conclusion

One must bear in mind the way in which the preceding results were obtained. It has been essentially the determination of a body of experimental data, which has been treated according to the models usually accepted for describing the transport processes in ionic crystals, i. e. diffusion by free vacancies and diffusion by vacancy pairs. The major result of this treatment is that the ratio D^*/D_σ is nearly equal to unity. However, when applied to the localized vacancy diffusion mechanism, the correlation theory implies a factor equal to 0.78 for the considered structure (NaCl), which is the result of mathematically perfect calculations[14, 24]. It is obvious that our results do not by any means affect the correlation theory. At present, this discrepancy remains an open question and we are restricted to only suggesting some hypotheses:

a) The present analysis of data contains for instance the assumption that the vacancy pairs give contributions to both diffusion of the anion and diffusion of the cation relative to the total diffusion coefficient which are of the same order of magnitude. This has been suggested by the theoretical calculations of the jump frequencies of THARMALINGAM and LIDIARD[15] and by transport number measurements. However, if these determinations of the jump frequencies and transport numbers were somewhat in error, this would require a new estimation of the diffusion coefficient of the cation via vacancy pairs, which could then lead to observe the correlation factor in the final ratio[25] D^*/D_σ.

b) The transport processes in the alkali halides considered have been interpreted according to the classical model of diffusion via vacancies and vacancy pairs. Any other diffusion mechanism, such as diffusion via dislocations, associated defects etc., which would add a greater contribution to the tracer diffusion coefficients than to the ionic conductivity, could also be a possible explanation of the discrepancy.

c) Finally, one could conceive that the vacancy is not so much localized as usually represented, as for example, in the model of NACHTRIEB and HANDLER[26].

Diffusion by delocalized defects would then lead to smaller correlation effects than those involved in the vacancy classical model. Existence of such a delocalized vacancy could thus also be a possible explanation.

New investigations, both experimental and theoretical, seem to be necessary in order to throw more light on the elementary transport processes in NaCl and KCl.

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[24] A. B. LE CLAIRE and A. B. LIDIARD, Phil. Mag. **1**, 518 [1956].

[25] A. B. LIDIARD, private communication.

[26] N. NACHTRIEB and G. HANDLER, Acta Met. **2**, 797 [1954].