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IONIC TRANSPORT PARAMETERS OF ALKALI HALIDES

I. NaCl

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The present study discusses the known facts about ionic transport parameters for NaCl, as they are described in literature. Data on enthalpy and entropy of the individual processes, obtained both experimentally and theoretically are listed at the end of the study in tables.

CONTENTS

LIST OF PRINCIPAL SYMBOLS

M, X	Cations and anions of the host lattice
□	Vacancy
1, 2	Single positive and negative excess charge (subscripts)
G, H, S ...	Increment of the Gibbs free energy, enthalpy and entropy
f	Subscript relating to the formation of the Schottky defects
m	Subscript relating to the migration of single defects
a	Subscript relating to the association impurity-vacancy
ma	Subscript relating to the migration of associates

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d	Subscript relating to the reorientation of the defect dipoles
s	Subscript relating to the segregation of the unassociated defects
n	Concentration of the charge carriers
e	Electronic charge
N	Numbers of cation (or anion) sites in cm^3
k	The Boltzmann constant
w	Jump probability
x	Molar fraction of incorporated defects
ITC	Ionic thermo-current, depolarization current upon linear heating
D	Diffusion coefficient
D_0	Pre-exponential factor for diffusion
E	Experimental activation enthalpy for diffusion
t_M, t_X	Transport numbers for cations and anions
σ	Conductivity
μ	Mobility
τ	Relaxation time
Δ_e, Δ_m	Electrical and mechanical relaxation
nnn	Next—nearest neighbour
δ	Loss angle
a	Lattice parameter
ε	Dielectric constant
f	Frequency factor

1. Introduction

The dominating defects in crystals of alkali halides are the Schottky defects (positive and negative ion vacancies). Their movement controls the transport of matter in crystals. At least six parameters are required for an adequate description of the transport enthalpy and entropy associated with the formation of the Schottky defects, with the motion of positive and negative ion vacancies. Moreover, for diffusion experiments also parameters of vacancy pair diffusion are required and for conductivity experiments the parameters of association between aliovalent impurities and vacancies.

Data on these parameters as obtained by various authors differ, the interval of the dispersion of data being sometimes quite wide. The reasons for these discrepancies can vary and their discussion for NaCl is included in the presented study. The other alkali halides, together with Ag and Cs halides and alkali earth halides will be dealt with in the following paper.

2. Ionic conductivity

Measurement of ionic conductivity σ as a function of temperature is an important method for the study of ionic process in alkali halide crystals. The general course of log σT vs $1/T$ of graphs is presented in Fig. 1 from experimental data for various crystals of alkali halides, including NaCl. Different slopes observed in conductivity graphs log σT vs $1/T$, I, II, III, etc. are connected with physical processes, determining n and μ. They latter are mutually dependent according to the equation

$$\sigma = n \, . \, e \, . \, \mu , \tag{1}$$

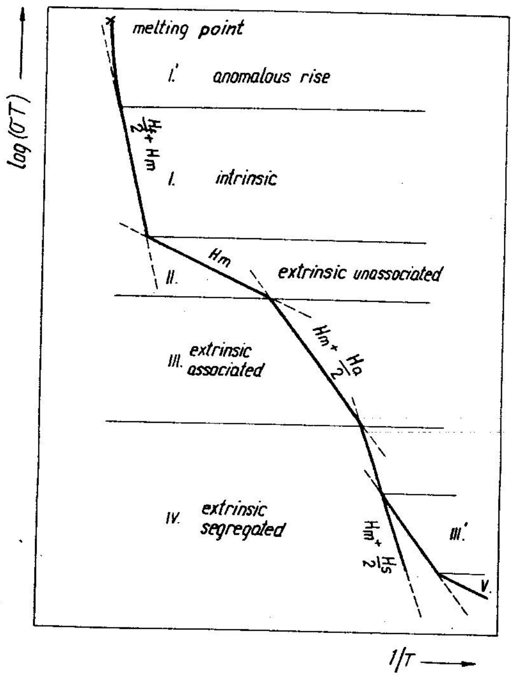

Fig. 1. Schematic conductivity — temperature plot for ionic crystals.

where n is the concentration of charge carriers, μ is their mobility and e is the electronic charge.

2.1. Intrinsic conductivity

Intrinsic conductivity I is determined by the concentration of thermally produced Schottky defects. The slope of this region is the sum of one half of the enthalpy of the formation of the Schottky defect and the migration enthalpy of Na ion vacancy ($H_m + H_f/2$) (Fig. 1, 2). For NaCl it is equal to 1.86 ±0.03 eV (Tab. 2).

At high temperatures (~750 °C), near the melting point, a break in the conductivity graph in the upward direction can be observed — region I'

Table 1

Ionic radii [Å]

Ion	r	Ion	r	Ion	r
H^-	2.08	Li^+	0.60	Be^{2+}	0.31
F^-	1.36	Na^+	0.95	Mg^{2+}	0.65
Cl^-	1.81	K^+	1.33	Ca^{2+}	0.99
Br^-	1.95	Rb^+	1.48	Sr^{2+}	1.13
J^-	2.16	Cs^+	1.69	Ba^{2+}	1.35
		Cu^+	0.96	Zn^{2+}	7.74
O^{2-}	1.40	Ag^+	1.26	Cd^{2+}	0.97
S^{2-}	1.84	Au^+	1.37	Hg^{2+}	1.10
Se^{2-}	1.98	Tl^+	1.44	Pb^{2+}	1.21
Te^{2-}	2.21			Sm^{2+}	1.8 (2.0)
				Mn^{2+}	0.80
				Fe^{2+}	0.75
				Co^{2+}	0.72
				Ni^{2+}	0.69

(Fig. 1, 2). This increase is usually ascribed to the additional movement of the anion. Conductivities produced by cation and anion vacancies are additive. Therefore the total conductivity σ_T will be

$$\sigma_T = n_1 e \mu_1 + n_2 e \mu_2, \tag{1a}$$

where the indices 1 and 2 belong to the cation or the anion. Since in the intrinsic region $n_1 = n_2$, by using the equation

$$\sigma = ne\mu = \frac{Ne^2}{kT} D = \frac{Ne^2 a^2 \nu_0}{kT} \exp\left(-E/kT\right) \tag{2}$$

we obtain

$$\sigma_T = \frac{Ne^2}{kT} (D_1 + D_2). \tag{3}$$

By means of the data for D_{Na} [1] and D_{Cl} [2], the curve of intrinsic conductivity can be reconstructed (Fig. 3). By separating the anion contrubution from the cation motion, we obtain the activation enthalpy of the anion 2.70

Table 2

Intrinsic defects

□1 – positive vacancy; □2 – negative vacancy

Crystal	Defects	H_f [eV]	S_f/k [eV/grad]	H_{m_1} [eV]	S_{m_1}/k [eV/gr]	H_{m_2} [eV]	S_{m_2}/k [eV/gr]
NaCl	□1, □2	2.34[1]) 2.12[2]) 2.38[3]) 1.30–2.20[8]), [19]) 2.18[9]), [10]) 2.07[11])	6.2[4]) 6[10]), [17])	0.75[1]), [5]) 0.80[2]) 0.65[3]) 0.85[6]) 0.66–0.76[9]), [10]), [13]) 0.30[12]) 0.70–0.92[12]), [14]) 0.76[18])	3.1[4]) 2.64[10]), [17])	0.86[7]) 0.9–1.1[3]) 0.72[12]) 0.75–1.00[12]), [14])	1.5–4.4[15]), [16])

[1]) [41] σ

[2]) [70] σ

[3]) [38] D, σ

[4]) [11] σ; $\nu_{Deb} = 5.9 \times 10^{12}\, s^{-1}$

[5]) [71] σ

[6]) [33] σ

[7]) calculated from [4], D with $H = 2.12$ eV

[8]) [19, 65, 72, 73–75], theoretical value

[9]) [14, 17] σ

[10]) [3] σ

[11]) [10] σ, anion conductivity using [2]

[12]) [76], theoretical value

[13]) [8] σ

[14]) [77], theoretical value

[15]) [2] D

[16]) [4] D

[17]) [78] σ

[18]) [79] σ

[19]) [80], theoretical value

±0.20 eV, which is in good agreement with the enthalpies for the anion diffusion 2.12–2.70 [2, 4, 5] obtained from diffusion studies.

It appears that the anion contribution is structurally sensitive: annealing at a high temperature for a longer time (700 °C, 24 hours) reduces the mentioned increase, so that at higher temperatures the cation motion is dominant. Tests were made in order to ascertain whether the increase was not caused by a change of dislocation density or by some other mechanical effect. **Kanzaki** et al. [6] demonstrated on zonally purified KCl that conductivity at high temperatures was sensitive to the defect state of the crystal. It is interesting that both in NaCl and KCl, the given magnitude of the diffusion coefficient of the anion changes by nearly an order depending on whether the crystal was annealed or not. This should be put into connection with the increase of the anion conductivity in unannealed and deformed samples and probably helps to explain the great dissipation of values of the transport numbers [7], where the defect state of the crystal is not specified. Results obtained by **Graham** et al. [8] have shown that the contribution of the chlorine ion can be substantial and should not be ignored, especially for samples with small-size ions. It is generally believed that the movement of the Cl ion in NaCl is a combination of two types of defects, free anion vacancy and a pair of vacancies [2, 4]. **Laurance** [2] studied the effect of doping with Ca^{2+} on the diffusivity of Cl^- and explained the obtained results as follows: a) the prevailing anion defect in a pure crystal is the free vacancy, b) in a doped crystal pair of vacancies predominate and c) at small concentrations of doping, a combination of both types can be seen. Enthalpies computed for the motion of the anion vacancy and the pair of vacancies are 1.11 eV or 1.07 eV. The study of **Barr** et al. [4] confirms the substantial contribution of the pair of vacancies to the anion diffusion in NaCl. This study provides the following data for migration enthalpy: 0.9 ±0.1 eV, or 1.0 eV. Autoradiographic studies showed that the movement of Cl^- in NaCl takes place predominantly in the region of grain boundaries [1, 9].

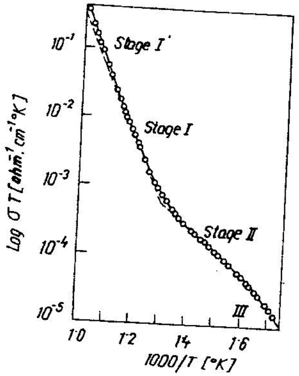

Fig. 2. High-temperature conductivity of a „pure“ crystal of NaCl [3].

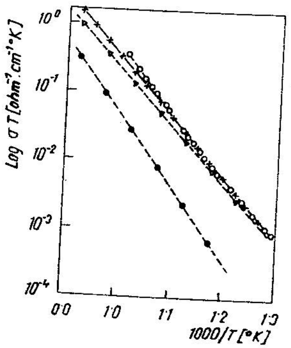

Fig. 3. Ionic conductivity results compared with diffusion data [3]. ● – anion contribution; △ – cation contribution; × – value calculated from diffusion; ○ – measured points.

The breakup of conductivity at high temperatures into an anionic one and a cationic one with activation enthalpies of 2.55 or 1.58 eV was observed also when measuring pure RbCl (550–700 °C) [10]. The comparison with relevant data for NaCl [2, 11] and KCl [11] shows that the difference between the activation enthalpies of anions and cations in alkali halides is the greatest for anions and cations of nearly the same radius. In KCl and RbCl anions contribute to the conductivity at 707 °C, even in a much greater measure than in NaCl, but their contribution decreases considerably with decreasing temperature. In alkali halides the difference between the activation enthalpies of anions and cations increases from 0.2 to 1.0 eV when the difference between the radii of anions and cations decreases from 0.42 Å in NaCl to 0.01 Å in RbCl [12]. This trend is the reverse of the one resulting from computations of **Guccione** et al. [13].

The motion of the anion, however, is not the only explanation of the region I', known in literature. **Allnatt** and **Pantelis** [14] explain the anomalous increase of conductivity beyond 750 °C in case of pure NaCl by a possibility of additional cation Frenkel defects to remove this anomaly. According to their analysis, interstitial Na ions carry 61 % of the electric current in NaCl at 794 °C. In agreement with equation (3), the mobile Na interstitial ions could also contribute essentially to the cation diffusion in NaCl. Nevertheless, nothing like it was ever observed in an experiment.

According to **Fuller** and **Reilly** [16] the anomalous distortion of I' for NaCl as well as KCl and RbCl can be a result of a trivacancy contribution, especially in case of heavily doped crystals. Here, apart from the dominating contribution of cation vacancies with increasing impurity concentration also the contribution of cation trivacancies to electrical conductivity ought to increase. The contribution of anion vacancies gradually decreases down to zero.

2.2. Impurity — unassociated conductivity

A significant dissipation of values of the activation enthalpy measured for this region of 0.72 eV [17] and 0.88 eV [18], (Tab. 3) is in a great measure caused by a short temperature range, above which the region is situated, causing possible overlapping of regions on the conductivity graph. Since thisconcentration of cation defects is in this region fixed, its activation enthalpy H_m applies to the movement of Na ion vacancy. Thus the difference between this enthalpy and the intrinsic enthalpy $(H_f/2 + H_m)$ is 1/2 of the Schottky enthalpy. This computation yields the value of e. g. 2.12 ±0.06 eV, which is in excellent agreement with the most reliable theoretical computations [19] $[2(1.86 \pm 0.03 - 0.80 \pm 0.03) = 2.12 \pm 0.06]$.

The short range of region II is not the only reason for the dissipation of the H_m data. As results from the experiment, H_m depends to a certain degree also on the introduced impurity and dissipation is mentioned by the same author for both pure and doped crystals. Data for doped crystals are generally higher than those for a pure material. For example, high values of H_m for Ba^{2+}in NaCl [18, 20, 21] can be interpreted in terms of precipitation. It is possible that the presence of precipitates in heavily doped crystals can cause a barrier, which then increases the activation enthalpy. The presence of precipitates is supported also by the shape of the conductivity isotherms σ vs n [20, 21], which shows a maximum for such crystals. A similar shape of curves σ vs n was not observed in doped crystals with other impurities of lower concentration. However, impurity solubility in the NaCl lattice depends not only on the concentration, but also on the radius of the impurity ion [22]. It is probable that impurity ions with their ion radius equal to or approaching the radius of Na^+ require for the transport of sodium ions a smaller energy.

Laredo and Dartyge [23] found that in haevily doped crystals the quality of the coat of paint of the electrode can influence the value of H_m. When observing NaCl crystals with a high concentration of Sr^{2+} $(n < 2\times10^{-2})$ they obtained for H_m 0.75 ±0.01 eV $(n = 4.6\times10^{-4})$. For higher concentrations, where precipitation begins, the behaviour of the region II becomes anomalous: the slopes are no more reproducible. Their mean values determined from the dynamic increase of temperature decrease with increasing concentration. This anomaly is explained by the authors as a high-temperature surface precipitation of $SrCl_2$, which occurs in case of application of a graphite („Dag“) coat of paint of the electrode. It seems that at high temperatures a part of Sr^{2+} is captured by the graphite-painted surfaces, forming $SrCl_2$ precipitates, which are non-active in crystal conductivity. In the same measurements (range of concentrations and temperatures) done with Ag-painted crystals the anomalous behaviour $H_m : H_m = 0.75 \pm 0.01$ eV disappears in all considered concentrations. It is probable that Ag electrodes capture a part of Sr^{2+}, but to a much lesser degree than graphite electrodes.

The plastic deformation of NaCl crystals causes a temporary increase in conductivity (the Gyulai—Hartly effect). The migrating defect has an activation enthalpy of 0.74—0.01 eV [24], which is a value characteristic for cation vacancy. The formation of cation vacancies by plastic deformation is not quite clear. Seitz [25] suggests that the mentioned effect is caused by cation vacancies produced by the motion of the dislocation. According to Fischbach and Nowick [26] the movement is caused by a cation vacancy, but its origin is connected with the breaking up of the complex of divalent impurity-vacancy. The correctness of the mechanism, for the Gyulai—Hartly effect as suggested by Seitz, can be verified by determining some suitable parameter of the migrating charge carrier, e. g. the activation enthalpy of migration and by comparing the obtained value with data from conventional conductivity measurements. Theoretical computations by Kear et al. [27] have shown the possibility of formations of interstitials in NaCl during the plastic deformation. Tharmalingam [28] made more exact computations for NaCl, KCl and KBr and arrived at the conclusion that anions can easily move in the (111) direction due to interstitial mechanisms and that this process is the most suitable compared to all the others. However, the origin of anion interstitials in NaCl during the plastic deformation has not been confirmed yet by any experiment.

In additively coloured NaCl single-crystals, heating in an atmosphere of sodium vapours at 550 °C for 16—72 hours causes the absence of the impurity-unassociated region II. Instead of it, the high temperature curve extends into the low temperature region [8].

2.3. Impurity — associated conductivity

The parameter, characterizing the association, the association enthalpy H_a (or the energy G_a) varies with different authors (Tab. 3). For example, the system $NaCl + MnCl_2$ is interesting by the fact that the introduction of paramagnetic impurity allows to study the associated complexes by means of the electron-spin resonance. These measurements give [29] values of 0.41 eV for the nearest neighbouring complexes. However, the agreement between data determined for this system by various techniques is rather poor: the impurity diffusion [30] gives the value 0.70 eV, while the conductivity measurement [3, 31] gives 0.29 or 0.28 eV. This difference can be also the result of a different impurity background of the crystal. Too high association enthalpies obtained from the impurity diffusion compared with the results obtained from conductivity measurements could be partially ascribed to the next-nearest interactions, since these are usually neglected in the current analysis of conductivity data. In the $NaCl + MnCl_2$ system the next-nearest neighbour complex is almost equally stable as the nearest neighbouring complex. The use of the simple association theory as it applies to interactions of the nearest neighbours

Table 3
Impurity defects

System	H_a or G_a [eV]	H_d [eV]	H_{ma} [eV]	H_s [eV]	H_m [eV]
NaCl : Mg^{2+}	0.34[1]	0.66[2]		0.94[1]	0.75[1], [18]
	0.04[32]				0.734[32]
				1.21 – 0 884[28]	0.79 – 0 77[28]
Zn^{2+}	0.48[10], [11]	0.66[2]	0.51[10], [12]	0.98[10]	0.65[2]
	0.65[31]			0.916[31]	
Cd^{2+}	0.40[1], [4]	0.69[2]		0.93[1]	0.85[42]
	0.28[29]	0.68[7]		0.71[30]	0.84[50]
	0.6[1]			1.24[33]	0.79[1]
	0.34[50]			1.14[1], [6]	0.75[18], [6]
	0.39[13]				0.67[2]
	0.38[34], [35]				0.68[37]
	0.24[42]			0.90[28]	
Ca^{2+}	0.30[1]	0.68[5]	0.92[9]	0.64[33]	0.79[1]
	0.31[3]	0.70[6]	0.96[4]	1.0[1], [6]	0.67[37]
	0.67[4]	0.67[7]		0.79[12]	0.78[39]
		0.70[8]			0.72[33]
		0.71[2]			0.85[3], [42]
	0.284[29]				0.635[36]
	0.38[34], [35], [45]				0.743[32]
	0.49[36]				0.68[41]
	0.57[38]				0.74[43]
	0.08[39]				0.7[44]
	0.19[32]				0.77[45]
	0.36[45]			0.87[28]	0.78 – 0 77[28]
NaCl : Ca^{2+} +OH$^-$		0.64[40]			
Sr^{2+}	0.5 – 0.53[46]	0.71[2]		0.78[1]	0.75[47]
	0.43[34], [35]			1.80[46]	0.72[46]
	0.44[2]			1.4[46]	0.82[1]
	0.45[34]			0.85[47]	0.74[3]
	0.22[32]				0.73[7]
	0.25[28]			1.15[28]	0.74 – 0.86[28]
Pb^{2+}	0.41 – 0.47[13]		0.98[13]		0.78[51]
	0.28[51]				
			0.80[28]		

Table 3 (continued)

System	H_a or G_a [eV]	H_d [eV]	H_{ma} [eV]	H_s [eV]	H_m [eV]
Ba^{2+}	0.76[1], [48]			0.99[1]	0.74 – 0.79[48]
	1.06[46]			2.00[46]	0.75[1]
	0.79[46]				0.78[32]
	0.45[2]				0.88[49]
	0.40[28]			2.03[28]	0.94 – 1.04[28]
Mn^{2+}	0.31[1]	0.68[2]	0.71[14]	0.78[1]	0.63[15]
	0.7[14], [21]	0.63[15]	0.78[16]		0.70[1]
	0.29[52]	0.7[8]	0.83[17]		0.69[2]
	0.27[19]		0.80[16]		0.58[22]
	0.28[19]				0.64[22]
	0.31[19]				
	0.41[15]				
	0.32[20]				
NaCl : Ni^{2+}	0.32[18], [23]				0.75[18]
Co^{2+}	0.30[18], [23]				0.75[23]
					0.72[24]
Be^{2+}					0.5[25]
Sm^{2+}		0.67[19]			
Cu$^+$					0.35[26]
K$^+$		0.9 – 1.1[20]			
KO$_4^{2-}$					0.722[27]
O^{2-}					0.69[27]

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[1] calculated from [70], assuming $H_{m_1} =$ = 0.80 eV [70]

[2] [82]Δ_e, σ

[3] [33] σ, 250 – 400 ^{2}°C with 10^4 – 10^5 cp with ac bridge

[4] [35] D, $S_a/k = 5.7$ (Ca^{2+})

[5] [46] Δ_e

[6] [11] Δ_e

[7] [81] Δ_e, *ITC*

[8] [92] Δ_m

[9] [93] Δ_e

[10] [38] D, σ (assuming association of nnn terms, H_a decreases)

[11] 700 °C

[12] from diffusion in heavily doped samples

[13] [54] D (321 – 528) °C – Pb^{2+}

[14] [30] D, $S_a/k = 2.2$

[15] [29] ESR, Δ_e

[16] [94] EPR, Δ_e

[17] [52] Δ_e

[18] [41] σ

[19] [31], H_a from D: 0.27 – 440 °C, 0.28 – 421 °C, 0.31 – 401 °C

[20] [95] EPR

[21] [96] EPR

[22] [97] σ, ESR (crystals were grown from aqueous solution: 0 – 140 °C, 140 – 230 °C),

[23] [98] σ

[24] [84] Δ_e

[25] [99] D

[26] [91] σ

[27] [100] σ

[28] [79] σ

[29] [101] σ, $S_a = 2.4 \times 10^{-5}$

30) [102] σ, $S_s = 0.88$
31) [103] σ, D, $S_a = 4 \times 10^{-4}$, $S_s = 0.132$
32) [20] σ
33) [22] σ, Δ_e, $S_s = 0.7$ (Ca^{2+}), $S_s = 10.6$ (Cd^{2+})
34) [34] theoretical value
35) [40] theoretical value
36) [36] Δ_m, 400—700 2°C
37) [105] *ITC*
38) calculated from [60], D using data [35]
39) [106] σ
40) [107] Δ_e
41) [51] Δ_e
42) [37] σ
43) [10] σ
44) [104] Δ_e
45) [43] σ, higher concentrations Ca^{2+}
46) [17] σ, $S_s = 15$ (Sr^{2+}), $S_a = 0.15 \times 10^{-3}$ (Sr^{2+}), $S_s = 9.4$ (Ba^{2+}), $S_a = 0.18 \times 10^{-3}$ (Ba^{2+})
47) [23] σ, high concentrations
48) [21] σ
49) [18] σ
50) [32] σ, for Cd^{2+} in NaCl — recalculated results from [37]
51) [108] σ
52) [3] σ

can be non-adequate in the case of the analysis of ionic conductivity, especially in systems, where the magnitude of the impurity ion is less than that of the host ion. It was actually shown that a refined analysis of conductivity data, considering the long-range interactions leads to an increase of the computed association enthalpy [32, 33].

The situation for other impurity ions, e. g. for calcium is not better. Theoretically **Bassani** and **Fumi** [34] obtained 0.38 eV for $T = 0$ °K, while the experimental data comprise 0.67 eV from **Murin** et al. [35] and 0.31 eV from **Kanzaki** et al. [33]. The value determined from measurements of the internal friction of NaCl + $CaCl_2$ is 0.49 eV [36].

With the exception of the most heavily doped crystals the region of association is distored. Therefore the determination of the association enthalpy H_a (or the energy G_a) from the slope of region III is for lower impurity concentrations not exact enough. However, the data can be analysed by the method of conductivity isotherms [32, 37] or by a similar computation, i. e. by using diffusion isotherms [38].

Theoretical computations of some binding energies [34, 39, 40] show that this energy should increase with an increasing ionic radius. This is confirmed by experimental studies with the exception of those limited to impurity ions of a similar or a smaller size compared to that of the host cation [30, 38]. It is assumed that in such cases it can be important, as previously mentioned, that an interaction between the impurity ion and the cation vacancy in the next-nearest neighbouring position takes place. An increase of the binding energy with an increasing ionic radius of impurity (Tab. 1) can be explained by some local pressure distortion.

The fact that the observed value of H_a is of the same order for Ni^{2+} an Cd^{2+} [41] and is smaller for Ca^{2+} [42] points to the fact that the electron configuration in the outer shell of the impurity ion has a great influence upon the association energy.

The absence of the association region in graphs of log σT vs $1/T$ e. g. for NaCl + $ZnCl_2$ [38] is explained by the assumption that the precipitation process often interferes and covers the region of association.

2.4. Impurity conductivity connected with precipitation and low-temperature association

After a further decrease of the crystal temperature (~150 °C) impurity in solutions segregates or is precipitated from the solid solution. This results in a steeper slope of the conductivity graph, thus forming the region IV — the region of precipitation. When the precipitation ends (~100 °C), the association between divalent impurity and vacancies — region III′ [3, 43] could go on. The isothermal analysis of this association reaction is difficult due to the indeterminable concentration of impurity in the solution, which determines the conductivity properties.

The interpretation of conductivity measurements at temperatures below region III (~150 °C) becomes complicated. The hysteresic effects at these temperatures indicate that the conductivity in this region is controlled by some time-dependent mechanism and that the equilibrium conductivity value is measured. The conductivity measured during the cooling period of the crystal evidently cannot be compared with the conductivity measured during its heating up. During the cooling of the crystal, e. g. by NaCl + Ca^{2+} region IV does not appear [43]. This difference indicates the complexity of the process by which aggregates consisting of Ca^{2+} and cation vacancy dissociate. In the system NaCl + Cd^{2+} region IV appears at lower temperatures and the final value of conductivity is higher (at 40 °C) than when measured at an increasing temperature. The formation of aggregation is simpler in NaCl + Cd^{2+} (cation vacancies remain in the aggregate [44] than in NaCl + + Ca^{2+}) (assumption of two different types of aggregates [45, 46]) and effects of the conductivity hysteresis can be explained purely on the basis of the dissolution of the $CdCl_2 \times 6$ NaCl aggregate.

Region IV is well-spaced, e. g., in crystals doped with Mn^{2+} (Fig. 4), but in pure crystals it is absent [3] as can be expected from a consideration of the kinetics of precipitation. To reach equilibria positions in low-doped crystals is time-consuming, while the decay of impurities is more rapid in crystals with a high concentration of impurity. An increase of the level of doping results in a longer period of precipitation and a steeper slope of region IV (1.21—1.48 eV), while at the same time the slope of the linear region of the low-temperature association — III′ — decreases [3] (Fig. 5).

Aggregation or precipitation is in most systems observed (during heating) within the range of 100—200 °C for samples cooled relatively slowly (1 °C/min) to room temperature. Exceptions are, e. g. NaCl + Zn^{2+} [38], NaCl + Ba^{2+} [17, 21], where precipitation occurs only at high temperatures (~400 °C) probably due to a greater disturbance of the environment of the impurity ion. Rapid cooling (~30 °C/min) of doped samples to room temperature eliminates the occurence of the region on the conductivity graph.

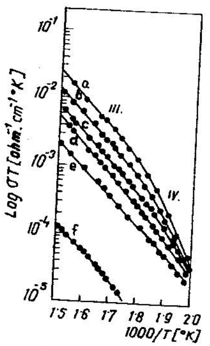

Fig. 4. Association region [3]. a – 686 m. p. p. m. Mn^{2+}; b – 325 m. p. p. m. Mn^{2+}; c – 186 m. p. p. m. Mn^{2+}; d – 130 m. p. p. m. Mn^{2+}; e – 90 m. p. p. m. Mn^{2+}; f – pure.

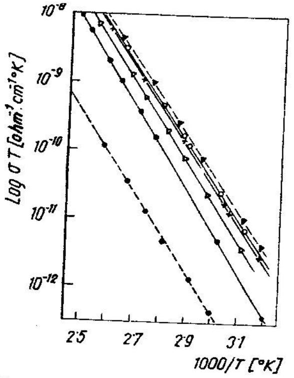

Fig. 5. Low-temperature association region [3]. ▲ – 760 m. p. p. m. Mn^{2+} + OH^-; ○ – 700 m. p. p. m. Mn^{2+}; × – 244 m. p. p. m. Mn^{2+}; △ – 166 m. p. p. m. Mn^{2+}; ● (solid line) – pure; ● (dashed line) – 71 m. p. p. m. Mn^{2+}.

The difference between the conductivity data of rapid-cooled (quenched) and slow-cooled crystals is caused by the fact that formation of aggregates or precipitation by the cooling of the crystal is a slower process and when the crystal which at high temperatures does not contain aggregates or precipitates is cooled down, it contains only isolated impurity ions and pairs in solid solution, while the slowly cooled crystals contain also higher aggregates or precipitates.

The presence of big aggregates of impurity ions or other point defects, preventing the motion of cation vacancies may also explain the observed decrease of conductivity with increasing concentration of impurity (from a certain limit), e. g. in systems of NaCl + Ni^{2+} [41], NaCl + Ba^{2+} [21]. Similarly as these experiments the decrease of conductivity with time also points to the formation of higher aggregates by a relatively slow process [21].

3. Dielectric relaxation

The formation of divalent ion-vacancy pairs and the motion of the vacancy can be studied also by dielectric losses measurement. Since the complex of divalent ion-vacancy forms an electric dipole, it will produce the Debye loss peak, having the characteristic maximum when the frequency of the applied electric field is approximatively equal to the rate at which the dipole can be reoriented.

The theory of dielectric losses caused by complexes of divalent ion-vacancy has been worked out by Lidiard [47].

The most important data, resulting from the dielectric relaxation are: the activation enthalpy for the dipole reorientation of H_d, determined by jumps (w_1) of the associated single defect (e. g. $\square_1$) and thus comparable with the enthalpy of its free motion H_m. On the other hand the study of the dipole decrease (due to the diffusion limited formation of higher aggregates) provides the activation enthalpy H_{ma} for the migration of the dipole, dependent on the jumps of the mutual exchange (w_2) and should be identical with the value H_{ma} obtained from the impurity diffusion (Tab. 3, 4).

Table 4

Comparison of activation enthalpies of free-cation vacancies and reorientation of impurity-vacancy pairs

System	Activation enthalpy [eV]	
	free vacancy*	bound vacancy
NaCl : Ca^{2+}	0.66 – 0.76	0.67 – 0.70¹), ²), ³)
Cd^{2+}		0.68 – 0.69³), ⁴)
Mn^{2+}		0.65 – 0.69³), ⁴), ⁵)
Co^{2+}		0.67 – 0.72⁶)

* The figures in the second column are the same as in Tab. 3,

¹) [51] Δ_e
²) [81] *ITC*
³) [82] Δ_e
⁴) [52] Δ_e
⁵) [83] σ
⁶) [84] Δ_e

The values of the activation enthalpies for the motion of lattice defects are obtained from the observed temperature and the frequency of the loss maximum

$$f_{\max} = A \exp(-H_m/kT) \tag{4}$$

(the frequency factors A in alkali halides are $4f_0/\pi$) and the number of lattice defects (impurity-vacancy complexes) is determined from the magnitude of the loss maximum

$$(\tan\delta)_{c\,\max} = \frac{2\pi\, e^2 N_c}{3\varepsilon a k T}. \tag{5}$$

The vacancy pair in alkali halides present a special problem. Their study using the method of dielectric losses is far from being simple. These pairs are intrinsic defects and in this equilibrium they are presented in significant concentrations only at high temperatures, when their rates of reorientation are necessarily very high. Thus high frequencies are required (1—10 MHz) [48] and background losses caused by a high conductivity of the crystal at these temperatures are considerable. Some apparently successful measurements have been made, but the observed dipolar losses are considerably larger than expected and therefore it is not certain, whether we have here really the Debye losses from vacancy pairs. The pair contribution appears as a small elevation in curves (Fig. 6) (Tab. 5). The magnitude of these losses could be explained better as the Maxwell—Wagner losses associated with interfacial polarization at the electrodes [49]. However, the temperature changes of τ and the magnitudes of the losses are not as expected. When the losses really represent the vacancy pair relaxation, the faster jump of the anion should be measured into a pair. The contribution to self-diffusion of either the cations or the anions are limited by the slower of the to jumps [50].

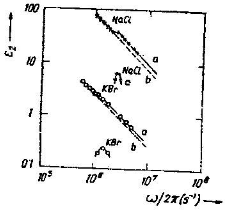

Fig. 6. Imaginary part ε_2 of the dielectric constant of NaCl (707 °C) and KBr (600 °C) [48]. a — experimental data; b — contribution $\sigma/\varepsilon_0 w$ of the dc conductivity σ; c — dipolar contribution.

Table 5

Vacancy pairs $\Box_1\ \Box_2$

Crystal	$H - H_a$ [eV]	H_d [eV]	H_{ma} [eV]	Activation energy for anion diffusion by means of vacancy pairs
NaCl	1.30[1]	1.25[1]	1.31[2] 1.073[3] 1.0[4]	2.49[3] 2.37[2]

[1] [48] Δ_e

[2] [4] D, calculated with $H = 2.12$ eV

[3] [2] D

[4] [85]

The measurements of dielectric losses are also used for the study of the aggregation of impurity-vacancy dipoles into high complexes, or eventually complete precipitation of the impurity from the solution. The kinetics of this aggregation provides information on the motion of the impurity-vacancy pairs. Dielectric losses for the study of aggregation were used for the first time by Dryden et al. [51, 52, 45] at about 20 °C. From among the NaCl system they examined the quenched crystals NaCl + Ca^{2+}, NaCl + Mn^{2+}, then KCl + Sr^{2+}, KCl + Ba^{2+} and LiF + Mg^{2+}. By annealing at temperatures of about 100 °C the main peak caused by dipoles decreases (Fig. 7), while at the beginning it follows the third order kinetics. The activation enthalpy H_{ma} of this process is slightly higher than H_d. This is reasonable, since the real diffusion of dipoles also contains jumps of the mutual exchange (w_2), i. e. $\exp(H_d/kT) \sim 1/w_1$, $\exp(H_{ma}/kT) \sim 1/w_1 + 1{:}w_2$ for closely bound associates. The comparison with H_{ma} data from the diffusion results is partially screened by dispersion [15].

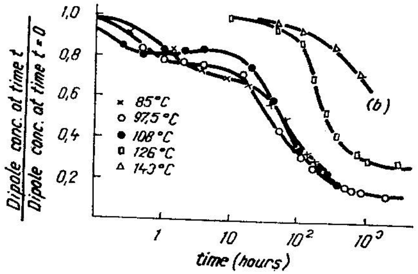

Fig. 7. Decay of dipole concentration in the sample of KCl containing 1.4×10^{-4} mol fraction of Sr^{2+} [52].

The decay of the dipoles is interpreted as an aggregation into clusters in threes (trimers) $(M_1^2 + \Box_1)_3$. The most probable model of these trimers is the smallest hexagon in a {111} plane consisting of cation positions. This model makes possible a rough theoretical estimate of the aggregation energy [52], which is in good agreement with experimental data of 0.7 eV for KCl + + Sr^{2+} and KCl + Ba^{2+} and of 0.9 eV for LiF + Mg^{2+} (Tab. 6). They are slopes of graphs in $\ln(x_3 x_d^{-3})$ vs $1/kT$, where x_3 and x_d correspond to the concentration of trimers, or dipoles in equilibrium.

In the second stage there occurs the aggregation into higher clusters. In NaCl + Ca^{2+} another type of aggregate was found than in the first stage, causing the secondary absorption on the side of the high frequencies and changing the kinetics of aggregation. The enthalpy of its reorientation is

Table 6

Activation energy and frequency factor for trimer formation in different systems (according to the equation $dn/dt = -\nu_0 n^3 \exp(-E/kT)$)

System	E [eV]	ν_0 [sek^{-1}]
NaCl : Mn^{2+}	0.83[1]	8 × 10^{17}
Cd^{2+}	0.5[2]	2.8 × 10^{16}
	0.37[3]	

[1] [52] Δ_e

[2] [53] *ITC*

[3] [110] data re-calculated from [53]

0.64 eV with at least one reorientation by 0.05 eV lower than the other. This can be computed from the model of a chain-like arrangement of some dipoles [46]. KCl + Sr^{2+} and KCl + Ba^{2+} similarly as NaCl + Mn^{2+} do not manifest any trace of a second absorption when aggregation occurs. All absorption curves are perfect Debye curves. The only conclusion, which can be arrived at on the basis of recent results is that in the plateaus of the decay curves there exist two types of aggregates in equilibrium with the dipoles; one type of aggregate — a trimer, similar to trimers occurring in KCl systems and another causing the second absorption observed in NaCl + Ca^{2+}. For the time being no sufficient data are available suitable for a succesful discussion as regards the character of the second type of aggregate.

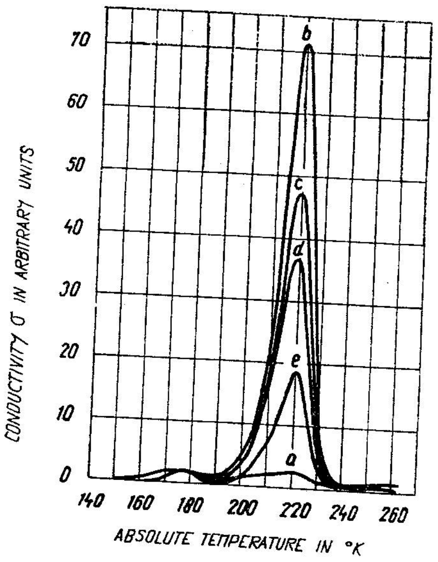

Fig. 8. *ITC* method used for NaCl + + CdCl$_2$ (impurity concentration: 1.2 × × 10^{18} cm^{-3} from chemical analysis). Curve a: sample not previously treated, curve b: sample heated at 230 °C for 45 min and quenched at room temperature; curve c: after an annealing of 85 min at room temperature; curve d: after an annealing of 225 min at room temperature; curve e: after an annealing of 1090 min at room temperature [53].

A prove of the existences of higher aggregates was found also by the *ITC* method (ionic thermocurrents), which is very suitable for the study of precipitation at relatively low temperatures, e. g. [53]. Graphs of ionic thermocurrents (Fig. 8) provide the data of τ, H_d and the area delineated by the *ITC* band gives the initial concentration of the dipoles.

4. Diffusion

Diffusion is a process of the transport of atoms or ions of the host substance or the impurity conditioned by thermal motion. In NaCl the mechanism of self-diffusion and as a rule also of the diffusion of divalent cation impurities is vacant, i. e. the ion migrates by jumps into the neighbouring vacancy. The diffusion is therefore accompanied by a migration of vacancies.

Diffusion studies provide direct information about the transport of the substance in both sub-lattices. Over large ranges of temperature the diffusion coefficient often behaves according to the equation

$$D = D_0 \exp(-E/kT) \tag{6}$$

(E is the activation enthalpy of the diffusion). For self-diffusion, when only one of the defects is capable of diffusion (a cation or an anion), $E = E/2 + E_m$. The influence of a few defects causes generally a bending of the graph log D vs $1/T$ (Fig. 9) (Tab. 7).

Measurements of the anion diffusion in pure crystals of NaCl, KCl and KBr show a considerable contribution of the cation vacancy — anion vacancy pairs [2, 4, 16], which by doping with divalent cation impurities is made even more conspicuous.

From the diffusion coefficients for the diffusion of single anion and cation vacancies (D_M or D_x) the transport numbers t_M and t_x can be defined as

$$t_M = \frac{D_M}{D_M + D_x}$$

and $t_M + t_x = 1$. In this way more exact transport numbers can be obtained than by using the Tubandt method [15].

Experimental investigations showed the dependency of the diffusion coefficient on concentration to be in general agreement with the theory — Ca [35] and Mn [30] in NaCl, Pb in NaCl [54], Cd in NaCl [55], Zn in NaCl [38] and Pb in KCl [55—59], Cd in KCl [60] and Cd in AgCl [61] and in AgBr [62].

The impurity diffusion is often considered in relation to the transport mechanism [10, 63] or to the magnitude of the diffusing ions [64, 65]. When diffusing impurities affect the concentration of the defect of the host crystal, D depends on concentration. In the case of the impurities taking up the interstitial positions, as well as the lattice positions, D is decreasing with increasing concentration [63]. Alliovalent impurities forming associates with vacancies of the excess charge diffuse much faster than the host ions which have only occasionally the opportunity of meeting vacancies and D increases with increasing concentration. This is confirmed by various systems: the study of impurity diffusions with Zn^{2+} [38] and Pb^{2+} [54] in NaCl and also Pb^{2+} [56, 57] and Cd^{2+} [58] in KCl confirms the general concentration dependence derived from the model of association. The agreement of the experimental data H_a with the theoretical data is better, when nnn association is included [38].

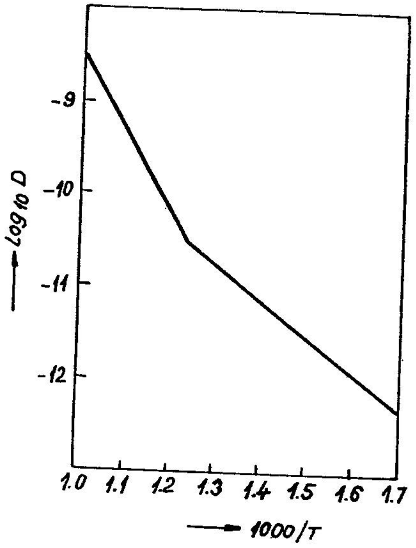

Fig. 9. The self-diffusion coefficient of Na^+ in NaCl as a function of temperature [66].

According to the trace diffusion [66, 67, 9] of the anion and cation movement, the importance of the anion movement is greater at temperatures of about 650 °C. The magnitude of the activation energy of this movement is structurally sensitive [16]. The coefficients of the anion diffusion measured at 650 °C are changing from 9.0×10^{-11} to 1.53×10^{-10} cm^2 sec^{-1} in comparison with the cation diffusion 8×10^{-10} cm^2 sec^{-1} at the same temperature [1, 4, 2].

The influence of the size of ions the diffusion of monovalent ions in alkali halides was observed by measurements of the diffusivity of NaCl, also of KCl and RbCl [68]. In agreement with the theory [64] the activation energy increases when the host cation becomes smaller. Values of the pre-exponential factor (D_0) cannot be explained by the quantitative method. Experiments with monovalent foreign anions (NaCl + J, KCl + J, KJ + Cl) showed [69] that the D_0 for impurities is higher than that for the host ions, while the activation energy is nearly the same.

Table 7

Impurity diffusion

Parameters D_0 and E according to equation (6)

System	T [°C]	D_0 [cm^2/s]	E [eV]	Ref.
NaCl : Zn^{2+}	590—800	2×10^{-2}	1.02	[38]
	550—780	1.5×10^{-4}	0.51	[38]
Cd^{2+}	350—500	1.2	0.64	[55]
Ca^{2+}	430—750	6×10^{-4}	0.90	[86]
			0.96	[60]
Sr^{2+}			0.91	[87]
Pb^{2+}	321—528	1.5×10^{-2}	0.98	[54]
Mn^{2+}	350—700	3.48×10^{-3}	0.95	[88]
	450—750	2×10^{-5}	0.66	[30]
Ni^{2+}	200—650		0.26	[89]
	620—750	2×10^{-2}	1.3	[90]
Co^{2+}	610—760	8×10^{-3}	1.1	[90]
K^+	400—600		0.5	[89]
Cu^+		33.8	1.43	[91]
Rb^+	600—787	205	2.11	[68]
J^-	530—700	500	2.24	[69]

5. Conclusion

In order to find one or more ion transport parameters a great number of experiments with NaCl crystals was performed. As can be seen from the obtained results and from their relatively good reproducibility in the region of high temperatures, the processes in this region have been thoroughly investigated. The problem which remains to be solved (at these temperatures) is the behaviour of the region below the melting point. In this respect the contribution of various defects to conductivity – as e. g. of vacancies of both types, trivacancies, interstitials – has not been determined satisfactorily.

The problem in the mechanism of the charge transport at low temperatures (about 0 °C) also remains to be solved. The occurrence of different regions in the plot of ln σT vs $1/T$ at these temperatures suggests the existence of various processes very sensitive to the previous treatment of the sample.

An insufficient analysis of the results by some authors and sometimes the absence of important details of the experiments, often make comparisons of the transport parameters and arriving at uniform conclusions difficult. A less satisfactory agreement between theoretical and experimental data is probably caused by the vagueness of theoretical models.

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