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IONIC TRANSPORT PARAMETERS OF ALKALI HALIDES

II. POTASSIUM, LITHIUM AND CAESIUM HALIDES, SILVER HALIDES AND ALKALI EARTH HALIDES

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The present study discusses the known facts about ionic transport parameters for potassium and lithium halides, silver halides and alkali earth halides, 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

□ .... Vacancy
● .... Interstitial site
1, 2 .... Single positive and negative excess charge (subscripts)
B1 .... NaCl structure
B2 .... CsCl structure
G, H, S ... Increment of the Gibbs free energy, enthalpy, and entropy
m .... Subscript relating to the migration of single defects
a .... Subscript relating to the association impurity – vacancy

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ma	Subscript relating to the migration of associates
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
k	Boltzmann constant
x	Molar fraction of incorporated defects
T	Melting point
ITC	Ionic thermo-current, depolarization current upon linear heating
ESR	Electron spin resonance
D	Diffusion coefficient
E	Experimental activation enthalpy for diffusion
σ	Conductivity
μ	Mobility
Δ_e, Δ_m	Electrical and mechanical relaxation
Φ	Working function
χ	Electronic affinity

1. Introduction

This paper is a continuation of the study on NaCl (presented as No. I). Transport parameters of potassium and lithium halides are given with an analysis of the experimental and theoretical results, while data on silver halides and alkali earth halides are only tabled.

2. Potassium halides

2.1. KCl

The greatest attention so far has been accorded to NaCl, KCl, less to Lif and KBr.

In KCl similarly as in NaCl, electrical conductivity of single crystals is created up to relatively high temperatures by cation vacancies [1]. Also the breakup of the conductivity grapf log σT vs $1/T$ is similar. Mechanisms of conductivity in regions II and III have been thoroughly studied. The existence of region IV and its extent depends on the heat history and the special rate of heating up during conductivity measurements. In formally pure crystals of KCl, Kumbartzki and Thommen [2] showed that region IV appears only during a sufficiently slow heating up (or cooling down) when following the conductivity as a function of temperature. This can be easily explained by the process of aggregation of multivalent cation impurities, requiring a relatively long period of time.

The graphs log σT vs $1/T$ are slightly curved (concavely downwards), which indicates association between cation vacancies and divalent cation impurity, e. g. Sr^{2+} (Fig. 1). Therefore parabolic isotherms σ vs n can be expected, intersecting the σ axis near σ_0, the conductivity of pure salt; the rate of bending decrease with increasing temperature.

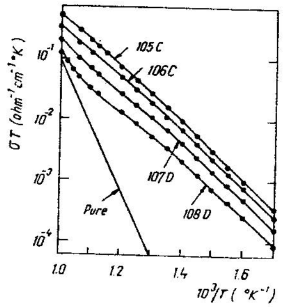

Fig. 1, Conductivity of KCl crystals doped with $SrCl_2$; the mole fraction of strontium impurity is: 105C — 502 ppm, 106C — 275 ppm, 107D — 146 ppm, 108D — 51 ppm [96].

The values of the activation energy for conductivity by cation vacancies are in mutual agreement e. g. the data by Jacobs and Maycock show 0.76 eV [3], Gründing lists 0.77 eV [4], Pierce 0.76 eV [5] and Kobayashi and Tomiki [6] (the latter authors do not mention the numerical value, but deduction from their graph yields ~0.75 eV).

A great dispersion can be observed in the data for the migration of the anion vacancy, e. g. Allnatt and Jacobs list 1.77 eV [7], while the value attained with crystals doped with SO_4^{2-} is 1.87 eV [8]; Pershic and Pavlov obtained 2.20 eV [9]. At the same time the theoretical value by Guccione et al. [10] is 1.18 eV.

Should the migration enthalpies of cations and anions be similar, i. e. $H_{m_1} \sim H_{m_2}$, the graph ought to manifest a curvature within the relevant temperature range. However, hardly any curvature was observed [3, 7]. Data found from conductivity are in good agreement with the diffusion value of Ewles and Jain [11] 1.86 eV and with the value computed from the Kerkhoff data on transport figures [12] 1.9 eV. (Tab. 1a, 1b, 1c.)

Considerable temperature dependence of the association energy within the temperature range of (27—623 °C) 0.43—0.20 eV can be understood when applying the Lidiard theory [1] of non-nearest-neighbour interactions between defects. For a quantitative confirmation of the importance of these interactions measurements are necessary at low concentrations and then it is important to use a material without hydroxyde. An independent confirmation of the importance of the mentioned interactions is to be found, e. g., in the paper by Watkins [13] (E. S. R.) and Dreyfus [14] (dielectric relaxations).

Table 1a

Intrinsic defects — alkali halides

□1 — positive vacancy, □2 — negative vacancy

Crystal	Defects	H [eV]	S/k	H_{m_1} [eV]	$S_{m}/_{1}k$	H_{m_2} [eV]	S_{m_2}/k
KCl	□1, □2	2.26$^{1)}$, $^{2)}$, $^{3)}$ 2.31$^{3)}$ 2.36$^{6}_{2}$) 1.66$^{6}_{1}$) 2.17$^{2}_{2}$), $^{9)}$ 1.84$^{2}_{1}$), $^{9)}$ 1.75–2.26$^{43)}$ 2.415$^{36a)}$ 2.1$^{37)}$ 2.30$^{7)}$ 2.40$^{38)}$ 2.59$^{33)}$ 2.49$^{14)}$	5.37$^{2)}$ 7.6$^{3)}$ 5.8$^{6}_{2}$) 1.05$^{6}_{1}$) 4.5$^{2}_{2}$) 2.25$^{2}_{1}$) 3.6$^{36)}$ 9.61$^{39)}$	0.71$^{2)}$ 0.59$^{3)}$ 0.74$^{7)}$ 0.67$^{6)}$ 0.77–0.96$^{8)}$, $^{10)}$ 0.78$^{36)}$ 0.73$^{39)}$ 0.76$^{14)}$	1.80–1.89$^{2)}$, $^{4)}$ 2.70	1.043$^{2)}$, $^{5)}$ 0.95$^{3)}$ 1.11$^{2)}$, $^{7)}$ 0.80–1.21$^{8)}$,$^{10)}$ 0.99$^{39)}$ 0.89$^{14)}$	4.2–6.3$^{2)}$, $^{3)}$ 4.14$^{39)}$ 3.95$^{14)}$
KBr	□1, □2	2.53$^{11)}$ 2.35$^{12)}$, $^{13)}$ 1.68–2.14$^{44)}$	7.4–9.9$^{11)}$, $^{12)}$	0.62–0.67$^{11)}$,$^{12)}$,$^{13)}$ 0.73$^{7)}$	1.7$^{12)}$	0.87–0.95$^{11)}$ 1.20$^{7)}$	3.7$^{12)}$
KF	□1, □2	2.64$^{15)}$ 2.04–2.51$^{16)}$		1.02$^{15)}$			
KJ	□1, □2	1.60$^{17)}$, $^{41)}$ 1.70–1.92$^{16)}$ 2.0$^{19)}$ 2.29$^{20)}$ 2.21$^{40)}$ 1.90$^{7)}$ 1.87$^{10)}$	8.9$^{40)}$	1.21$^{17)}$ 0.65$^{18)}$ 0.73$^{7)}$ 0.58$^{21)}$ 0.63$^{40)}$ 0.72$^{41)}$	1.58$^{40)}$	1.36$^{7)}$ 1.29$^{40)}$ 1.50$^{41)}$	9.36$^{40)}$

Table 1a (continued)

Crystal	Defects	H [eV]	S/k	H_{m_1} [eV]	S_{m_1}/k	H_{m_2} [eV]	S_{m_2}/k
NaBr	□1, □2	1.72$^{22)}$ 1.31–2.01$^{16)}$, $^{24)}$, $^{25)}$	4.04$^{22)}$	0.80$^{22)}$		1.18$^{23)}$	
LiF	□1, □2	2.70$^{26)}$ 2.74$^{30)}$ 2.34–2.68$^{27)}$ $^{32)}$ 1.24–2.57$^{16)}$, $^{24)}$	9.6$^{27)}$	0.65$^{26)}$, $^{28)}$ 0.65–0.7$^{31)}$ 0.70$^{30)}$ 0.75$^{33)}$ 0.58$^{34)}$ 0.65–0.73$^{27)}$, $^{32)}$, $^{29)}$ 0.74$^{42)}$	1$^{29)}$	1.1$^{30)}$	3.5$^{29)}$
LiCl	□1, □2	2.2$^{32a)}$ 1.08–2.56$^{16)}$ 1.49$^{36b)}$ 1.68$^{36a)}$	2.91$^{40)}$	0.41$^{32a)}$ 0.52$^{36)}$			
LiBr	□1, □2	1.8$^{32a)}$ 0.86–1.32$^{16)}$		0.39$^{32a)}$			
LiJ	□1, □2	1.34$^{32a)}$ 1.06$^{35)}$ 0.64–1.00$^{16)}$	4.5$^{32a)}$	0.38$^{32a)}$			
RbCl	□1, □2	2.55$^{9}_{2}$) 2.47$^{9}_{2}$) 1.58$^{9}_{1}$) 1.53$^{9}_{1}$)					

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1) [62] σ, $\nu_{\mathrm{Deb}} = 5.9 \times 10^{12}\ \mathrm{s}^{-1}$

2) [74] σ

3) [75] D

4) $\nu = 4.25 \times 10^{12}\ \mathrm{s}^{-1}$

5) [76]

6) [77] σ, anion and cation conductivity

7) [9] σ

8) [78] theoretical value

9) [79] σ, anion conductivity by using [80]

10) [81] theoretical value
11) [31] σ
12) [82] D
13) [18] σ
14)
15) [84] σ
16) [85] theoretical value
17) [42] σ
18) [41] σ
19) [39] σ
20) [40] theoretical value
21) [34] Δe
22) [36, 37] σ
23) [38] D
24) [86] theoretical value
25) [87] theoretical value
26) [88] σ
27) [52] σ
28) [59] Δe
29) [50] σ, D
30) [89] σ
31) [90] σ, *ESR*
32) [53, 56] a, b; σ
33) [91] σ, *ESR*
34) [60] Δe
35) [63] σ
36) [93] a, b; σ theoretical values
37) [94]
38) [95]
39) [96] σ
40) [97] σ
41) [46] σ
42) [98], temperature dependence of electrical signals (407 °C)
43) [33, 68, 32, 85–87, 81, 92], theoretical value
44) [68, 32, 85–87], theoretical value

Table 1b

Intrinsic defects — alkali earth halides

Crystal	Defects	H [eV]	S/k	H_{m_1} [eV]	S_{m_1}/k	H_{m_2} [eV]	S_{m_2}/k
CaF_2	F_0, $\square_2$	2.80$^{1)}$ 5.1$^{11)}$ 2.3$^{11)}$	13.6$^{1)}$	1.64$^{1)}$	10.6$^{1), 2)}$	0.87… …0.52$^{1), 3)}$	8.1… …1.3$^{1), 2), 3)}$
BaF_2	$\square_2$, F_0	1.58$^{8)}$ 1.78$^{2)}$ 5.2$^{11)}$ 1.9$^{11)}$		0.78$^{7)}$		0.85$^{7)}$	
SrF_2	F_0, $\square_2$	1.74$^{4)}$ 2.28$^{6)}$ 5.3$^{10)}$ 2.3$^{11)}$	5.5$^{4)}$	0.94$^{4)}$ 1.0$^{6)}$	2.2$^{4), 5)}$	0.94$^{4)}$ 1.0$^{6)}$	2.2$^{4), 5)}$

1) [104] D, σ
2) $\nu_{Deb} = 9.9 \times 10^{12}\ s^{-1}$ [105]
3) decreasing from 200 to 600 °C [105]
4) [106] σ
5) $\nu_{Deb} = 8 \times 10^{12}\ s^{-1}$ [105]
6) [107]
7) assuming $\mu_{\square\ vac} > \mu_{\bigcirc\ int}$ [105]
8) assuming $\mu_{\bigcirc} > \mu_{\square}$ [105]
9) [108], theoretical value
10) [109] σ

Crystals of KCl are very often used for the investigation of the effect of colouring upon their properties. The qualitative effect of the additive colouring is the same as, e. g., in the case of irradiation.

In the interpretation of the temperature coefficient of conductivity of additively coloured alkali halides [15–22] there is a discrepancy, which can be found also in the problem of the source of carriers. According to **Mott** and **Gurney** [15], who used the experiments done by **Smakula** [16] and **Shamovski** et al. [17] as well as **Maycock** [18], the conductivity is of an ionic character, while the mechanism is provided by negative ion vacancies.

On the other hand, **Jain**, **Sootha** and **Kothari** [19–21] interpret the increased conductivity of coloured crystals as caused by the thermionic emission of electrons from colloidal metal particles, which has been confirmed also by the diffusion experiments of **Jain** and **Parashar** [22]. The electronic character of conductivity appears therefore as the most suitable explanation of the excess conductivity in such crystals. (Tab. 2a, 2b, 2c.)

Table 1c

Intrinsic defects — silver halides
$\bigcirc_1$— positive excess charge in interstitial site

Crystal	Defects	H [eV]	S/k	H_{m_1} [eV]	S_{m_1}/k	H_{m_2} [eV]	S_{m_2}/k
AgCl	Ag $\bigcirc_1$, $\square_2$	1.28$^{1)}$ 1.44$^{2)}$ 1.96–1.98$^{6)}$	6.0$^{1)}$ 9.4$^{2)}$ 11.5$^{3)}$	0.16$^{1), 3)}$ 0.055$^{2), 3)}$ 0.151$^{3)}$	−0.71$^{1), 4)}$ −2.76$^{2), 4)}$	0.35$^{1)}$ 0.27$^{2)}$ 0.32$^{3)}$	0.68$^{1), 4)}$ −0.76$^{2), 4)}$
AgBr	Ag $\bigcirc_1$, $\square_1$	1.06$^{1)}$	6.1$^{1)}$	0.15$^{1)}$	−0.88$^{1), 5)}$	0.34$^{1)}$	1.75$^{1), 5)}$

1) [101] σ
2) [102] σ
3) [103] σ
4) $\nu_{Deb} = 3.8 \times 10^{12}\ s^{-1}$
5) $\nu_{Deb} = 3.0 \times 10^{12}\ s^{-1}$
6) [86], theoretical value

The mobility of electrons in KCl is approximately independent from temperature, so that electronic conductivity can be computed by the application of the theory of contact between metal and insulator:

$$\sigma_e = \sigma_c - \sigma_u = BT^{3/2}S \exp\left[-(\Phi - \chi)/kT\right],$$

where B is a constant, S is the sum of the surface areas of all colloidal particles, Φ is the working function for the thermionic emission from the pure potassium into the vacuum and χ is the electronic affinity of KCl, i. e. the energy of the bottom of the conductivity band with respect to the vacuum. When the temperature increases, the exponential factor S decreases, since at higher

Table 2a
Impurity defects — alkali halides

H_m^* — is obtained most exactly from „pure crystal“ without added impurities; however the type of impurity, high concentration of it, and its form can affect H_m in impurity crystal; H_d — reorientation of dipole; H_{ma} — migration of dipole; H_s — solubility.

System	H_a or G_a [eV]	H_d [eV]	H_{ma} [eV]	H_s [eV]	H_m^* [eV]
KCl : Cd^{2+}	0.51[1] 0.32[2], [3]		0.54[1]		
Ca^{2+}	0.52[4] 0.32[2], [3] 0.46[8]	0.63[5] 0.62[6] 0.61[9] 0.64[10]	0.66[6]		0.63[7]
Sr^{2+}	0.42[11] 0.58[15]	0.66[5] 0.63[9] 0.67[10]	0.73[12]		0.76[13], [14] 0.77[4] 0.75[16] 1.86_2[17] 1.9_2[18] 0.657[7] 0.74[19] 1.8_2[19]
Pb^{2+}	0.58 – 0.41[20] 0.26[21]	0.65[9]	1.18[20]		0.78[21]
Ba^{2+}	0.57; 0.61; 0.55[22]	0.70[12]	0.74[12]	0.88[22]	0.78 – 0.87[22]
Co^{2+}					0.75[23]
Be^{2+}					0.45[24]
KCl : $Ce^{2(3+)}$			1.03[25], [26]		
Cu^{2+}					0.09[27]
SO_4^{2-}					1.77_2[19] 1.87_2[28] 2.20_2[29] 1.18_2[30]
KBr : Cd^{2+}	0.22[31]			1.28[32] 1.22[31]	0.64[31]
Ca^{2+}	0.42[32] 0.46[32]			0.72[32]	0.665[32] 0.65[4] 0.66[33]
Sr^{2+}		0.65[10]		1.14[32]	0.65[10]
Pb^{2+}	0.27[21]			1.14[21]	0.68[21]
Ba^{2+}	0.28[35]	0.69[5]		1.88[32]	0.68[10] 0.84[35] 0.67[7]
CO_3^{2-}				2.12[32]	0.87_2[32]

Table 2a (continued)

System	H_a or G_a [eV]	H_d [eV]	H_{ma} [eV]	H_s [eV]	H_m^* [eV]
SO_4^{2-}					1.02_2[31] 0.94_2[36]
KJ : Mg^{2+}	0.48[37]				1.21[37]
Cd^{2+}					0.87[38] 0.65[39]
Ca^{2+}	0.38[37]				1.21[37]
Sr^{2+}	0.42[37] 0.54[41]	0.58[10]			1.21[37] 0.58[10] 0.86[40]
Pb^{2+}	0.28[21]				0.69[21]
Ba^{2+}	0.26[42]			0.56[42]	0.72[42]
CO_3^{2-}					1.5_2[42] 1.12_2[44]
NaBr : Ba^{2+}					1.80[45], [46] 1.18_2[46]
LiF : Mg^{2+}	0.7 – 0.8[47] 0.4[55] 0.36[59]	0.75[48] 0.65[51] 0.64[56], [57]	0.79[49] 0.75[52]		0.70[50] 0.72[53], [54] 0.75[58], [57]
Cd^{2+}		0.54[57]			
Sr^{2+}		0.51[57]			
Mn^{2+}		0.51[57]		0.8[55]	
Ni^{2+}		0.62[57]			
Co^{2+}		0.61[57]			
$Ti^{2(3+)}$	0.48[43]				0.70[43]
LiJ : Mg^{2+}					0.43[34] 0.42[54]
LiCl : Cd^{2+}				–0.25[22]	0.52 – 0.46[22]

[1] [110] *D*, 380 – 500 °C
[2] [111], theoretical value
[3] [112], theoretical value
[4] [4] σ
[5] [113] Δ_e, *ITC*
[6] [114] Δ_e
[7] [29] *ITC*
[8] [115] σ, using $H_m = 0.81$ eV [4]
[9] [116] *ITC*
[10] [34] Δ_e
[11] [74] σ
[12] [27] Δ_e
[13] [3] σ
[14] [5] σ
[15] [96] σ
[16] [6] σ
[17] cited in [52]
[18] [56] σ
[19] [7] σ
[20] [117, 118] *D*, 373 – 500 °C
[21] [119] σ
[22] [93] σ

[23] [120] σ

[24] [30] D

[25] [121] D

[26] from diffusion in heavily doped samples [105]

[27] [122] σ

[28] cited in [3]

[29] [9] σ

[30] [10], theoretical value

[31] [123] σ

[32] [31] σ, $S_s = -4.8$ (Ca^{2+}), $S_s = 7.3$ (Sr^{2+}), $S_s = 13$ (Ba^{2+}), $S_s = 3.6$ (Cd^{2+}), $S_s = 8.4$ (CO_3^{2-})

[33] [18] σ

[34] [63] σ

[35] [124] σ

[36] [35] σ, Δ_e

[37] [42] σ

[38] [39] σ, $S_m/k = 4.1$ (Cd^{2+} in KJ)

[39] [41] crystals coloured with I_2 in temperature range 90–200 °C

[40] [40] theoretical value

[41] [97] σ

[42] [46] σ

[43] [54] σ

[44] [48] D

[45] [36, 37] σ, $S_m/k = 3.58$ (Ba^{2+} in KBr)

[46] [38] σ, D

[47] [125] σ

[48] [126] Δ_c

[49] [127] Δ_e

[50] [52] σ

[51] [128] Δ_e

[52] [129] Δ_e

[53] [50] σ

[54] [53] σ

[55] [91] σ, *ESR*

[56] [130] *ITC*, Δ_e

[57] [58] *ITC*

[58] cited in [52]

[59] [56] σ

Table 2b*

Impurity defects – silver halides

H_d^* relates to the strongest side-peak, mostly unidentified, [105]

System	H_a [eV]	H_d [eV]	H_d^* [eV]	H_{ma} [eV]
AgCl : Cd^{2+}	0.47[1] 0.27[2] 0.37[15]	0.37[3] 0.39[4]		0.61[15]
Cr^{2+}		0.37[3]		
Cr^{3+}			0.30[3], [5]	
Fe^{2+}	0.27[2]			
Co^{2+}		0.37[3]		
Ni^{2+}		0.37[3]		
S^{2-}	0.5[2], [6]		0.17[4], [7]	
Se^{2-}		0.039	0.12[4], [7]	
Na^+				0.54[8]
Cu^+	0.55[2], [9] 1.03[1], [9]			0.40[10]

* Tab 2b is from reference [105]

Table 2b (continued)

System	H_a [eV]	H_d [eV]	H_d^* [eV]	H_{ma} [eV]
AgBr : Cd^{2+}	0.16[2] 0.21[11]	0.31[3] 0.29[4]		0.55[11], [12]
Cr^{2+}		0.36[3]		
Cr^{3+}			0.25[3], [5]	
Mn^{2+}				0.74[12], [14]
Fe^{2+}	0.16[2]	0.32[3]		
Co^{2+}		0.33[3]		
Ni^{2+}		0.34[3]		
O^{2-}		0.06[4]		
S^{2-}	0.4[2], [6]	0.075[4]	0.22[4]	
Se^{2-}		0.75[4]		
Te^{2-}		0.045[4]		
Cu^+	0.56[2], [9]			0.45[10]

[1] [102] σ

[2] [101] σ

[3] calculated from [131] Δ_e

[4] [132] Δ_e

[5] halogenated crystal

[6] rough estimate

[7] 4 additional side-peaks

[8] [133] D, interchange with $\square_1$

[9] reaction enthalpy for $Cu_1 - Cu_0 + \square_1$

[10] [134] D interstitial migration of Cu_0

[11] [135] D

[12] from diffusion in heavily doped samples

[13] [135] Δ_e

[14] [137] D

[15] [138] D

temperatures more and more colloids are changed into F-centers. These two processes yield a maximum on the curve σ_c/σ_u vs T (°C). When the temperature of the peak is attained, the factor S is decreasing so quickly that the surplus electronic conductivity begins to decrease. From the graph $(\sigma_e/AT^{3/2})$ vs $1/T$ it follows that $\Phi - \chi = 1.94 \pm 0.04$ eV. A is the area of absorption band, σ_c, σ_u the conductivity of the coloured or uncoloured crystal, respectively, under the assumption that $\Phi = 2.26$ eV for potassium is $\chi = 0.32$ eV [19].

A long-term application of the electric field to the coloured crystal at constant temperatures in the interval 300–470 °C causes a decrease of the excess

Table 2c
Impurity defects — alkali earth halides

System	H_a [eV]	H_d [eV]
$CaF_2 : Na^+$	0.07[1]	0.53[5], [8]
Y^{3+}	1.43[1] 0.12[7]	1.2[2] 1.16[7]
Al^{3+}		0.74[3]
$SrF_2 : Na^+$	0.50[6]	
Y^{3+}	0.16[6] 0,09[7]	1.01[7]
O_2^-	0.46[6]	
$BaF_2 : K^+$	0.32[4]	
Y^{3+}	0.06[7]	0.86[7]

[1] [104] D, σ
[2] [139] Δ_m
[3] [140] Δ_e
[4] [107] σ
[5] [141] Δ_e, Δ_m
[6] [106] σ
[7] [142] Δ_e
[8] [143] Δ_e, Δ_m

conductivity. By the field effect the excess alkali metal is partially removed from the crystal (the colloids move from the cathode end of the crystal) so that the excess conductivity is decreasing [19].

The properties of an additively coloured ,,pure“ KCl listed in literature are in essence identical [19, 20, 23, 24]. When divalent cation impurities are added, the properties of such coloured crystals compared with the ,,pure“ ones are undergoing a change according to the type of impurity applied, e. g. in the system $KCl + Mg^{2+}$ [25], the excess conductivity caused by potassium colloids (observed in pure crystals in the interval 300—500 °C) is not observed. Results of conductivity measurements [25] (as well as E. S. R. and optical measurements) support the opinion, that in $KCl + Mg^{2+}$ no potassium colloids are formed. Excess conductivity caused by potassium colloids was observed in a barium-doped crystal [19], however not in a cadmium doped one [19].

Quenched crystals of KCl doped with strontium and barium were used for the investigation of the kinetics of aggregation of dipoles into higher complexes by the method of dielectric relaxation [26, 27] listed for the sake of comparison with the NaCl system in [49].

Confirmation of the formation of higher complexes was obtained also from

Table 3
Comparison of activation enthalpies of free cation vacancies and reorientation pairs of impurity-vacancy

(Values in the second column are from Tab. 2.)

System	Activation enthalpy [eV]	
	free vacancy	bound vacancy
$KCl : Ca^{2+}$ Sr^{2+} Ba^{2+}	0.71	0.63—0.64[1], [3] 0.66—0.67[3], [5] 0.70[5]
$KBr : Sr^{2+}$ Ba^{2+}	0.62—0.67	0.65[1] 0.68—0.69[1], [3]
$KJ : Sr^{2+}$	1.21	0.58[1]
$NaBr : Ca^{2+}$	0.80	0.62[1]
$NaF : Ca^{2+}$		0.87[1]
$LiF : Mg^{2+}$	0.65—0.73	0.65—0.75[1], [2]
$LiCl : Mg^{2+}$	0.41	0.42[1]
$LiBr : Mg^{2+}$	0.39	0.40[1]
$LiJ : Mg^{2+}$	0.38	0.35[1]
$AgCl : Cd^{2+}$	0.27—0.34	0.37[8]
$AgBr : Cd^{2+}$	0.31	0.31[8]

[1] [34] Δ_e
[2] [126] σ
[3] [144] *ITC*
[4] [14] Δ_e
[5] [27] Δ_e
[6] [145] σ
[7] [146] Δ_e
[8] [105] D, σ

the conductivity decrease of quenched crystals of $KCl + Ca^{2+}$ during annealing; the number of free vacancies was decreasing exponentially with time, the activation energy of the decrease being 0.63 ± 0.1 eV [28]. (Tab. 3.)

For the observation of the association and the aggregation of KCl crystals doped with Sr^{2+} and Be^{2+} the *ITC* method was used [29, 30], the results of which are summarized in table at the end of the study.

2.2. KBr, KJ

The conductivity results for KBr crystals, obtained by Rolfe [31] are in Figs. 2 and 3. The difference of the effect of cation and anion impurities on the temperature dependence is quite evident. The activation energy for the formation of a pair of the Schottky vacancies — according to Rolfe — is 2.53 eV, which is in agreement with the experimental data of 2.3—2.4 eV according to Maycock. The theoretical value from the original computation of Mott and Littleton [32] is 1.92 eV. More precise computations of these activation energies for alkali halides, however, were not applied by **Fumi** and **Tosi** [33] to KBr. The activation energy for the migration of the cation vacancy is 0.665 eV [31] and the anion vacancy 0.87 eV [31]. The migration energy of the cation vacancy was measured by several authors. **Gründing** [4] obtained the value of 0.65 eV and **Maycock** 0.66 eV from the conductivity measurements. **Dryden** and **Meakins** [34] found the values of 0.65 eV and 0.68 eV from dielectric losses measurements. **Jacobs** et al. [35], by doping KBr with K_2SO_4, obtained from measurements of the conductivity for the migration energy of the anion vacancy — 1.02 eV and 0.94 eV from measurements of dielectric losses. (Tab. 4.)

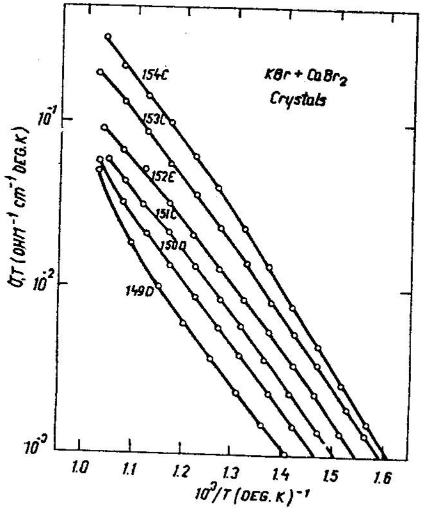

Fig. 2. Conductivity of KBr crystals doped with $CaBr_2$, the mole fraction of calcium impurity is: 149D — 24.7 ppm, 150D — 41.9 ppm, 151C — 82.9 ppm, 152E — 129.5 ppm, 153C — 254.2 ppm, 154V — 412 ppm [31].

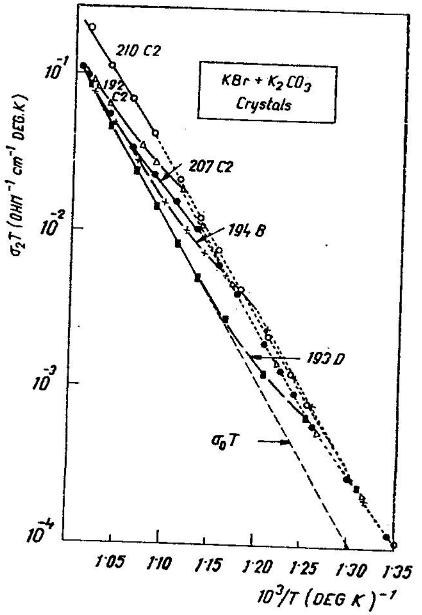

Fig. 3. Conductivity of KBr crystals doped with K_2CO_3, the mole fraction of carbonate impurity is: 193D — 0.9×10^{-5}, 194B — 3.0×10^{-5}, 207C2 — 4.8×10^{-5}, 192C2 — 9.6×10^{-5} [31].

The energy of association is according to **Rolfe** [31] 0.46 eV. This value differs from that of **Gründing** [4] who found the value of 0.56 eV in measurements of low-temperature conductivity in KBr crystals doped with Ca^{2+}. This difference can be caused by some precipitation, taking place together with the association in the case of Gründing's results. Rolfe's results, obtained at higher temperatures, should not be influenced by such a mistake.

Table 4

Vacancy pairs $\square_1$ $\square_2$

Crystal	$H - H_a$ [eV]	H_a [eV]	H_{ma} [eV]	Activation enthalpy for anion diffusion via vacancy pairs
KCl	1.34[1], [2]	1.04[1], [2]	1.50[3]	2.65[3]
KBr	1.41[1]	1.19[1]		2.60[4]
LiF	1.56[5] 1.33[6]			
AgCl	0.82[7], [8]		1.0[7], [9]	
AgBr			1.65[10]	

[1] [147] Δ_e

[2] [148] Δ_e

[3] [75] D, calculated with $H = 2.31$ eV

[4] [82] D

[5] [53] σ, calculated with $H = 2.68$ eV ($\Delta S = 5.376$ k)

[6] [149], measuring of density after quenching, $H = 2.41 \approx 0.10$ eV

[7] [150] σ

[8] Assuming $H = 1.25$ eV

[9] may apply to $\square_2$

[10] [151] D

The investigation of NaBr crystals pure and doped with divalent cations, e. g. Ba^{2+}, well soluble in this substance, yields according to **Hoshino** and **Shimoji** [36, 37] the following data of activation enthalpies: the enthalpy of the Schottky defect formation is 1.72 eV and the migration enthalpy of the cation vacancy is 0.80 eV, which is in agreement with the data of **Schamp** and **Katz** [38] obtained from the comparison of the results of conductivity and self-diffusion. The migration enthalpy of the Br^--vacancy is 1.18 eV [38].

The contribution of the anion vacancies to conductivity at high temperatures, observed in some alkali halides, e. g. KCl, KBr, RbCl is observed also in KJ. As regards this alkali halide there are among the published activation enthalpies of e. g. the migration of cation vacancy, considerable discrepancies; according to **Itami** et al. [39] the migration enthalpy of cation vacancy is 0.87 eV (conductivity measurement on KJ + Cd J_2 crystals). This value is in agreement with the theoretical result of [40] 0.86eV, based upon Einstein's model of solids. However, the values obtained from measurements of dielectric losses [34] (pure KJ crystals) of 0.58 eV, and from other conductivity measurements of 0.65 eV [41] (KJ crystals coloured with I_2 in the temperature range 90°—200 °C), and of 1.21 eV [42] (KJ crystals containing Mg^{2+}, Ca^{2+}, Sr^{2+}) are scattered. The experimental value for the formation of the Schottky deffect of 2.00 eV [39] is in relatively good agreement with the theoretical value of [40] 2.29 eV, while the value of Ecklin et al. [42] of 1.59 eV is too low. (Tab. 3, 5.)

The values of the effective activation enthalpy $\frac{1}{2}H + H_m$ from experimental measurements [43–45] (1.87–1.48 eV) are too scattered compared with the theoretical value of 2.00 eV [40].

Ba^{2+} is very easily soluble in KJ. The behaviour of KJ + Ba^{2+} is similar to that of NaCl and KCl crystals when they are doped with impurities of divalent cations. The solubility of some impurities in KJ, of e. g. Ca^{2+}, Pb^{2+}, Cd^{2+} is very weak and causes only an insignificant increase of the impurity conductivity [42]. An important rôle here is played obviously by the ionic radius of Ba^{2+}, which is slightly bigger that of K^+, while radii of other impurity ions are considerably smaller than r_K. This view is supported also by the well-known high solubility of the Tl^+ ion in KJ [47]. The radius of Tl^+ is very similar to that of $r_{Ba^{2+}}$.

Table 5

Calculated binding energies of pairs of anion-cation vacancies in the nearest (nn) and the nextnearest neighbour sites (nnn) [83]

Crystal	Binding energy [eV]	
	Nearest neighbours	Next-nearest neighbours
NaCl	0.60[1])	0.28[2])
KCl	0.72–0.76[1–3])	0.38[2])
KBr	0.61[3])	
KJ	0.40[3])	
RbCl	0.83[3])	
RbBr	0.68[3])	
RbJ	0.53[3])	

[1]) [152]
[2]) [112]
[3]) [81]

The conductivity graph of a pure KJ crystal contains a few regions (Fig. 4). At high temperatures, near to the melting point, the conductivity of the crystal is the intrinsic conductivity of anion vacancies (slope 2.30 ± 0.05 eV), then the intrinsic conductivity of cation vacancies (slope 1.50 ± 0.05 eV). The activation enthalpy for the migration of the cation vacancy determined from the slope of region II is 0.72 eV. The slope of region III is 0.85 eV, from which the value for the association energy is approximately 0.26 eV. The shape of the conductivity graph at lower temperatures indicates the formation of higher impurity-vacancy aggregates (or a precipitation of impurity in this region). A rough analysis of this region yields for the energy of the solubility of barium in KJ the value of about 0.56 eV.

The solubility of the anion impurity CO_3^{2-} in KJ is also satisfactory [46]. Qualitatively the behaviour of this impurity is the same as that of KBr crystals doped with K_2CO_3 [31], but the solubility of the carbonate in KJ is higher.

The doping of KJ with CO_3^{2-} causes a conductivity increase at lower temperatures due to the suppression of the concentration of cation vacancies according to the mass action law. The contribution of the anion vacancies to conductivity is insignificant at lower temperatures. The activation energy for

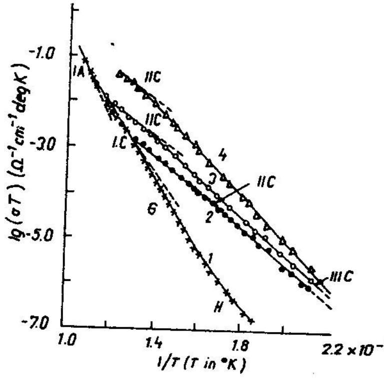

Fig. 4. Plots of lg σT vs $1/T$ for pure and Ba^{2+} – doped KJ crystals. Curve 1, pure KJ crystals; curves 2–4, KJ crystals doped with 0.4, 1.0 and 2.5 wt % $BaCl_2$ in the melt (IA — at temperatures greater than about 620°C, IC — at temperatures between 620 and 510°C, G — at temperatures between 510 and 350 °C and H — at temperatures below 350 °C) [46].

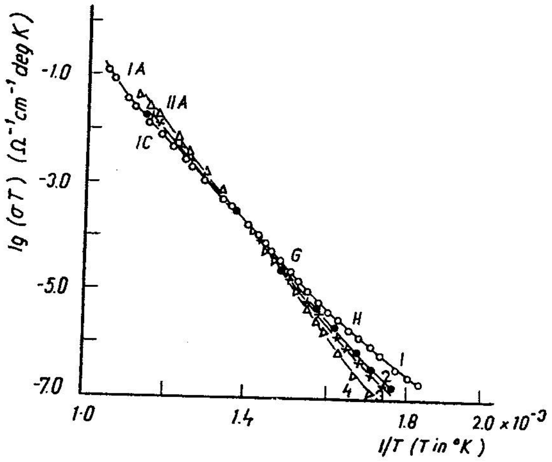

Fig. 5. Plots of log σT vs $1/T$ for pure and carbonate – doped KJ crystals. Curve 1 pure KJ crystal; curves 2–4, KJ crystals doped with 0.1, 0.5 and 1.0 wt % K_2CO_3 in the melt [46].

the migration of anion vacancy is 1.5 eV (Fig. 5), which is slightly higher than the value of 1.12 eV for the migration obtained from the diffusion of iodine in KJ [48].

3. Lithium halides

3.1. LiF, LiJ

Measurements of ionic conductivity of LiF crystals show that the course of conductivity, log σT vs $1/T$ has the expected character (Figs. 6, 7). The intrinsic region, especially for highly doped crystals is expressed in the graph by a continuously curved line, which makes impossible the direct determination of the activation energy.for the process of the intrinsic conductivity. It can be said that the conductivity within this temperature range, similarly as in the prevailing number of alkali halides is the result of the motion of the cation and the anion vacancies. In a similar way as described in the case of NaCl [49], making use of the diffusion data, the effect of the anionic influence upon the intrinsic region of the conductivity graph can be confirmed. For LiF the diffusivities were measured by applying NMR techniques. The self-diffusion coefficient F can be determined from Eisenstadt's data [50] as D_F $64 \times \exp(-2.2/kT)$ cm^2 s^{-1}; the two values for D_{Li} result from data of Stoebe and Huggins [51] $4.25 \exp(-1.87/kT)$ cm^2 s^{-1} and $2.4 \exp(-1.81 : kT)$ cm^2 s^{-1} from Eisenstadt's paper [50]. Using of D_{Li} from Eisenstadt, which is somewhat greater in magnitude and of a slightly lower slope the D_{Li} determined by Stoebe and Huggins beyond this temperature range, bigger values are obtained than those observed below ~ 725 °C [52], but which are in agreement with the observed data beyond this temperature [52]. (Tab. 6.)

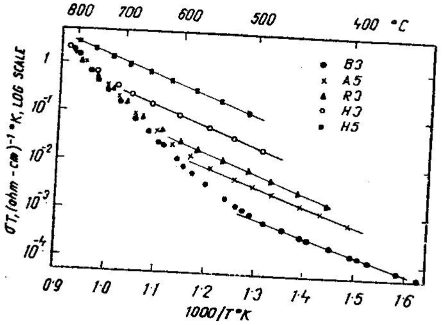

Fig. 6. Ionic conductivity results of LiF + + MgF$_2$ crystals in regions I and II (B3 — 1 Mg^{2+} ppm, A5 — 17 Mg^{2+} ppm, R3 — 82 Mg^{2+} ppm, H5 — 320 Mg^{2+} ppm) [52].

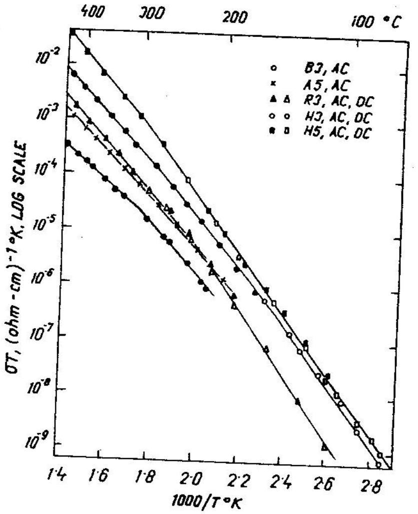

Fig. 7. Ionic conductivity results of LiF + + MgF$_2$ crystals in low-temperature regions (using the method of a. c. conductivity, d. c. conductivity) [52].

Table 6

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

System	E [eV]	ν_0/sec^{-1}
KCl : Sr^{2+}	0.73¹)	4×10^{13})
Ba^{2+}	0.74¹)	8×10^{15})

¹) [27] Δ_e

Comparison of the observed intrinsic curve proper with the intrinsic conductivity of Haven [53] indicates that his results correspond roughly to the slope and magnitude of the data by Stoebe and Pratt [52] beyond 675 °C; i. e. Haven's results correspond to the high-temperature tangent of the intrinsic curve. This was to be expected, as Haven used for doping high concentrations and therefore observed region I only in this interval, where there are important contributions of anions. The activation energy of region I given by Jain and Sootha [54] was also determined at the high-temperature end of the curve. This illustrates the difficulty in determing the real enthalpies for the vacancy motion and its formation by using the slope of region without the additional help of diffusion data or the numerical analysis, which latter separates contributions of anions from those of cations. This difficulty can explain some differences in the slope of region I as presented by various authors for some alkali halides. As known from literature, the contribution of anions at high temperatures was found (curvature of region I of pure crystals) also for NaCl contributions [49, 77, 79], KCl, e. g. [7], KBr [31].

The impurity — unassociated region yields the value of activation energy for the motion of cation vacancy, which for LiF is equal to 0.70 ± 0.02 eV [52], where the limits of error are determined first of all by the uncertainty of temperature limits of region II for a pure crystal, from which the value comes. This value is in agreement with data by **Jain** and **Sootha** [54] for Ti in LiF 0.70 eV. It is slightly lower that the value obtained by **Eisenstadt** [50] and **Haven** [53] 0.72 and **Bergé** [55] 0.75 eV. This is obviously caused by the inclusion of parts of the transition region in the mentioned measurements. (Tab. 7a).

Table 7a

Impurity diffusion — alkali halides

parameters D_0 and E are according to equation (6) from [49)

System	T [°C]	D_0 [cm²/s]	E [eV]	Ref.
KCl : Rb^+	600—760	26.8	2.04	153
Ag^+	200—650		0.42	154
Tl^+	270—400 250—550 550—730	1×10^{-3} 2×10^{-8} 2	0.88 0.43 1.70	155 156
Cu^+		10.6	1.23	122
Cd^{2+}	350—500	4.68×10^{-5}	0.54	110
Pb^{2+}	229—474 275—465	1.02×10^{-3} 1.82×10^{-2}	1.01 1.11	117, 118 155
Co^{2+}	200—650		0.20	154
$(Ce^{3+})Ce^{2+}$	500—700	1.1×10^{-3}	1.03	121
J^-	500—650	50	2.0	157
P^-	650—740	1×10^{9}	3.2	158
H_2O	200—770	35.5	0.8	159
KBr : Tl^+	350—500 550—700	50 4×10^{-5}	2.01 1.03	160
Pb^{2+}	275—400	1.5×10^{-3}	0.91	161
KJ : Tl^+	100—390 440—650	 8×10^{-3}	0.4 1.17	163 162
Cl^-	500—650	1.5×10^{-3}	1.13	157

Below region II the slope of the conductivity curve is steeper and the impurity-associated region III appears. The activation energy of this region is 0.9 eV [52] and using the migration energy of cation vacancy, 0.70 eV is the energy of association. e. g. for Mg^{2+} in LiF 0.4 ± 0.1 eV [52], 0.48 eV for Ti^{2+} in LiF [54] and 0.36 eV for Mg^{2+} in LiF [56].

At even lower temperatures the activation energy increases up to 1.1 eV [52]. This is probably caused by the aggregation or precipitation and the value is similar to that, which was found by **Barsis** et al. [56]. This behaviour is even more evident by the presence of OH^- ions in the crystal [57].

The presence of OH^- ions in LiF crystals diminishes their conductivity similarly as in other alkali halides. This decrease is equal to about two orders compared with crystals of the same doping, but without OH^- [57]. Crystals, containing free OH^-, but nearly without cation impurities, show a decrease of the conductivity knee and a nearly linear intrinsic region down to 450 °C compared with 520 °C for a pure crystal (without OH^-) (Fig. 8). The total slope of the intrinsic region for these crystals indicates an activation energy of 2.05 ± 0 05 eV [57], which is nearly by 10 % higher than for crystals without OH^-.

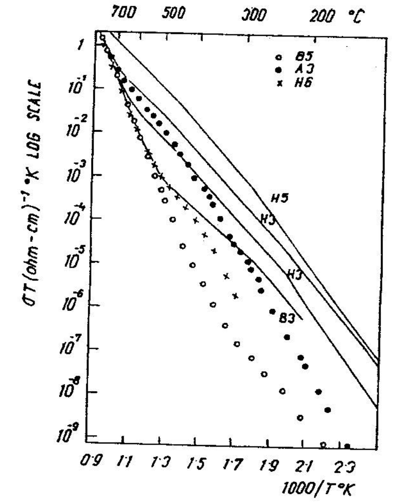

Fig. 8. Conductivity plot for LiF crystals doped with OH^- (B5, H6 and A3 compared with the conductivities of crystals B3, R3, R4 and H5, which are relatively free of OH^- ions [57]; B5 — 3 ppm, H6 — 10 ppm, A3 — 100 ppm) [57].

The impurity-unassociated region II is barely visible, as the slope of the conductivity graph immediately increases again below the knee of the curve. A low-temperature slope yields an activation energy of 1.1 eV or 1.4 eV. This behaviour can be explained by means of Mg^{2+} — OH^- complexes (confirmation by optical absorption). When the crystal is even more doped with divalent cation impurity, e. g. Mg^{2+}, the slope of the conductivity curve yields activation energies of 1.0 eV between 700—525 °C, of 1.2 eV between 500—400 °C and of 1.4 eV between 390 and 225 °C. These values can be compared with values for a crystal containing relatively less OH^- : 0 70 eV for region II and 0.9 eV for the association region As the slopes in the crystal with the highest OH^- concentration indicate higher activation energies, these can be connected with the formation of Mg^{2+}-vacancy complexes and with an equilibrium between these complexes and the impurity vacancies.

By the method of ionic thermocurrents (*ITC*) applied to LiF crystals doped with various divalent cation impurities [58] it is possible to determine with great accuracy the concentration of impurity-vacancy dipoles and the activation energy of the dipole rotation which decreases with increasing ionic radius (0.64 eV for Mg^{2+} to 0.51 eV for Sr^{2+}).

Dielectric losses of LiF measured in the interval 0–130 °C [59] yield the activation energy of 0.65 eV. Breckenridge quotes the value of 0.58 eV [60], but as he determined it only from measurements at one frequency he had to assume the value of the preexponential factor A (equation (4) in [49]). Haven's [53] value from the conductivity measurements is also 0.65 eV, although he performed the measurements in a higher temperature region than Dryden and Rao [59]. (Tab. 7b.)

Table 7b
Impurity diffusion – silver halides
(parameters D_0 and E are according to eq. (6) from [49]) [105]

System	T [°C]	D_0 [cm²/s]	E [eV]	Ref.
AgCl : Na^+	180–300	8.81	1.19	133
Cu^+	170–445	9.79×10^{-3}	0.40	134
Cd^{2+}	150–280	2.35×10^{-5}	0.56	164
	350–400	32.8	1.36	
		2	0.93	165
Mn^{2+}	210–300	5.3×10^{-4}	0.80	137
	300–430	7.7	1.27	
Co^{2+}	300–425	2.5×10^{-5}	0.76	166
Sr^{2+}		0.33	0.98	167
		0.30	0.96	168
Zn^{2+}		12	1.07	168
AgBr : Cu^+	70–405	5.04×10^{-2}	0.46	134
Cd^{2+}	190–300	(0.26)	0.95	
	300–405	(1×10^{-4})	1.45	135
	185–360	(2.6×10^{-3})	0.55	
Mn^{2+}	215–350	16.5	1.17	
	350–420	2×10^{-7}	1.93	137
	210–360	1.6×10^{-2}	0.74	

LiJ is an exception among the Li-halides due to the following properties: the concentration of defects near the melting point is by an order higher than for the common halides; no systematic dependence of the slope of region II on impurity concentration exists here. According to Stasiw and Teltow [61], no association theory as formulated by Dreyfus and Nowick [62] can be applied to LiJ. When the most reproducible value of $H_m = 0.43$ eV [63] is used, the enthalpy of the formation of H (from slope of region I — 0.96 eV) equals 1 06 eV. These values contrast with those of Haven [53] $H = 1.32$ eV and $H_m = 0.42$ eV. Since the concentration of defects at melting point is by Jackson and Young [63] — x_0/T_m 0.18 at %, which is in agreement with other alkali halides (it never goes beyond 0.2 at %), it is possible that Haven used a material with a high concentration of an electrically non-effective Mg combined with oxygen.

4. Caesium halides

4.1. CsCl, CsBr, CsJ

It is known that alkali halides crystallize under normal temperature and pressure in the NaCl structure (B1) with the exception of CsCl, CsBr and CsJ, which produce the CsCl structure (B2). CsCl is the only alkali halide known to display the phase transition at normal pressure. Measurements with X-rays show that at temperatures below 470 °C it is stable in the CsCl structure (B2) and at higher temperatures in the NaCl structure (B1).

In pure CsCl the activation enthalpy H determined from conductivity measurements by Arends and Nijboer [64] for B1 and B2 is considerably different, $H_{B1} > H_{B2}$. This observation is in disagreement with the data established by Harpur et al [65] and Morlin [66]. From diffusion measurements done by Laurent et al. [67] it is known that in CsCl the anion diffuses with a higher rate than Cs in both phases. Apart from this, the determined migration enthalpy of the anion for the B2 phase in CsCl is of the order of 0.2–0.3 eV, while for CsBr it is 0.27 and 0 30 eV for CsJ. Thus, when the Schottky defects prevail in CsCl, we can compute from the activation enthalpy 1.34 eV, for the B2 phase the enthalpy of the vacancy formation of 2.18 eV. This value is in good agreement with the values of 2.0 and 1.9 eV for CsBr or CsJ [67]. For the B1 phase the migration energy for the anion in CsCl is not known. Computation of Mott and Littleton [32] yields the theoretical value of enthalpy for the Schottky defect formation as equal to 2.05 eV. In this way we may obtain for the B1 phase the migration enthalpy of the anion vacancy equal to 0.7 eV, compared with 0.95 eV for KCl and 1.06 eV for NaCl [68]. (Tab. 8.)

Table 8
Intrinsic defects — cesium halides

Crystal	Defects	H [eV]	H_{m_1} [eV]	H_{m_2} [eV]
CsCl	□₂, □₁	1.1[1] 1.03 – 1.78[5], [6] 1.86[4] 1.78[7] 1.64[8] 2.05[2] 2.18[11]	0.6[4]	0.5[1] 0.34[4] 0.38[8] 0.2 – 0.3[10] 0.7[11]
CsBr	□₂, □₁	2.0[2] 1.03 – 1.65[6]	0.58[2]	0.27[2]
CsJ	□₂, □₁	0.78[3] 1.9[2] 1.11 – 1.98[6]	1.10[3] 0.58[2]	0.3[2]

[1] [66] σ, assuming only mobile cation vacancy
[2] [69] D, σ
[3] [99] σ
[4] [71] D, σ
[5] [81], theoretical value
[6] [100], theoretical value
[7] [71] D, (B2)
[8] [70] σ, (B1)
[9] [32], theoretical value
[10] [67] D, (B2)
[11] [64], theoretical value; calculated from $H = 2.05$ eV; experimental value for (B1) phase is unknown

Very small amounts of divalent impurity influence both the behaviour of the conductivity in the transition region, and the activation enthalpy of B1. It can be computed from graph results that, e. g. 0.02 mol% of Ca^{2+} diminishes the H_{B1} by 0.16 eV [64]. The activation enthalpy H_{B2} is less sensitive to impurity concentration. The mentioned amount of calcium diminishes it by 0.04 eV. The activation enthalpy of the jump of vacancies of Cs^+ introduced by Ca^{2+} ions is 0.64 ± 0.03 eV, in agreement with the published data [66, 69]. (Tab. 9.)

The general behaviour of σ at the phase transition is hardly affected by the magnitude of the concentration of impurity, as it was found by Weijma and Kottnerus investigating the system of $CsCl + Ba^{2+}$ [70]. (Fig. 9). From the impurity slopes II they found directly the migration enthalpy of cation vacancies in two phases, i. e. $H_{mB1} = 0.77$ eV and $H_{mB2} = 0.64$ eV. Morlin found in $CsCl + Sr^{2+}$ that $H_{mB2} = 0.5$ eV [66]. The difference is probably due to the size of ions, which was found also in KCl doped wita Ca, Sr and Ba By making use of the self-diffusion results in CsCl [71], it is possible to determine the enthalpy of the formation of the Schottky pair defects in B2 — CsCl as $H_{B2} = 1.78$ eV. This value is in good agreement with theoretical computations. Apart from this, combination of H_{B2} and the results in [71] yields the value of the migration enthalpy of the anion vacancy $H_{mB2} = 0.38$ eV.

Table 9
Impurity defects — cesium halides

System	H_a or G_a [eV]	H_s [eV]	H_m [eV]
CsCl : Ba^{2+}	0.88[1]		0.77_1 (B1)[1] 0.64_1 (B2)[1]
Ca^{2+}			0.64[3], [4]
Sr^{2+}			0.5 (B2)[4]
Br^-			1_1 (B2)[2] 2.1_2 (B1)[2]
CsJ : Ba^{2+}		1.34[5]	0.61_1[5]
Sr^{2+}			0.3_2[5]

[1] [70] σ, cation migration in both phases
[2] [72] σ, anion migration in both phases
[3] [69] σ
[4] [66] σ
[5] [73] σ

When considering the conductivity exclusively through the vacancies in the B1 phase, we obtain the enthalpy of the formation $H_{B1} = 2\,(1.59 - 0.77) = 1.64$ eV, since experimentally it is possible to include into the conductivity also the contribution of anion vacancies.

In the third region of the conductivity graph association and precipitation

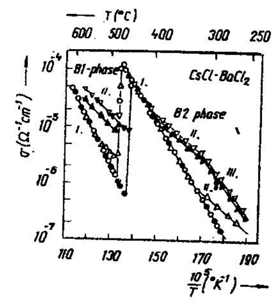

Fig. 9. Conductivity σ of pure and with Ba^{2+} — doped CsCl single crystals as a function of temperature (○ — pure, increasing temperature, ● — pure, decreasing temperature; △ — 15 ppm Ba^{2+}, increasing temperature; ▲ — 75 ppm Ba^{2+}, increasing temperature; ▽ — 80 ppm Ba^{2+}, increasing temperature; ▼ — 80 ppm Ba^{2+}, decreasing temperature) [70].

are taking place. By considering purely the association of impurity ions and cationic vacancies, the enthalpy of the association 0.88 eV can be computed. However, the role, effect of precipitation in region III is not yet known. Therefore the real association enthalpy could be smaller than this value.

Measurements were performed also on single crystals of CsCl doped with Rb^+, K^+ and Br^- [72]. Results show that already a small concentration of these monovalent ions is of considerable importance for the activation enthalpies in both phases as well as for the hysteresis behaviour. It appeared that decrease of the activation enthalpies in crystals doped with Rb^+ and K^+ and the theoretical computation yield the value $H_{BI} = 2.05$ eV [72]. Possibly, the independence of these enthalpies on the Br^- concentration can be ascribed to the size of ions. The introduction of cations with the ionic radius smaller than the host ion Cs ($r_{Cs^+} > r_{Rb^+} > r_{K^+}$) significantly increases the contribution of the cations to conductivity (a 5 % increase of K^+ causes a 70 % increase of σ). The effect of K^+ ions on the activation enthalpy is far stronger than the effect of Rb^+. (Tab. 10.)

Table 10

Impurity diffusion — cesium halides
(parameters D_0 and E are according to eq. (6) from [49]) [105]

System	T [°C]	D_0 [cm²/s]	E [eV]	Ref.
CsJ : Tl^+	200—440	1×10^{-6}	0.37	156
	440—570	9×10^{-2}	1.09	

The numerical values of the migration enthalpy for Br^- ions are 1 and 2.1 eV for the CsCl, or the NaCl phase respectively; the value for the Cl^- ions in CsCl equals 0.34 eV. Theoretically, the migration enthalpy can be computed according to the simple model of Mullen [40], extended to Cs halides.

The conductivity of pure CsJ and one doped with Ba^{2+} and Sr^{2+} is, below the temperature of 300 °C, irreproducible and depends upon the heat history of the sample. The activation enthalpy in this region varies between 0.4—1.1 eV [73]. Beyond 300 °C its value is in all pure crystals 1.37 ± 0.4 eV. In doped crystals, a region connected with the dissolving of impurities in the lattice was observed. Its analysis yields the value 1.34 eV for the heat of solubility and 0.61 eV for the migration enthalpy of the cation vacancy. The assumption that region I is predominantly the result of simple anion vacancies leads to the value of 0.3 eV for the migration of the cation vacancy. The enthalpy of the formation of the Schottky defects in the lattice is 2.14 eV. The heat cycle produces a hysteresis effect in conductivity.

5. Conclusion

On the whole, we can say about the other alkali halides in essence the same as about NaCl in Part I.

In order to find one or more ion transport parameters, a great number of experiments with alkali halide 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, e. g., of vacancies of both types, trivacancies, interstitials, has not been determined satisfactorily.

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