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F BAND IN X- AND ELECTRON-IRRADIATED CaF_2

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ANION CONTRIBUTIONS TO THE ELECTRICAL CONDUCTIVITY OF ALKALI CHLORIDES

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The measured electrical conductivity of pure RbCl is separated into the usual anion and cation contributions with activation energies of 2.55 and 1.58 eV, respectively. By comparison with corresponding results for KCl and NaCl it is found that the alkali-chloride anion and cation activation energies differ most for nearly equal anion and cation radii. We conclude from this anomalous trend that an extension of conventional theory is required.

The intrinsic electrical conductivity of alkali-halide crystals is, in principle, the sum of the anion (−) and cation (+) contributions and is expressible as the sum of two exponentials in the following way:

$$\sigma T = \sigma_a T + \sigma_c T = A_0 \exp(-W_a/kT) + C_0 \exp(-W_c/kT), \qquad (1)$$

where σ is the conductivity ($\Omega^{-1}\ \mathrm{cm}^{-1}$); σ_a and σ_c are the anion and cation contributions to σ, respectively; T is the absolute temperature (°K); W_a and W_c are the anion and cation activation energies for conduction, respectively; and A_0 and C_0 are constants. In general, W_a is not equal to W_c. Therefore, $\ln\sigma T$ is not a linear function of $1/T$. Experimental data from many experiments[1-6] have indicated, however, that σT could be expressed as a single $\exp(-W/kT)$ term. These same experiments gave evidence that the electric current was carried by mobile cations, and quite naturally the idea developed that anions were relatively immobile. Allnatt and Jacobs[7] observed curvature in a plot of $\ln\sigma T$ vs $1/T$ for pure KCl, which they associated with additional anion conductivity. This was substantiated by subsequent chlorine-ion diffusion measurements on KCl.[8]

The intrinsic electrical conductivity of RbCl crystals has been measured in the temperature range 550 to 700°C to look for evidence of anion contributions to the conductivity. Figure 1 shows the results, plotted in the usual way. The measurements were made using standard ac bridge techniques at 1 kHz. The tempera-

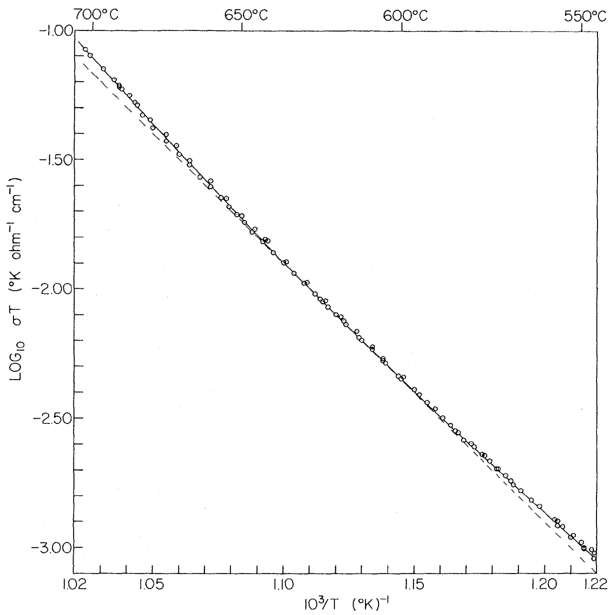

FIG. 1. Temperature dependence of the electrical conductivity of "pure" RbCl. The least-squares fit of the experimental data and 1.23 times $\sigma_c T$ [see Eq. (1) of text] inferred from G. Arai and J. G. Mullen [Phys. Rev. 143, 663 (1966)] are shown as solid and dashed lines, respectively.

ture uncertainty was 0.2°C and the experimental error in the magnitude of the conductivity was ±2% (represented by the circles in Fig. 1).

The analysis of the RbCl data was done using Eq. (1) and the method of least squares. The solid curve in Fig. 1 is the sum of the anion and cation contributions to the conductivity as determined by this analysis. The numerical results from our analysis of the RbCl data are shown in Table I along with values reported for NaCl by Laurance[9] and Dreyfus and Nowick,[6] and for KCl by Beaumont and Jacobs.[10] The estimated computational uncertainties for RbCl are a factor of 2 for A_0 and C_0 and ±0.05 eV for W_a and W_c. The analysis of the RbCl data was modified to include the existence of long-range Coulomb interactions between the cation and anion vacancies. This modification was made using the Debye-Hückel theory for electrolytic solutions,[11] and the results are given in parentheses in Tables I and II. Our identification of anion and cation components of the RbCl conductivity is based on the 1.99-eV activation energy of Rb-ion diffusion in RbCl.[12] This value sets an upper limit on W_c, since it was not corrected for the vacancy-pair contribution to the diffusion. It therefore appears consistent with our value of 1.58 eV.

The electrical conductivity data of Fig. 1 can be compared with diffusion coefficient (D_{Rb}) for Rb^+ in RbCl.[12] If the vacancy pair contribution is neglected, the Einstein relation gives the cation contribution to the conductivity $\sigma_c T = 3.23\times10^7 D_{Rb}$.[13] This expression, multiplied by the constant 1.23 for closer comparision with the measured values of σT, is represented by the dashed line in Fig. 1. Thus, as for NaCl and KCl, the intrinsic electrical conductivity cannot be explained as only cation conductivity. The curvature of the plot of $\ln\sigma T$ vs $1/T$ for RbCl is greater than the similar curvature reported for KCl.[10] It follows that for RbCl the values for the difference in activation energies, $W_a - W_c$, and the ratio of the pre-exponential constants, A_0/C_0, must be even larger than the KCl values[10] of 0.33 eV and 80.

Values for the anion transport number, the fraction of current carried by the anion, were calculated from Table I and are shown in Table II. These values agree with the two values obtained by the direct measurements of Haven.[14] Apparently, the reported linearity[6] of a plot of $\ln\sigma T$ vs $1/T$ for NaCl occurred not because of low anion mobility but because a precise measurement of the conductivity of NaCl had not been

Table I. Contributions to ionic conductivity.

	(°K/Ω cm) Anion (−) $A_0\exp(-W_a/kT)$	Cation (+) $C_0\exp(-W_c/kT)$	A_0/C_0
NaCl	$1.2\times10^9\exp(-2.07\text{ eV}/kT)$[a]	$4.7\times10^8\exp(-1.86\text{ eV}/kT)$[b]	2
KCl	$3.85\times10^9\exp(-2.17\text{ eV}/kT)$[c]	$4.63\times10^7\exp(-1.84\text{ eV}/kT)$[c]	80
RbCl	$8.85\times10^{11}\exp(-2.55\text{ eV}/kT)$	$3.58\times10^6\exp(-1.58\text{ eV}/kT)$	25×10^4
	$[2.55\times10^{11}\exp(-2.47\text{ eV}/kT)]$	$[1.79\times10^6\exp(-1.53\text{ eV}/kT)]$	$[14\times10^4]$

[a]Ref. 9. [b]Ref. 6. [c]Ref. 19.

Table II. Anion transport numbers.

Temp. (°C)	$\sigma_{anion}/\sigma_{total}$ NaCl	KCl	RbCl	RbCl[b]
747	0.20	0.65	···	
707	0.18 (0.14[a])	0.62	0.70 (0.68)	0.33
620	0.15	0.52 (0.54[a])	0.43 (0.41)	0.19
546	0.12	0.43	0.19 (0.19)	0.28

[a]Transport numbers measured by Y. Haven, Proc. Brit. Ceram. Soc. 1, 93 (1964).

[b]Transport numbers computed using our conductivity data and Rb^+ diffusion in RbCl (Ref. 12) uncorrected for vacancy pairs.

made for the entire intrinsic region (550 to 790°C) In KCl and RbCl the anions make contributions to the conductivity at 707°C which are even larger than that of NaCl but which decrease significantly with decreasing temperature.

For the alkali chlorides, as the difference between anion and cation radii decreases from 0.42 Å in NaCl to 0.01 Å in RbCl,[15] the difference between anion and cation activation energies increases from 0.2 to 1.0 eV. This trend is opposite to that shown in the calculations of Guccione, Tosi, and Asdenti.[16]

The ratio of pre-exponential terms can be expressed as

$$\frac{A_0}{C_0} = \frac{\nu_a}{\nu_c} \exp[(\Delta s_a - \Delta s_c)/k], \tag{2}$$

where ν is a vibration frequency and Δs is an activation entropy. Typical values for ν and Δs in these crystals are 5×10^{12}/sec and $3k$, respectively.[6] Assuming $\nu_a = \nu_c$, the A_0/C_0 values (Table I) give rise to unusually large values for the difference between anion and cation activation entropies, i.e., $(\Delta s_a - \Delta s_c) = 4.4k$ for KCl and $12k$ for RbCl. These anomalous values for $(\Delta s_a - \Delta s_c)$ are a direct consequence of the curvature of $\ln\sigma T$ vs $1/T$ and the assumed temperature independence of W_a and W_c. Curvature could be explained and more physically acceptable values of A_0/C_0 obtained if the activation energies were assumed to be slightly temperature dependent. Temperature-dependent activation energies could possibly be related to the apparent discrepancy between the low-temperature[17] and high-temperature[8] values for the anion migration energy in KCl.

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$$D_{\text{anion}} = (22^{+22}_{-11}) \exp\left(-\frac{(2.07\pm0.05)\text{ eV}}{kT}\right)\text{cm}^2/\text{sec},$$

$$D_{\substack{\text{vacancy}\\\text{pairs}}} = (990\pm90) \exp\left(-\frac{(2.50\pm0.02)\text{ eV}}{kT}\right)\text{cm}^2/\text{sec}.$$

For NaCl,

$$\sigma_{\text{anion}} T = 5.25\times10^7 D_{\text{anion}}.$$

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$$(\epsilon-1)/(\epsilon+2) = 0.544 \exp(1.65\times10^{-4}T)$$

and

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