decreases with the temperature, but the temperature dependence of the excess change seems to be smaller at higher temperatures. It is probably not possible to experimentally find the temperature at which the excess is zero (Fig. 2).

The solid state

There are three phases of particular interest, the f.c.c. phase in pure Li$_2$SO$_4$ and in mixtures with up to 40 mole\% Na$_2$SO$_4$, the b.c.c. phase with 40 to 60 mole\% Na$_2$SO$_4$ and the hexagonal phase with 60 to 100 mole\% Na$_2$SO$_4$ (I.e.9).

Diffusion in Cubic Sulphates

IV. $^{22}$Na and $^{24}$Na in f.c.c. Li$_2$SO$_4$

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Simultaneous diffusion of $^{22}$Na$^+$ and $^{24}$Na$^+$ in cubic lithium sulphate has been studied. The relative difference in diffusion coefficients for the two ions is (2.8 ± 0.4)\%.

The results are compared with previously obtained values for the $^6$Li and $^7$Li mobilities in lithium sulphate.

Some years ago LUNDÉN measured the relative mobility of the $^6$Li$^+$ and $^7$Li$^+$ ions in cubic lithium sulphate of natural composition and also the electrical conductivities of Li$_2$SO$_4$ and $^{7}$Li$_2$SO$_4$ have been studied. The obtained relative differences in mobilities (b) were 2.1 and 4.2\% respectively.

These values are lower than expected from a simple inverse mass root relation for the mobilities. The difference between $\Delta b$ for the isotopic pure salts and the mixture can easily be explained by assuming a cooperative transport model for the cations, where two ions are cooperating.

In a recent paper we have reported on diffusion measurements of Na$^+$ ions in pure lithium sulphate and we have assumed that the same mechanism is responsible for the lithium and sodium ion transport. This might, however, be confirmed by measuring the difference in diffusion coefficient of $^{22}$Na$^+$ and $^{24}$Na$^+$ in lithium sulphate.

The experimental technique has mainly been described elsewhere. The surface layer contained $^{22}$Na$^+$ and $^{24}$Na$^+$ of about the same radioactive strength. Gamma ray spectra were obtained by using a NaI(Tl)-crystal coupled to a multichannel analyzer. In the spectra, the intensity of the 0.54 MeV and 2.75 MeV peaks were compared and it was then possible to calculate $\Delta D/D$ by comparing the intensities with the spectrum of pure $^{22}$Na. The experimental time was between two and three hours.

The results are given in Table 1. No definite temperature dependence of the difference can be found from these measurements. The mean value of $\Delta D/D$ is (2.8 ± 0.4)\% with the higher diffusion coefficient for $^{22}$Na$^+$.

For two isotopes, one generally uses the relation

$$b_1/b_2 - 1 = - f \Delta K (m_1/m_2)^{1/2} - 1$$

where $m_1$ is the mass of the ion, $f$ a correlation factor and $\Delta K$ has been related to the share of the kinetic energy at the diffusive saddle point, which is associated with the diffusing ion rather than the surroundings.

For small isotope differences we obtain in our case with $f = 1$:

$$\Delta K = 2(\Delta D/D)/(\Delta m/m)$$

For $^{22}$Na$^+$ and $^{24}$Na$^+$ $\Delta K$ is 0.64 and this value should be compared, not with the electromigration value, but with the conductivity results, which gave $\Delta K_{Li} = 0.55$. The two $\Delta K$ values are in fair agreement, but the results support our previous transport model, where the ions mainly are diffusing between the octahedral positions in the lattice.

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A. KVIST and A. BENGTZELIUS, unpublished.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta D/D$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>694</td>
<td>3.1</td>
</tr>
<tr>
<td>721</td>
<td>2.7</td>
</tr>
<tr>
<td>730</td>
<td>2.5</td>
</tr>
<tr>
<td>771</td>
<td>2.3</td>
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<tr>
<td>774</td>
<td>2.5</td>
</tr>
<tr>
<td>776</td>
<td>2.3</td>
</tr>
</tbody>
</table>

5 L. BROMAN and K. KARLSSON, Nucl. Instr. and Meth. 44, 174 [1966].
9 A. BENGTZELIUS and A. KVIST, unpublished.