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).

It is possible to use our previous model for a calculation of the number of cooperating ions, but no conclusions can at present be drawn from this approximation.

The solid state

There are three phases of particular interest, the f.c.c. phase in pure Li_2SO_4 and in mixtures with up to 40 mole% Na_2SO_4, the b.c.c. phase with 40 to 60 mole% Na_2SO_4 and the hexagonal phase with 60 to 100 mole% Na_2SO_4 (l.c.[9]).

The transformation temperatures obtained from the conductivity experiments are in good agreement with the DTA results. For the three pure phases equations are given in Table 3. In the f.c.c. and b.c.c. phases, the activation energies are almost equal, about 8.4 kcal/mole. In the hexagonal phase, Q decreases when the lithium sulphate and also the disorder concentration increases. The diffusion coefficient of Na^+ in pure Li_2SO_4 has recently been determined[12] and diffusion experiments in lithium sulphate with different concentrations of sodium sulphate are in progress. A discussion of the transport mechanisms must therefore wait until the diffusion measurements are finished (l.c.[13]).

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Diffusion in Cubic Sulphates

IV. ^{22}Na and ^{24}Na in f.c.c. Li_2SO_4

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Simultanous 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 $(2.8 \pm 0.4)\%$. The results are compared with previously obtained values for the ^{6}Li and ^{7}Li mobilities in lithium sulphate.

Some years ago Lundén[1] measured the relative mobility of the $^6Li^+$ and $^7Li^+$ ions in cubic lithium sulphate of natural composition and also the electrical conductivities of $^6Li_2SO_4$ and $^7Li_2SO_4$ have been studied[2]. 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 $\Delta b/b$ 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[3] 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[4]. 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[5]. 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 ^{24}Na. The experimental time was generally between two and three hours.

Temperature (°C)	$\Delta D/D$ (%)
694	3.1
721	2.7
730	3.2
771	2.9
774	2.5
776	2.3

Table 1. The relative difference between the diffusion coefficients of $^{22}Na^+$ and $^{24}Na^+$ in cubic lithium sulphate.

The results are given in Table 1. No definite temperature dependence of the difference can be found from these measurements. The mean valueof $\Delta D/D$ 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_i is the mass of the ion, f a correlation factor and ΔK has been related to the share of the kinetic energy at the diffusitive saddle point, which is associated with the diffusing ion rather than the surroundings[6].

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 $^{24}Na^+$ $\Delta K_{Na} = 0.64$ and this value should be compared, not with the electromigration value, but with the conductivity results[2], which gave ΔK_{Li}, = 0.55. The two ΔK 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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