Self-Diffusion and Transport Mechanisms in Cubic Lithium Sulphate

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The self-diffusion coefficient of the lithium ion in cubic lithium sulphate has been measured from 640 to 790 °C. From electrical conductivity and electromigration experiments it has been found that several cations are moving in phase and the mean value of the number of ions in each group has been estimated to be about 2.0. The measurements of the self-diffusion coefficient indicate that we also have transport mechanisms, which contribute more to the diffusion than to the electrical conduction.

Several investigations of the transport mechanism of cubic lithium sulphate have been performed in this institute: In electromigration experiments Lundén [1] has studied the isotope effect of the two cations, Kvist and Lundén [2] have measured the electrical conductivity of the salt and Kvist [3] the electrical conductivity of $^6Li_2SO_4$ and $^7Li_2SO_4$. From the electromigration experiments Lundén has estimated the self-diffusion coefficient of the cations. It was, however, difficult to find a mechanism of transport, which could coordinate the obtained results and we found it probable, that the discrepances were caused by a too high self-diffusion coefficient of the cations (D^+). We decided therefore to remeasure D^+.

Experimental

Reagent grade lithium sulphate and potassium sulphate (Hopkin & Williams AnalaR) and enriched lithium sulphate (Oak Ridge National Laboratory) were used without furthter purification. The salts were dried at 180 °C before use. All measurements were performed in air.

About ten different experimental arrangements were tried in preliminary investigations, but it was found that it is not possible to get complete and immediate contact between two salt slabs, which had been cooled to room temperature before use.

In our final measurements, we therefore used the following experimental technique.

An approximately 40 mm long salt column (diameter 13 mm) was obtained in a quartz tube which was placed in a big thermostate bath, by melting pure lithium sulphate of natural composition and cooling it to just below the melting point, 860 °C. If one mole percent of potassium sulphate is added to lithium sulphate, the melting point decreases by about 10 °C (l. c. [4]). Such a mixture, in which we had changed the concentration of $^6Li_2SO_4$ by about four percent by adding enriched salt, was poured on the top of the other salt in the quartz tube, and when thits salt had molten, the salt column was cooled to the desired temperature as fast as possible. The total time from the pouring of the second salt to the reaching of the final temperature was only a few minutes. This time was very short compared with the difusion time, 3 to 5 hours.

After an experiment the salt column was cut into one mm thick samples, the lithium sulphate was converted into lithium nitrate and the $^7Li/^6Li$ isotope abundance ratio of every third sample was measured with a mass spectrometer.

Results and Discussion

If the end surfaces of two salt columns of infinite length containing different concentrations of $^6Li^+$ are brought in contact, it is possible to calculate the diffusion coefficient of the lithium ion from the distribution of $^6Li^+$ in the salt column after the time t, by using the relation [5]

$$\operatorname{erf} y = \left(\frac{c_1+c_2}{2} - c \right) \frac{2}{c_1-c_2} \qquad (1)$$

where $$y = x/2\sqrt{D^+ t}\,.$$

c_1 and c_2 are the concentrations of $^6Li^+$ in the two columns at $t=0$, and c the concentration of $^6Li^+$ at the distance x from the contact surface after the time t.

Since the diffusion time was only $3-5$ hours, Eq. (1) can be used with satisfactory accuracy.

The distribution curve of $^6Li^+$ on both sides of the contact surface gave the same diffusion coefficient and there was no indication that the addition of potassium ions had influenced the results.

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[1] A. Lundén, Z. Naturforschg. **17 a**, 142 [1962].

[2] A. Kvist and A. Lundén, Z. Naturforschg. **20 a**, 235 [1965].

[3] A. Kvist, Z. Naturforschg. **21 a**, 487 [1966].

[4] A. A. Nacken, Neues Jahrb. Mineral. Geol., Beilage Bd. **24 A**, 43 [1910].

[5] W. Jost, Diffusion in Solids, Liquids, Gases, Academic Press, New York 1960.

The results are tabulated in Table 1, and we have also plotted D^+ as a function of temperature in Fig. 1. The results differ from those obtained by Lundén[1] as a byproduct of his electromigration experiments.

Temp. °C	$D^+ \cdot 10^5$ cm²/s
640	2.62
680	2.93
735	(4.35)
760	4.46
780	4.43
790	4.66

Table 1. The self-diffusion coefficient of the lithium ion in cubic lithium sulphate. The measurement at 735 °C is uncertain, due to too long diffusion time.

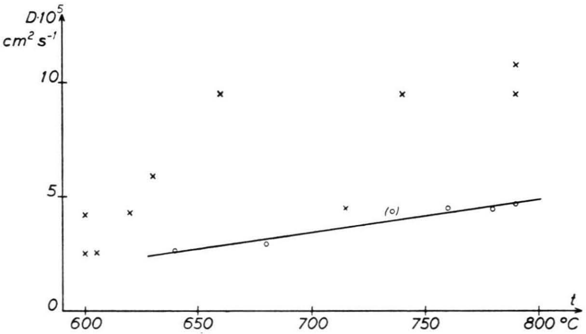

Fig. 1. The self-diffusion coefficient of the lithium ion in cubic lithium sulphate as a function of temperature. o: this investigation; ×: according to Lundén[1].

In a recent paper[3] we have proposed that there is a cooperative motion of cations in cubic lithium sulphate. From conductivity and electromigration measurements, we have estimated a mean value k of the number of cations moving in phase. We then obtained $k = 2.0$.

The relation between the equivalent conductivity Λ and the diffusion coefficient D^+ can be expressed by the Nernst–Einstein relation factor

$$\alpha^+ = \frac{t^+ \Lambda}{F^2} \cdot \frac{R\,T}{D^+ Z^+} \tag{2}$$

Temp. °C	$D^+ \cdot 10^5$ cm²/s	$\varkappa$ Ω^{-1}cm^{-1}	α^+
600	1.95	1.07	1.1
700	3.38	1.86	1.3
800	4.82	2.70	1.4

Table 2. The Nernst–Einstein relation factor, α^+, of cubic lithium sulphate. The density was taken to 2.08 g/cm³ at all temperatures[7].

where t^+ is the transport number, z^+ the valency of the cation, F the Faraday constant, T the temperature in °K and R the gas constant. Table 2 shows α^+ at three different temperatures.

The temperature dependence of the diffusion coefficient is generally written as an Arrhenius' equation

$$D = D_0\, e^{-Q_{\mathrm{D}}/RT} \tag{3}$$

where Q_{D} is the activation energy of diffusion.

In the same way the equivalent conductivity is often written

$$\Lambda = \Lambda_0 \exp\{-Q_\Lambda / R\,T\}\,. \tag{4}$$

If, however, we want to compare the activation energies of diffusion and conduction, we should write[6]

$$\Lambda\,T = (\Lambda\,T)_0 \exp\{-Q_{\Lambda T}/R\,T\}\,. \tag{5}$$

From Eqs. (3) and (5) we obtained

$$Q_{\mathrm{D}} = (7850 \pm 960)\ \text{cal/equiv.},$$
$$Q_{\Lambda T} = (10\,150 \pm 700)\ \text{cal/equiv.}$$

Less energy is thus needed for diffusion than electrical conduction and this indicates that we have different mechanisms of transport.

From the conductivity and electromigration experiments we found that the mean value of the number of ions taking part in a cooperative motion is two and we have assumed that we have the same coupling mechanism in diffusion. A jump of several ions in the same direction contributes more to the conduction than to the diffusion, and if we had the same mechanism of transport we should get $\alpha^+ \geqq 2$, but α^+ is only about 1.3. We must then also have a motion of ions, which contributes more to diffusion than to conduction.

If some ions move forewards and some ions at the same time move backwards, we get a kind of ring mechanism[2], which probably will need less energy than simple jumps and α^+ is then smaller than k.

According to Table 2, α^+ increases somewhat with the temperature and this indicates that the ring mechanisms are more important at low than at high temperatures.

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[6] A. J. Dekker, Solid State Physics, Academic Press, London 1962, p. 172 and 177.

[7] H. Øye, Theses, Trondheim 1963.