Phase Diagram and Transport Properties of Cubic Lithium Sulphate with Small Quantities of Thulium Sulphate and Aluminium Sulphate

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The phase diagram and electrical conductivity of cubic lithium sulphate with small quantities of thulium sulphate and aluminium sulphate have been measured. We have also measured the tracer diffusion coefficients of Tm^{3+} and Al^{3+} in pure cubic lithium sulphate. The diffusion coefficients of the trivalent ions are much lower than those of the univalent and divalent cations. The results indicate that the trivalent ions are trapped in the lattice.

In several previous papers we have reported on investigations of cubic lithium sulphate with small quantities of univalent or divalent impurity cations.

We have thus performed differential thermal analyses [1–3] (DTA) in f.c.c. lithium sulphate with up to a few mole% of Na_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4, $MnSO_4$, $MgSO_4$, $ZnSO_4$, $CdSO_4$ and $SrSO_4$, and studied the electrical conductivity [4, 5] with up to about 5 mole% of Na_2SO_4, K_2SO_4, Rb_2SO_4, $MgSO_4$, $CdSO_4$ and $BaSO_4$. We have also measured the tracer diffusion coefficients [6–8] of Na^+, Ag^+, K^+, Rb^+, Tl^+, Cd^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+} and Pb^{2+} in cubic lithium sulphate.

In a previous paper [7] we proposed a model for the diffusion of univalent and divalent ions in pure lithium sulphate. To check that model and to get further information on the transport mechanisms in the salt we decided to study lithium sulphate with trivalent impurity cations. We have thus made differential thermal analyses and measured the electrical conductivity of lithium sulphate with small quantities of $Al_2(SO_4)_3$ and $Tm_2(SO_4)_3$ and we have also measured the tracer diffusion coefficients of Al^{3+} and Tm^{3+} ions in the pure salt.

Experimental

Aluminium sulphate and thulium sulphate are not thermally stable upon melting, but decompose into Al_2O_3 and Tm_2O_3 far below the melting points of the salts [9]. If the salts, however, are well dried it is possible to dissolve about 2 mole% of $Al_2(SO_4)_3$ in molten lithium sulphate, and for $Tm_2(SO_4)_3$ this quantity is still greater (at least 3 mole%).

All salts used were of reagent quality, were very well dried, but were used without further purification.

a) DTA-measurements. The same experimental technique as has been described previously was used [10]. The thermocouple [11] (Platinel II) was brought in direct contact with the salt, which gives high precision and sensitivity in the measurements.

b) Electrical conductivity measurements. The electrical conductivities were measured in capillary cells of pure quartz glass. No corrosion by the salts was observed, but to avoid decomposition of the salt, it was molten for as short a time as possible. The resistance and capacitance (negligeable) of the circuit were measured with a Radiometer impedance bridge, model GB 11a. A complete description of our experimental technique can be found in a previous paper [12].

c) Tracer diffusion measurements. A thin layer of salt, containing the impurity cation, was placed on top of a semi-infinite salt column of pure lithium sulphate. For the diffusion of thulium ions radioactive tracer technique was used; thulium has a radioactive isotope ^{170}Tm with a half-life of 127 days. For the diffusion

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measurements of aluminium ions, no suitable radioactive isotope is available, and flame spectrometer analyses of the samples were therefore necessary. The experimental equipment is described in a previous paper[6].

The diffusion coefficients were calculated from a plot of the logarithm of the concentration of the tracer ion versus x^2, where x is the distance from the top of the salt column. In all cases a completely straight line was obtained and there was no indication of a too high tracer ion concentration in the surface layer. There is then probably no decomposition of the salts.

Results and Discussion

The phase diagrams of lithium sulphate with $0-3$ mole% of $Tm_2(SO_4)_3$ and $0-1.5$ mole% of $Al_2(SO_4)_3$ are shown in Figure 1.

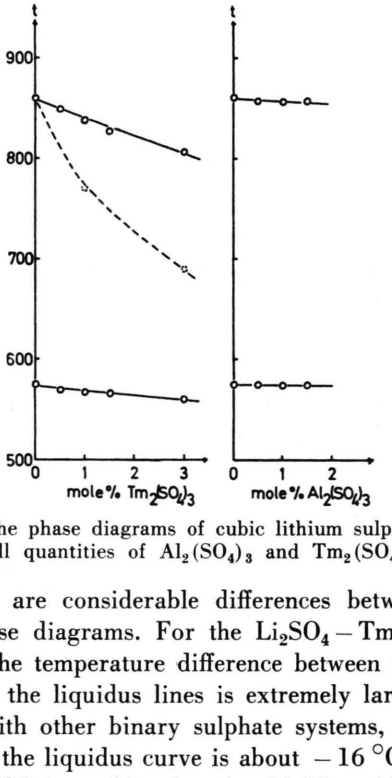

Fig. 1. The phase diagrams of cubic lithium sulphate with small quantities of $Al_2(SO_4)_3$ and $Tm_2(SO_4)_3$.

There are considerable differences between the two phase diagrams. For the $Li_2SO_4-Tm_2(SO_4)_3$ system the temperature difference between the solidus and the liquidus lines is extremely large compared with other binary sulphate systems, and the slope of the liquidus curve is about -16 °C/mole% of $Tm_2(SO_4)_3$, while for the $Li_2SO_4-Al_2(SO_4)_3$ system, the liquidus and the solidus lines almost coincide and the decrease in the melting point is only about -2 °C/mole% of $Al_2(SO_4)_3$. In both phase diagrams we have only drawn the liquidus lines. For the $Li_2SO_4-Tm_2(SO_4)_3$ system we found it very difficult to determine the exact position of the solidus line, and in the phase diagram we have only given two dotted circles, which indicate the position of this line. The transition temperature at 1.0 mole% $Tm_2(SO_4)_3$ was obtained from the conductivity measurements, and the one at 3.0 mole% from the DTA measurements.

In the $Li_2SO_4-K_2SO_4$ system a transition has been found between the liquidus and the solidus lines[1], and in the $Li_2SO_4-Cs_2SO_4$ system there is also a transition above the $\alpha-\beta$ transition[2]. For binary systems with lithium sulphate, where the other cation has an ionic radius of less than 1 Å, no such extra transitions have been detected, neither for the univalent nor the divalent cations.

The electrical conductivity was measured with 1.0 mole% and 1.5 mole% of $Al_2(SO_4)_3$ and with 1.0 mole% of $Tm_2(SO_4)_3$. With 1.0 mole% of $Al_2(SO_4)_3$ two completely independent measurements were performed, for which the results are in excellent agreement. The obtained results are shown in Fig. 2 for $Li_2SO_4-Al_2(SO_4)_3$ and in

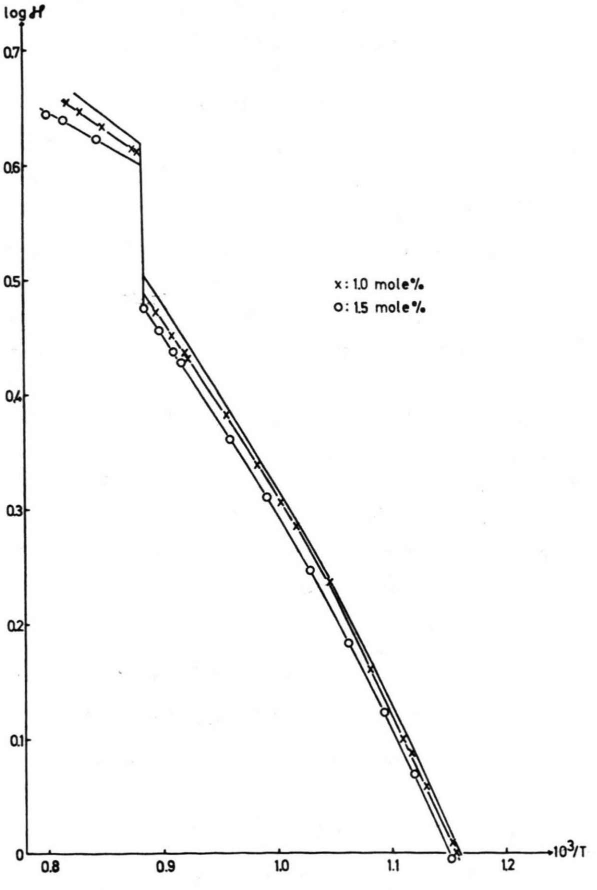

Fig. 2. The electrical conductivity of lithium sulphate with (a) 1.0 and 1.5 mole% of $Al_2(SO_4)_3$. The curve for pure Li_2SO_4 is also shown.

Fig. 3 for $Li_2SO_4 - Tm_2(SO_4)_3$. The electrical conductivity of f.c.c. Li_2SO_4 decreases considerably when $Al_2(SO_4)_3$ is added, while the addition of $Tm_2(SO_4)_3$ has little or no influence on the conductivity.

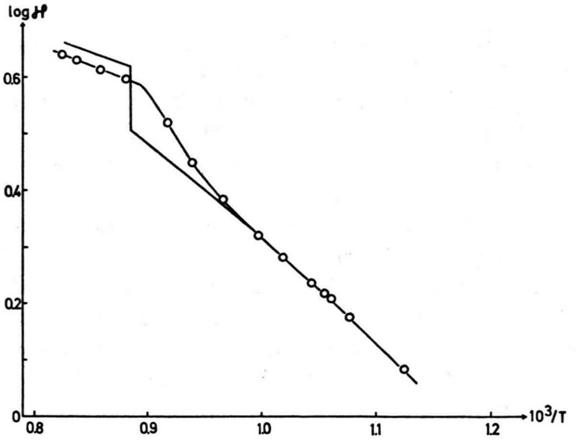

Fig. 3. The electrical conductivity of lithium sulphate with 1.0 mole% of $Tm_2(SO_4)_3$. The curve for pure Li_2SO_4 is also shown.

The diffusion experiments with Al^{3+} ions were especially difficult, mainly because of the flame spectrometer analyses, where much higher temperatures are necessary than for other ions. Due to very low diffusion coefficients of Al^{3+} and Tm^{3+} we also had to use much longer diffusion times (up to 500 hours) than for univalent and divalent tracers.

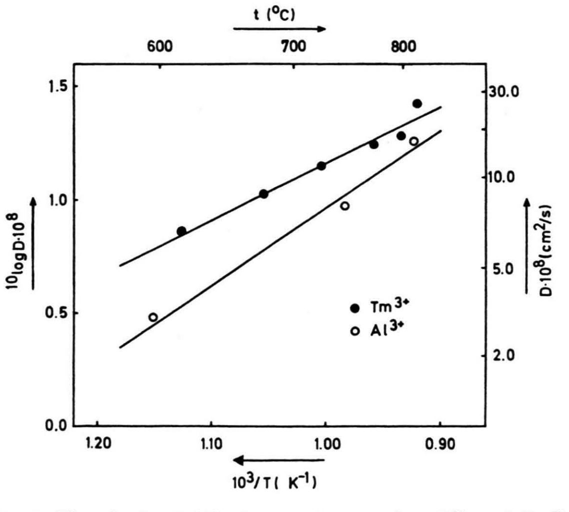

Fig. 4. The obtained diffusion coefficients for Al^{3+} and Tm^{3+} ions in cubic lithium sulphate.

The diffusion results are given in Fig. 4 and can be written

$$D_{Al^{3+}} = 54.7 \cdot 10^{-5} \exp(-15.5/RT) \text{ cm}^2/\text{s}$$

and $$D_{Tm^{3+}} = 4.51 \cdot 10^{-5} \exp(-11.4/RT) \text{ cm}^2/\text{s},$$

where R is the gas constant in kcal/mole K and T is the temperature in K.

The obtained diffusion coefficients are much lower than expected from our previous experiments with univalent and divalent cations (Fig. 5). For the univalent ions D is about 10^{-5} cm²/s, for the divalent ions about 10^{-6} cm²/s, and for the trivalent ions about 10^{-8} cm²/s. Preliminary measurements of the diffusion coefficient of the sulphate ion in cubic lithium sulphate have shown that $D_{SO_4^{2-}}$ is somewhat smaller than 10^{-8} cm²/s at 700 °C[13].

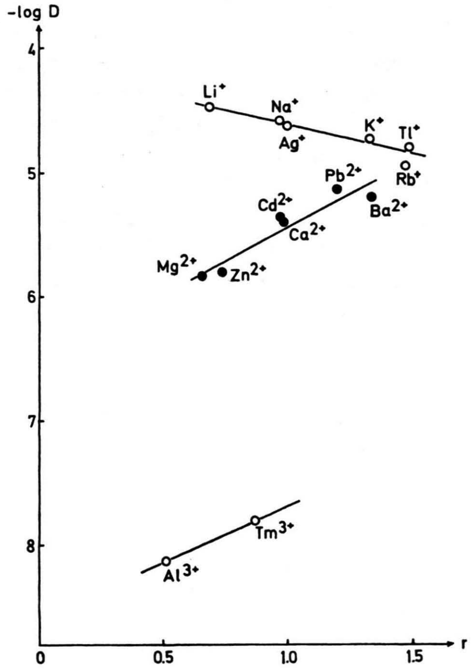

Fig. 5. The diffusion coefficients of univalent, divalent and trivalent cations in cubic lithium sulphate at 700 °C.

From our previous diffusion measurements one should expect the values of the diffusion coefficients of the trivalent ions to be about $5 \cdot 10^{-7}$ cm²/s, but the obtained results are considerably lower. There is, however, an evident connection between the diffusion coefficients and the valency of the cations and their ionic radii.

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[13] A. Bengtzelius and A. Kvist, unpublished.

In some conductivity measurements[5] we have found that the electrical conductivity of lithium sulphate increases, if an amount greater than a critical percentage of large cations like K^+ or Ba^{2+} is added. For smaller ions like Na^+ and Zn^{2+} a similar behaviour has not been found.

There are octahedral and tetrahedral lattice positions in the sulphate lattice of lithium sulphate and there are three available lattice positions for every two lithium ions in the pure salt. The aluminium ions are like the lithium ions small enough to be accommodated in the tetrahedral positions, while larger ions must be situated in octahedral positions. We have previously assumed that the migration of lithium ions takes place between tetrahedral lattice positions via an octahedral position. If the aluminium ions are accommodated by the tetrahedral positions, they should probably be more or less trapped in the lattice and we should obtain a very low diffusivity of the aluminium ions. The mean decrease in electrical conductivity per mole% of $Al_2(SO_4)_3$ corresponds to a mechanism, where the mobility of the lithium ions is the same as in the pure salt and the aluminium ions are immobile.

The tracer diffusion coefficient of the thulium ion is almost the same as that of the aluminium ion, but the thulium ion has a somewhat greater ionic radius than the aluminium ion. The electrical conductivity of lithium sulphate with 1.0 mole% $Tm_2(SO_4)_3$ is well within the experimental errors equal to the electrical conductivity of the pure salt. Since the thulium ions are somewhat too large for the tetrahedral positions it is possible that the conductivity decrease due to the slowly migrating thulium ions is compensated by a slight deformation of the lattice, or by the increase in the number of empty lattice positions.

Another aspect on the diffusion mechanism should also be discussed: the diffusion coefficients of the sulphate ions and the trivalent cations are almost equal and there might thus be a strong coupling between these ions.

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