In Table 3 we have tabulated Λ at 900 °C and in Table 4 the ARRHENIUS activation energies (Q) obtained from

$$\Lambda = \Lambda_0 \exp(-Q/RT).$$

The standard deviation of Q is generally a few hundred cal/mole.

Anion / Cation	SO_4^{2-}	$(SO_4WO_4)^{2-}_{1/2}$	WO_4^{2-}
Li^+	121.1	89.7	69.6
$(LiK)_{1/2}^+$	61.3	50.7	44.3
K^+	67.3	60.7	55.0

Table 3. The equivalent conductivities of the investigated salts at 900 °C.

Anion / Cation	SO_4^{2-}	$(SO_4WO_4)^{2-}_{1/2}$	WO_4^{2-}
Li^+	2590	5180	5460
$(LiK)_{1/2}^+$	6420	6280	7530
K^+	4910	5440	5600

Table 4. The ARRHENIUS activation energies of the investigated salts.

Some regularities in Λ and Q can be observed.

a) If we have the same cation [Me = Li, K, $(LiK)_{1/2}$]

$\Lambda(Me_2SO_4) > \Lambda(Me_2(SO_4WO_4)_{1/2}) > \Lambda(Me_2WO_4)$ and $\Lambda(Me_2(SO_4WO_4)_{1/2})$ is not far from the mean value of the conductivities of the pure salts.

b) $\Lambda(LiKX)$ [X = SO_4, WO_4, $(SO_4WO_4)_{1/2}$] is much smaller than both $\Lambda(Li_2X)$ and $\Lambda(LiKX)$.

c) $Q(Me_2SO_4) < Q(Me_2(SO_4WO_4)_{1/2}) < Q(Me_2WO_4)$ except for LiKX, where

$$Q(LiK(SO_4WO_4)_{1/2}) \approx Q(LiKSO_4).$$

d) $Q(LiKX)$ is much greater than $Q(Li_2X)$ and $Q(K_2X)$. For instance for the mixture of Li_2SO_4 and K_2WO_4, where $Q(Li_2WO_4) \approx Q(K_2WO_4)$, the activation energy is almost 40% higher than for the pure salts.

In the mixtures there is thus an increase in Q and a decrease in Λ compared with the pure salts if we have the same anion but different cations. This agrees with observations made for nitrate mixtures by others [8, 9]. On the other hand the conductivities and activation energies are almost ideal if we mix two salts with a common cation.

The difference in radius between the potassium ion and the lithium ion is the same as the difference between the tungstate ion and the sulphate ion (0.7 Å). The TOBOLSKY parameter [10] is thus approximately the same for LiKX and $Me_2(SO_4WO_4)_{1/2}$, but the deviations from ideality of the conductivities are very different. A possible explanation to this is that the transport mechanism mainly is determined by the cations in this system.

This work was supported financially by Magnus Bergvalls Stiftelse.

[8] V. WAGNER and S. FORCHERI, Z. Naturforschg. **22 a**, 891 [1967].

[9] B. DE NOOIJER, Thesis, Amsterdam 1965; B. DE NOOIJER and J. A. A. KETELAAR, Rec. Trav. Chim. Pays-Bas **83**, 573 [1964].

[10] A. KVIST, Z. Naturforschg. **22 a**, 467 [1967].

Differential Thermal Analysis of Lithium Sulphate with Small Quantities of Sodium, Rubidium and Cesium Sulphate

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Previously obtained results for the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4 show a second order transition below the solidus curve, probably due to the rotation properties of the sulphate ions. To obtain more information about the high temperature behaviour, the systems $(Li,Na)_2SO_4$, $(Li,Rb)_2SO_4$ and $(Li,Cs)_2SO_4$ have been studied. From differential thermal analysis we have constructed the phase diagrams for Li_2SO_4 with small quantities of Na_2SO_4, Rb_2SO_4, and Cs_2SO_4.

Mechanical properties and electrical conductivity of the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4 have recently been studied in this laboratory [1]. At a certain temperature below the solidus curve, a notable change in the temperature dependence of the apparent viscosity takes place, and a similar behaviour of the electrical conductivity is also observed. Our interpretation was that the sulphate lattice is affected by the presence of small amounts of foreign cations, and that this effect should depend on the size of the added ion. Considering data from X-ray measurements [2, 3] this effect would vanish if the foreign cation is small enough, but would appear for larger cations. A differential thermal analysis of the system $(Li,K)_2SO_4$ shows a change in the slope of the thermal curve at the considered temperature [1]. Similar systems could then be studied with this method.

[1] B. AUGUSTSSON and A. KVIST, Z. Naturforschg. **22 a**, 1177 [1967].

[2] H. ØYE, Thesis, Trondheim 1963.

[3] A. KVIST, Thesis, Göteborg 1967.

Three different systems have been studied in this work: Li_2SO_4 with less than 10 mole % Na_2SO_4, Li_2SO_4 with less than 3 mole % Rb_2SO_4 and Li_2SO_4 with less than 3 mole % Cs_2SO_4. The experimental technique of the measurements is described elsewhere [1]. The measurements were performed with increasing temperature of about ten degrees per minute, and the cooling curves were also registered. In all experiments reagent grade salts have been used without further purification. Al_2O_3 was used as reference.

$(Li,Na)_2SO_4$

Measurements were performed for the concentrations 0.5, 1.0, 3.0, 5.0, and 10 mole % Na_2SO_4. The results show good agreement with available data in the literature [4]. Between the transition, corresponding to the $\beta-\alpha$ transition in pure Li_2SO_4 at about 570 °C, and the solidus curve we could not detect any second order transition. Fig. 1 shows the probable phase diagram up to 10 mole % Na_2SO_4. Considering the transition at about 470 °C, the heat of transition increases with increasing concentration of Na_2SO_4.

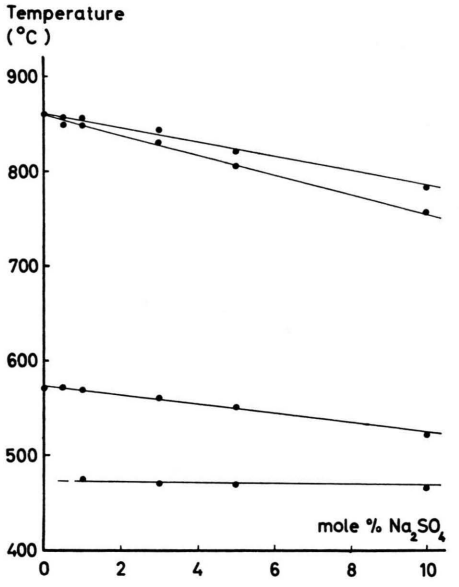

Fig. 1. The phase diagram of Li_2SO_4 with small quantities of Na_2SO_4.

$(Li,Rb)_2SO_4$

Measurements were performed for the concentrations 0.5, 1.0, 1.5, 2.0 and 3.0 mole % Rb_2SO_4. For concentrations less than 2 mole % Rb_2SO_4 a notable change in the slope of the differential thermal curve was registered between the $\beta-\alpha$ transition at about 570 °C and the solidus curve. A second order transition similar to the one in the system $(Li,K)_2SO_4$ is then to be expected. At about 520 °C a transition appears for concentrations above 1.5 mole % Rb_2SO_4. The heat of transition increases with increasing concentration. For 3.0 mole % Rb_2SO_4 an additional transition appears at about 500 °C. Fig. 2 shows the result of the measurements.

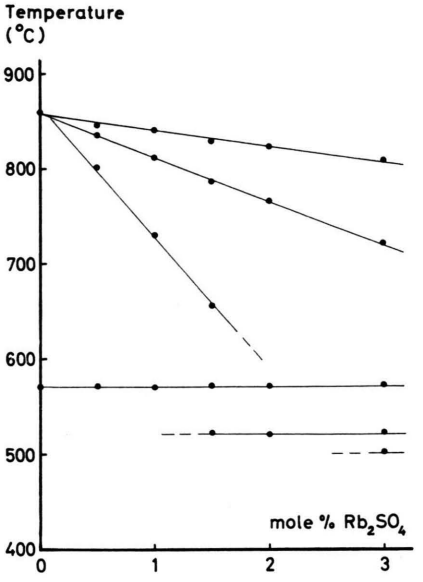

Fig. 2. The phase diagram of Li_2SO_4 with small quantities of Rb_2SO_4.

$(Li,Cs)_2SO_4$

Mixtures with 0.5, 1.0, 1.5, 2.0 and 3.0 mole % Cs_2SO_4 were studied. For concentrations less than about 2 mole % we could clearly detect a second order transition below the solidus curve. In this system a

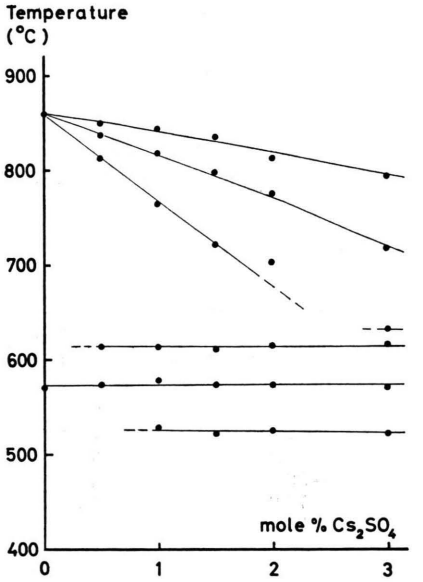

Fig. 3. The phase diagram of Li_2SO_4 with small quantities of Cs_2SO_4.

[4] R. Nacken, Neues Jahrb. Mineral. Geol., Beilageband **24**, 32 [1907].

transition appears also at about 615 °C, i. e. above the $\beta-\alpha$ transition (at 570 °C in the pure Li_2SO_4). For concentrations above 1.0 mole % Cs_2SO_4 a transition was obtained at about 525 °C with increasing heat of transition for increasing concentration. For 3.0 mole % Cs_2SO_4 an additional change in the structure was obtained at about 630 °C. Fig. 3 shows the phase diagram constructed from the differential thermal curves.

Discussion

According to the previous measurements of the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4 a structural change in the sulphate lattice below the solidus curve is to be expected for the system $(Li,Rb)_2SO_4$ and $(Li,Cs)_2SO_4$ for concentrations less than about 2 mole % Rb_2SO_4 and Cs_2SO_4 respectively. A similar effect was not observed in the system $(Li,Na)_2SO_4$, as the available space for the sodium ion is probably large enough and the sulphate lattice fairly intact. Fig. 4 shows a typical differential thermal curve for Li_2SO_4 with 1.0 mole % Cs_2SO_4. The second order transition at about 760 °C can easily be detected in the heating curve, but does not appear in the cooling curve. A similar behaviour in the corresponding temperature interval is found in the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4, where the change in the temperature dependence of the electrical conductivity is more striking for increasing than for decreasing temperature [1, 3].

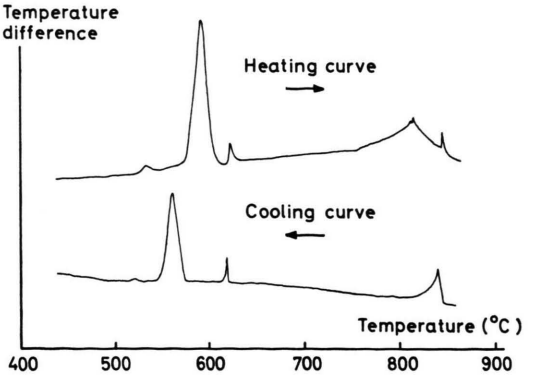

Fig. 4. Differential thermal curve for Li_2SO_4 with 1.0 mole % Cs_2SO_4.

Usually the transition temperatures are taken as mean values from heating and cooling curves. Several measurements of a certain transition temperature show that a variation of about 5 °C from the mean value is possible. Thus, this method only gives a rough picture of the structural changes. A further discussion of the structure must wait until X-ray investigations have been performed.

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Bemerkung zur Anisotropie der diamagnetischen Suszeptibilität der Alkalifluoride

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The diamagnetic susceptibility of TlF and TlBr was measured by the usual cylinder-method. The anisotropy of the diamagnetic susceptibility of these molecules as measured by the molecular-beam-resonance-spectroscopy-method is compared with these values.

	ξ		$\xi_\perp-\xi_\parallel$	
	in 10^{-30} erg/Gauss^2			
H_2	− 6,6		−0,915	(54)
NaF	−27,2		−1,59	(120)
KF	−39,2		3	(1)
RbF	−52,9		12	(6)
CsF	−73,9		14,7	(60)
TlF	−75,2	(13)	9,60	(480)

Tab. 1. Literaturwerte [1]. Die in Klammern angegebenen Zahlen sind die einfachen Fehler in Einheiten der letzten Stelle der Meßwerte.

Mit Hilfe der Molekularstrahl-Resonanzspektroskopie ist es neuerdings möglich, die Anisotropie $\xi_\perp-\xi_\parallel$ der diamagnetischen Suszeptibilität freier zweiatomiger Moleküle zu messen. Dabei ist $\xi_\perp$ bzw. $\xi_\parallel$ die diamagnetische Suszeptibilität, wenn die Molekülachse senkrecht bzw. parallel zum äußeren magnetischen Feld steht. Die bisher gemessenen Werte sind in Tab. 1 zusammengestellt.

Nur diese Differenz, nicht $\xi_\perp$ und $\xi_\parallel$ getrennt, kann man aus den Molekülspektren gewinnen. Zur Bestimmung der über alle Orientierungen des Moleküls gemittelten Suszeptibilität $\xi=\frac{2}{3}\xi_\perp+\frac{1}{3}\xi_\parallel$ muß auf andere experimentelle Methoden zurückgegriffen werden. Eine Messung an freien Molekülen in der Gasphase ist leider undurchführbar, da wegen der zu geringen Dichte der verdampften Salze der übliche Nachweis des diamagnetischen Effektes als Gewichtsdifferenz an einer Mikrowaage nicht mehr möglich ist. Um die Anisotropie der diamagnetischen Suszeptibilität mit der gemittelten Suszeptibilität ξ vergleichen zu können, kann nur der im festen Zustand pro Molekül gemessene Wert herangezogen werden. Wir haben deshalb die dia-

[1] $\xi_\perp-\xi_\parallel$, H_2: N. J. Harrick u. N. F. Ramsey, Phys. Rev. **88**, 228 [1952]. — RbF: G. Gräff, R. Schönwasser u. M. Tonutti, Z. Phys. **199**, 157 [1967]; dort Literatur zu den Messungen an den anderen Fluoriden.