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

$$A = A_0 \exp\left(-\frac{Q}{RT}\right).$$

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

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cation</th>
<th>$\text{SO}_4^{2-}$</th>
<th>($\text{SO}_4\text{WO}_4$)</th>
<th>$\text{WO}_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>(LiK)$_2^+$</td>
<td>121.1</td>
<td>89.7</td>
<td>69.6</td>
</tr>
<tr>
<td>K$^+$</td>
<td>(LiK)$_2^+$</td>
<td>61.3</td>
<td>50.7</td>
<td>44.3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cation</th>
<th>$\text{SO}_4^{2-}$</th>
<th>($\text{SO}_4\text{WO}_4$)</th>
<th>$\text{WO}_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>(LiK)$_2^+$</td>
<td>2590</td>
<td>5180</td>
<td>5460</td>
</tr>
<tr>
<td>(LiK)$_2^+$</td>
<td>6420</td>
<td>6280</td>
<td>7330</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>(LiK)$_2^+$</td>
<td>4910</td>
<td>5440</td>
<td>5600</td>
</tr>
</tbody>
</table>

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

Some regularities in $A$ and $Q$ can be observed. a) If we have the same cation [Me = Li, K, (LiK)$_2^+$]

$$A(\text{Me}_2\text{SO}_4) > A(\text{Me}_2(\text{SO}_4\text{WO}_4)_{1/2}) > A(\text{Me}_2\text{WO}_4)$$

and $A(\text{Me}_2(\text{SO}_4\text{WO}_4)_{1/2})$ is not far from the mean value of the conductivities of the pure salts.


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

Bengt Augustsson and Jan Gustafsson
Department of Physics, Chalmers University of Technology, Göteborg
(Z. Naturforsch. 22 a, 1534—1636 [1967]; received 12 August 1967)

Previously obtained results for the system (LiK)$_2$SO$_4$ with small quantities of K$_2$SO$_4$ have recently been studied in this laboratory. 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, this effect would vanish if the foreign cation is small enough, but would appear for larger cations. A differential thermal analysis of the system (LiK)$_2$SO$_4$ shows a change in the slope of the thermal curve at the considered temperature. Similar systems could then be studied with this method.


b) $A(\text{LiK}) [X = \text{SO}_4, \text{WO}_4, (\text{SO}_4\text{WO}_4)_{1/2}]$ is much smaller than both $A(\text{Li}_2\text{X})$ and $A(\text{LiK})$.

c) $Q(\text{Me}_2\text{SO}_4) < Q(\text{Me}_2(\text{SO}_4\text{WO}_4)_{1/2}) < Q(\text{Me}_2\text{WO}_4)$ except for LiKK, where

$$Q(\text{LiK}(\text{SO}_4\text{WO}_4)_{1/2}) = Q(\text{LiKSO}_4).$$

d) $Q(\text{LiK})$ is much greater than $Q(\text{Li}_2\text{X})$ and $Q(\text{K}_2\text{X})$. For instance for the mixture of Li$_2$SO$_4$ and K$_2$WO$_4$, where $Q(\text{Li}_2\text{WO}_4) \approx Q(\text{K}_2\text{WO}_4)$, 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 $A$ compared with the pure salts if we have the same anion but different cations. This agrees with observations made for nitrate mixtures by others. 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 is thus approximately the same for LiKK and Me$_2$(SO$_4$WO$_4$)$_{1/2}$, 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 Bergvall Stiftelse.


Mechanical properties and electrical conductivity of the system (LiK)$_2$SO$_4$ with small quantities of K$_2$SO$_4$ have recently been studied in this laboratory. 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, this effect would vanish if the foreign cation is small enough, but would appear for larger cations. A differential thermal analysis of the system (LiK)$_2$SO$_4$ shows a change in the slope of the thermal curve at the considered temperature. Similar systems could then be studied with this method.


Three different systems have been studied in this work: Li$_2$SO$_4$ with less than 10 mole % Na$_2$SO$_4$, Li$_2$SO$_4$ with less than 3 mole % Rb$_2$SO$_4$ and Li$_2$SO$_4$ with less than 3 mole % Cs$_2$SO$_4$. The experimental technique of the measurements is described elsewhere. 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$_2$O$_3$ was used as reference.

(Li,Na)$_2$SO$_4$

Measurements were performed for the concentrations 0.5, 1.0, 3.0, 5.0, and 10 mole % Na$_2$SO$_4$. The results show good agreement with available data in the literature. Between the transition, corresponding to the $\beta - \alpha$ transition in pure Li$_2$SO$_4$ 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$_2$SO$_4$. Considering the transition at about 470 °C, the heat of transition increases with increasing concentration of Na$_2$SO$_4$.

(Li,Rb)$_2$SO$_4$

Measurements were performed for the concentrations 0.5, 1.0, 1.5, 2.0 and 3.0 mole % Rb$_2$SO$_4$. For concentrations less than 2 mole % Rb$_2$SO$_4$ 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)$_2$SO$_4$ is then to be expected. At about 520 °C a transition appears for concentrations above 1.5 mole % Rb$_2$SO$_4$. The heat of transition increases with increasing concentration. For 3.0 mole % Rb$_2$SO$_4$ an additional transition appears at about 500 °C. Fig. 2 shows the result of the measurements.

(Li,Cs)$_2$SO$_4$

Mixtures with 0.5, 1.0, 1.5, 2.0 and 3.0 mole % Cs$_2$SO$_4$ 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 transition appears at about 470 °C.

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Fig. 1. The phase diagram of Li$_2$SO$_4$ with small quantities of Na$_2$SO$_4$.

Fig. 2. The phase diagram of Li$_2$SO$_4$ with small quantities of Rb$_2$SO$_4$.

Fig. 3. The phase diagram of Li$_2$SO$_4$ with small quantities of Cs$_2$SO$_4$.

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transition appears also at about 615 °C, i.e. above the \(\beta - \alpha\) transition (at 570 °C in the pure \(\text{Li}_2\text{SO}_4\)). For concentrations above 1.0 mole % \(\text{Cs}_2\text{SO}_4\) a transition was obtained at about 525 °C with increasing heat of transition for increasing concentration. For 3.0 mole % \(\text{Cs}_2\text{SO}_4\) 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 \((\text{Li,K})_2\text{SO}_4\) with small quantities of \(\text{K}_2\text{SO}_4\) a structural change in the sulphate lattice below the solidus curve is to be expected for the system \((\text{Li,Rb})_2\text{SO}_4\) and \((\text{Li,Cs})_2\text{SO}_4\) for concentrations less than about 2 mole % \(\text{Rb}_2\text{SO}_4\) and \(\text{Cs}_2\text{SO}_4\) respectively. A similar effect was not observed in the system \((\text{Li,Na})_2\text{SO}_4\), 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 \(\text{Li}_2\text{SO}_4\) with 1.0 mole % \(\text{Cs}_2\text{SO}_4\). 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 \((\text{Li,K})_2\text{SO}_4\) with small quantities of \(\text{K}_2\text{SO}_4\), where the change in the temperature dependence of the electrical conductivity is more striking for increasing than for decreasing temperature.³

**Fig. 4. Differential thermal curve for \(\text{Li}_2\text{SO}_4\) with 1.0 mole % \(\text{Cs}_2\text{SO}_4\).**

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.

This work was financially supported by the Swedish Council for Applied Research. We are indebted to Dr. A. Lundén for valuable criticism of the manuscript.

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**Bemerkung zur Anisotropie der diamagnetischen Suszeptibilität der Alkalifluoride**

G. Gräff und W. Schauer

Physikalisches Institut der Universität Bonn


The diamagnetic susceptibility of TIF and TIBr 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.

| \(\xi\) | \(\xi_{\perp} - \xi_{||}\) |
|--------|---------------------|
| in \(10^{-30}\text{erg/Gauss}\) |                     |
| \(\text{H}_2\) | -6.6 | -0.915 (54) |
| \(\text{NaF}\) | -27.2 | -1.59 (120) |
| \(\text{KF}\) | -39.2 | 3 (1) |
| \(\text{RbF}\) | -52.9 | 12 (6) |
| \(\text{CsF}\) | -73.9 | 14.7 (60) |
| TIF | -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.