The Dependence on the ^{6}Li-content of the Electrical Conductivity of Solid and Molten Lithium Sulphate

KJELL SCHROEDER and ARNOLD KVIST

Department of Physics, Chalmers University of Technology, Göteborg

The electrical conductivity of solid and molten lithium sulphate has been measured as a function of temperature and ^{6}Li-content. The electrical conductivity is higher for ^{6}Li$_2$SO$_4$ than for ^{7}Li$_2$SO$_4$. For f.c.c. lithium sulphate the conductivity is independent of temperature and $\Delta\varkappa/\varkappa = 4.73\%$ for the isotopically pure salts. For the melt

$$\Delta\varkappa/\varkappa^1 = [4.29 + 1.6 \cdot 10^{-3} (t - 860)] \% \ (t \text{ in } °C).$$

There is, within the experimental errors, no excess conductivity in the mixtures of ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$.

Some years ago we published results of conductivity measurements in ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$ [1]. We have now made a more thorough investigation of the temperature dependence of this effect both in the solid f.c.c. phase and in the melt up to 1200 °C. We have also measured the electrical conductivity of the equimolar mixture of ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$.

Experimental

Two calibrated quartz capillary cells [2] with approximately the same cell constants were placed in an air thermostat in a furnace. Since the electrical conductivity increases by about 0.3% per °C in cubic Li$_2$SO$_4$ it is necessary to keep the temperature difference between the two cells within at least 0.3 °C to get an accuracy of 0.1%. More than ten independent experiments were performed with small modifications.

The used salts contained 0.0, 50.0 and 95.5 mole % ^{6}Li$_2$SO$_4$ and were delivered by Oak Ridge National Laboratory. They were used without further purification, but were very well dried before use. According to analyses of the salts (performed by Oak Ridge National Laboratory) there was no difference in the chemical composition of the different salts, but we have found that there was a small difference in the corrosion of our quartz cells by the ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$ samples. ^{6}Li$_2$SO$_4$ did not even at the highest studied temperatures corrode the glass, while ^{7}Li$_2$SO$_4$ also at the melting point caused some corrosion of the glass. However, no time dependence of the electrical conductivity has been found and since the same conductivity results were obtained with increasing and decreasing temperatures, there is no reason to believe that the corrosion has influenced the conductivity difference between ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$.

The conductivities were measured with a commercial impedance bridge (Radiometer, Copenhagen, type GB 11 a)

and the temperatures were measured with Platinel thermocouples and a potentiometric microvoltmeter (Medistor, model A-75).

Results and discussions

Fig. 1 shows the relative conductivity differences between ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$, and also between the equimolar mixture and ^{7}Li$_2$SO$_4$. The values for ^{6}Li$_2$SO$_4$ have been obtained by linear extrapolation of the results for 95.5 mole % enriched ^{6}Li$_2$SO$_4$.
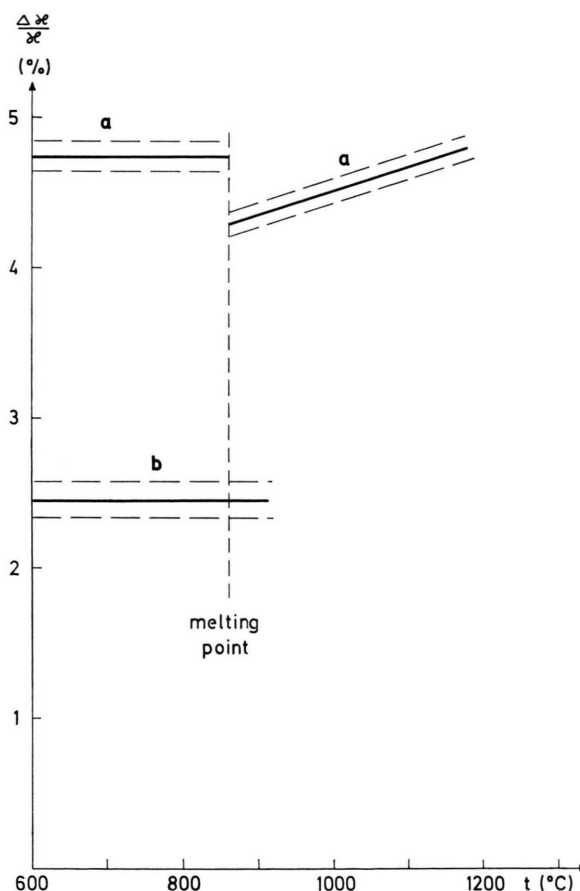

Fig. 1. The relative difference in conductivity between ^{6}Li$_2$SO$_4$ and ^{7}Li$_2$SO$_4$ (a) and between the equimolar mixture and ^{7}Li$_2$SO$_4$ (b). The dotted lines show the maximal errors.

The results given in the figure are mean values from a great number of measurements. All measurements fall within the limits given in the figure.

In the solid no temperature dependence of the relative conductivity difference has been found and $\Delta\varkappa/\varkappa = 4.73\%$.

[1] A. KVIST, Z. Naturforsch. **21 a**, 487 [1966].
[2] A. KVIST, Z. Naturforsch. **22 a**, 208 [1967].

This value is somewhat higher than the results reported previously[1], but the accuracy is somewhat better in this investigation. We have now also used two conductivity cells with a very small temperature difference in the same furnace and we have thus obtained conductivity values for the two cells at the same temperature.

For the melt there is a significant increase of $\Delta\varkappa/\varkappa$ with temperature:

$$\Delta\varkappa/\varkappa = [4.29 + 1.6 \cdot 10^{-3}\,(t - 860)]\,\% \quad (t\text{ in }°\text{C}).$$

The temperature dependence of $\Delta\varkappa/\varkappa$ for the melt is similiar to that of molten lithium nitrate and lithium chloride[3].

The increase in the relative conductivity difference with temperature is probably due to a weakening of the coupling between the cations.

Since great deviations from additivity for binary sulphate systems[2,4,5] have been found we have also measured the conductivity of the equimolar $^6Li_2SO_4$-$^7Li_2SO_4$ mixture. As is seen in Fig. 1, there is within the experimental errors no excess conductivity in this system.

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5 A. KVIST and K. SCHROEDER, Z. Naturforsch. **23a**, 676 [1968].