It is important to note that this value of the statistical sum is obtained either using the orthogonality and completitude relations for the wave functions, or integrating $(e^{-\beta H_0})_{\varepsilon \boldsymbol{K}_\perp, \varepsilon \boldsymbol{K}_\perp}$ in the variable ε, between the limits $(-e E L_z/2, \; +e E L_z/2)$ that is cutting the domain of integration in its upper part.

$$(j_i)_{12} = -\frac{e K_{i1}}{m L_i} \delta_{\varepsilon_1, \varepsilon_2} \delta_{\boldsymbol{K}_{\perp 1}, \boldsymbol{K}_{\perp 2}} \approx -\frac{e K_{i1}}{m L_i} [\eta(\varepsilon_1) \, \eta(\varepsilon_2)]^{-1/2} \delta(\varepsilon_1 - \varepsilon_2) \, \delta_{\boldsymbol{K}_{\perp 1}, \boldsymbol{K}_{\perp 2}} \; (i = x, y) \tag{A.9}$$

$$\begin{aligned}(j_z)_{12} &= -\frac{1}{m E L_z^2} [\eta(\varepsilon_1) \, \eta(\varepsilon_2)]^{-1/2} \sum_{K_z} K_z \exp\left\{\frac{i}{e E} K_z (\varepsilon_1 - \varepsilon_2)\right\} \delta_{\boldsymbol{K}_{\perp 1}, \boldsymbol{K}_{\perp 2}} \\ &\approx -\frac{e^2 E}{i m L_z} [\eta(\varepsilon_1) \, \eta(\varepsilon_2)]^{-1/2} \frac{\mathrm{d}}{\mathrm{d}\varepsilon_1} \delta(\varepsilon_1 - \varepsilon_2) \, \delta_{\boldsymbol{K}_{\perp 1}, \boldsymbol{K}_{\perp 2}} .\end{aligned} \tag{A.10}$$

Thermal Expansion of Alkali Sulphate Mixtures

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The linear thermal expansivities of polycrystalline samples of mixtures of Li_2SO_4 with K_2SO_4 and with Na_2SO_4 have been measured with a "Fused-Quarz Tube" apparatus [1]. Phase transitions are accompanied by changes in the expansion coefficient and also by volume changes. The observed expansion coefficient is constant over wide temperature intervals. Simple crystal structures show higher expansivities than more complex structures. The "pre-melting" phenomenon in Li_2SO_4 does not measurably influence the thermal expansion.

A method has been devised to correct the observations for the plastic flow of the crystals close to the melting points.

The present investigation of the thermal expansion of alkali sulphate mixtures is a part of a program in this laboratory for an extensive study of the rheology of these mixtures. Since lithium sulphate is a purely cationic conductor a study of the electrical conductivity primarily gives information about the cations. Information of the same kind is obtained from diffusion studies since D_{Li^+} (and the interdiffusion coefficients of other monovalent cations) is of the order of $10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ while $D_{\text{SO}_4^{--}}$ is several magnitudes smaller (about $10^{-10}\,\text{cm}^2\,\text{s}^{-1}$ at 800 °C) [2, 3]. Thus anion diffusion studies are much more difficult to perform accurately than cation diffusion studies and they are only able to give a qualitative information of the transport parameters. The difference in magnitudes of the cation and anion diffusion coefficients is due to the fact that a Li_2SO_4 crystal consists of a rigid anion lattice in which the cations are able to move very freely. Studies of the mechanical properties of these crystals are, however, comparatively easy to perform and they will give direct information about the anion lattice. Semiquantitative preliminary studies of the rheology of solid lithium sulphate have been performed in this laboratory, plastic flow investigations by AUGUSTSSON and LUNDÉN [4] and thermal expansion investigations by AUGUSTSSON and EKHED [5]. The present work is a quantitative investigation of the linear thermal expansivity of pure lithium sulphate and of mixtures of lithium sulphate with potassium and sodium sulphates.

Experimental

Reagent grade lithium sulphate was obtained from Mallinckrodt Chemical Works, New York, USA, and potassium and sodium sulphates from E. Merck AG., Darmstadt, Germany. After drying in a drying oven for over 50 hours at 120 °C the salts were melted and mixed in a quartz crucible and then cast

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under vacuum into a cylindrical quartz mould giving a specimen with 40 mm length and 10 mm diameter. The sulphate mixtures were found to adhere very strongly to quartz glass. Thus the mould was clad with a 0.01 mm thick platinum foil in order to avoid sticking of the salt. This foil covered the specimen after solidification and a very good (but not sticky) fit was obtained with the sample holder inside the cylindrical thermal expansion apparatus. This fit is very critical since the length to diameter ratio of the sample is comparatively small.

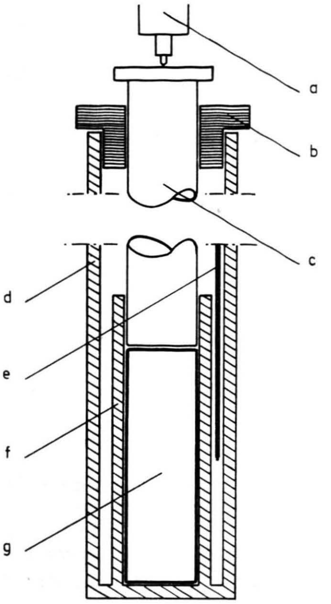

Fig. 1. "Fused quartz tube" thermal expansion apparatus. a) strain gauge, b) metal bearing for the inner tube, c) inner quartz tube, d) outer quartz tube, e) thermocouple, f) sample holder, g) platinum clad salt sample.

The overall experimental arrangement[1] is similar to the apparatus used by AUGUSTSSON and EKHED[5] but several improvements were made in order to increase the accuracy of the readings and to facilitate the collection of the data: No "wiggling" of the sample in the horizontal plane may be permitted, thus the ends of the specimen were ground flat and it was mounted in a "sample holder". This holder consists of a quartz glass tube with an inner diameter 0.5 mm wider than the platinum-clad sample. The inner quartz tube penetrates about 15 mm into the holder. The length changes of the sample are transmitted by the inner tube to the sensing device (a strain gauge) and finally they are recorded on a Philips potentiometric recorder type PR 2500 connected to the gauge.

The temperature close to the middle of the specimen was measured with a Platinel[6] thermocouple inserted between the outer tube and the sample holder. The observations were automatically recorded on a Philips temperature recorder (PR 2210-A 21). A Knick mV-source was connected in series opposition in the thermocouple circuit, thus a range covering only 300 °C could be used on the recorder in order to increase the reading accuracy to ±1 °C. A Frigistor zero-point temperature reference chamber was used.

Changing the temperature continuously with time was found to result in a considerable time lag between the temperature and the corresponding changes in sample length. This effect has to be eliminated since otherwise the length change due to a temperature change cannot be separated from the length change due to sample plasticity (see below). Moreover, measurements of thermal expansion are very time-consuming since several series of increasing and decreasing temperatures must be traversed in order to increase the accuracy of the result. Covering a temperature interval of 800 °C in 15 °C steps takes about 50 hours (minimum). Consequently some kind of programming for continuous day and night observation is imperative: A programmed temperature controller was constructed from a Monostat controller[7] and a program unit[8]. The controller was connected to a thermocouple close to the furnace windings and the specimen temperature was kept constant to better than 1 °C. The program unit changed the temperature by 15 °C every two hours since this time interval was found to be a minimum for a thermal equilibrium to be reached by the sample.

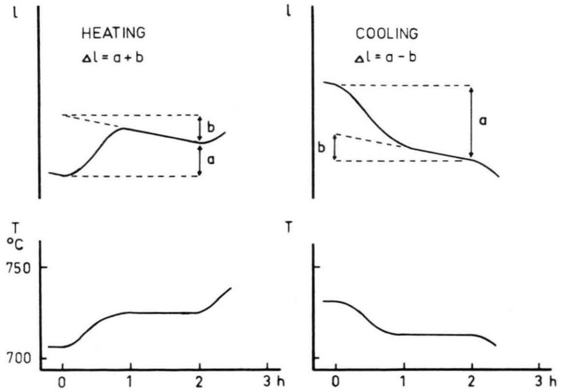

Fig. 2. Correction for sample plasticity. a) observed length change after 2 hours, b) calculated plasticity correction. For clarity the magnitude of the correction is exaggerated.

Mixtures containing sodium or potassium sulphate show a marked plasticity close to the melting point[4]. In some cases this effect was comparable to the thermal expansion of the specimen (see Fig. 2. For clarity the magnitude of the correction is exaggerated in the figure). Within experimental error the length change due to plastic flow is linear with time and the change dur-

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[6] Obtained from Baker Platinum Division, Engelhard Industries Ltd., Sutton, England.

[7] Made by AB Nordquist & Berg, Stockholm, Sweden.

[8] Program unit type P 12 M (cycling time 24 h) made by Sandblom & Stohne AB, Stockholm, Sweden.

ing a time interval (two hours) can be graphically constructed on the sample length versus time diagram obtained on the PR 2500 recorder. This correction is added to the measured length change if the temperature is rising and substracted if the temperature is decreasing.

Results and Discussion

The observed thermal expansion coefficients of the polycrystalline samples are given in Table 1. The statistical error in the $Li_2SO_4 - K_2SO_4$ data is less than 10% and in the $Li_2SO_4 - Na_2SO_4$ data less than 20%. Some phase transitions are accompanied by volume changes which are given in Table 2. Figures 3 and 4 show the relative change in length versus temperature. A “temperature hysteresis” effect (not shown) was sometimes found in the temperature region ±10 °C around a phase transition. It is found that over wide temperature intervals even mixed phases may be well described by a constant thermal expansion coefficient. Changes in the thermal expansivity occur at temperatures where phase transitions are found by SCHROEDER and KVIST[9, 10] (the $Li_2SO_4 - Na_2SO_4$ phase diagram has been considerably modified around the equimolar mixture[11]).

WEYL[12] has discussed different approaches towards a theoretical treatment of thermal expansion of ionic crystals. His approach is based on the Gibbs function *G* and its structural interpretation. If during heating a crystal is assumed to retain the lowest possible value of *G* it follows that it will expand only as much as is needed in order to increase its entropy *S*. If the crystal has mechanisms other than volume expansion to increase *S* it might even contract upon heating. An example of this behaviour is silver iodide[13–15] in the low temperature phase below 146.5 °C which has a negative thermal expansivity and also shows a considerable contraction during the transition from the low-temperature to the high-temperature phase. These properties are ascribed to the partial melting of the high-temperature AgI in which the cations have a very high mobility while the anions form a rigid network. Con-

Sample composition	Phase transition	Volume change (cm³/equiv.)
Pure Li_2SO_4	II to I	1.16
1.0 mole% K_2SO_4	I + II to I	0.59
2.5 mole% K_2SO_4	I + II to I	0.57
4.0 mole% K_2SO_4	II + m to I + m	0.58
48.0 mole% K_2SO_4	II + VII to II + VI	0.55
48.0 mole% K_2SO_4	VI to V	0.06
45.0 mole% Na_2SO_4	II to XI	1.78
50.0 mole% Na_2SO_4	(II) to XI	2.70

Table 2. Volume changes at the phase transitions. A transition from a low to a high temperature form always results in a volume expansion. For an explanation of the phase notation see the text to Table 1.

Phase	$\alpha \times 10^5$ (°K⁻¹)	Temp. range (°C)	Phase	$\alpha \times 10^5$ (°K⁻¹)	Temp. range (°C)	Phase	$\alpha \times 10^5$ (°K⁻¹)	Temp. range (°C)	Phase	$\alpha \times 10^5$ (°K⁻¹)	Temp. range (°C)
0 mole% K_2SO_4			1 mole% K_2SO_4			2.5 mole% K_2SO_4			4 mole% K_2SO_4		
II	2.2	200–550	II + VII	1.5	260–360	II + VII	1.0	260–360	II + VII	1.3	260–310
I	4.3	600–750	II + VII	1.9	360–432	II + VII	2.0	360–432	II + VII	1.4	310–432
			II + VI	2.4	432–515	II + VI	2.4	432–515	II + VI	1.8	432–515
			I	4.2	600–770	I	2.9	600–666	I + m	2.6	605–695
			I + m	3.7	770–815	I + m	(0.33)	666–710	(I + m)′	1.5	695–745
48 mole% K_2SO_4			45 mole% Na_2SO_4			50 mole% Na_2SO_4					
II + VII	1.9	300–350	II	3.9	200–260	(II)	2.9	390–500			
II + VII	3.6	350–432	II	3.6	260–360	XI	3.5	535–595			
II + VI	3.2	455–500	II	4.4	360–474						
VI	4.0	500–630	XI	6.2	525–580						
V	5.9	653–690									

Table 1. The linear thermal expansion coefficient α of mixtures of Li_2SO_4 with K_2SO_4 and with Na_2SO_4. Structures: I: f. c. c., II: monoclinic, V: unknown, VI and VII: hexagonal, X: unknown, XI: b. c. c., m: melt.

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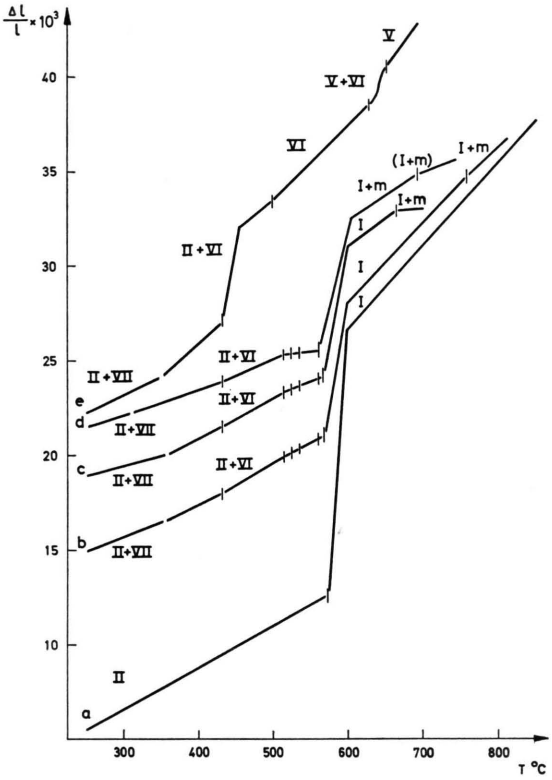

Fig. 3. Relative length change $\Delta l/l$ versus temperature T of different $Li_2SO_4-K_2SO_4$ crystals. K_2SO_4 content: a) 0 mole%, b) 1.0 mole%, c) 2.5 mole%, d) 4.0 mole%, e) 48 mole%. The individual curves are vertically shifted with respect to the origin. For an explanation of the phase notation see the text to Table 1.

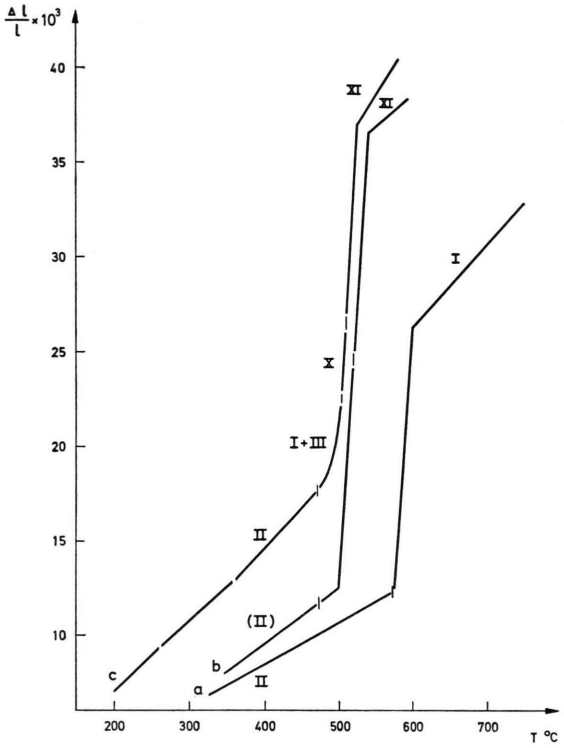

Fig. 4. Relative length change $\Delta l/l$ versus temperature T of different $Li_2SO_4-Na_2SO_4$ crystals. Na_2SO_4 content: a) 0 mole%, b) 50 mole% Na_2SO_4, c) 45 mole% Na_2SO_4. The individual curves are vertically shifted with respect to the origin. For an explanation of the phase notation see the text to Table 1.

sequently the electrical conductivity of the high-temperature AgI is very high [16, 17]. The Li^+ ion plays the same role in the high temperature form of Li_2SO_4 which also has a very high electrical conductivity. In this case, however, the transition between low- and high-temperature forms results in a volume expansion (1.16 cm^3/equivalent) and the low-temperature Li_2SO_4 expands upon heating in the normal way. None of the mixtures investigated in the present work shows evidence of extra mechanisms for entropy increase upon heating more powerful than volume expansion.

The thermal expansion is influenced by the complexity of the crystal, simple close-packed structures generally having high expansivities [18]. This fact is clearly borne out by Fig. 3 and Table 1: An increasing amount of K_2SO_4 results in a decreasing expansivity. Moreover the complex low-temperature forms of each mixture have smaller thermal expansion coefficients than the simpler high-temperature modifications.

There is a priori no reason to expect the coefficient of thermal expansion

$$\alpha = \Delta l / l \, \Delta T$$

(l = sample length, T = temperature) to be a constant. Nevertheless the present investigation (and most previous investigations also [12]) shows that α is essentially constant between the different phase transitions. Even mixed phases may to a good approximation be described by a constant α provided the equilibrium composition of the sample does not

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change upon heating. In the present case an observed mixed phase α may be considered as a weighted average of the expansivities of the pure components (a similar situation has been considered by HOBBS[19]). A non-linear change in l with T is to be expected close to a phase transition (cf. for instance the transition from phase VI to phase V in the mixture 52 mole% $Li_2SO_4 - 48$ mole% K_2SO_4). Such transitions are generally accompanied by a temperature hysteresis which obscures the expected nonlinearity.

For geometrical reasons transitions from one crystal structure to another are accompanied by volume changes. Entropy considerations require that a transition from a low- to a high-temperature form results in a volume increase (cf. however AgI above). This general rule is obeyed by the investigated mixtures. Table 2 shows that even a small amount of K_2SO_4 results in a 50% reduction of the volume change but it is not further reduced by an increase of the K_2SO_4 content. This fact is quite remarkable since (according to the phase diagram by SCHROEDER and KVIST[9]) in pure Li_2SO_4 the transition takes place between a monoclinic (II) and a f. c. c. (I) structure, in mixtures containing 1.0 and 2.5 mole% K_2SO_4 between I + II and I, and in the mixture containing 4.0 mole% K_2SO_4 between II + m (m = melt) and I + m. While it is obvious that a different volume change may be expected for mixtures it is not at all clear why it is independent of composition. It is possible that the phase diagram must be modified in order to be able to explain this feature.

In the I + m region the published $Li_2SO_4 - K_2SO_4$ phase diagram includes a dotted line with little experimental confirmation. It is supported by our measurements on the mixture containing 4.0 mole% K_2SO_4 which show a change in thermal expansivity from 2.6×10^{-5} to 1.5×10^{-5} $^{\circ}K^{-1}$ at the predicted temperature.

Around the equimolar $Li_2SO_4 - Na_2SO_4$ mixture there exists above 550 °C a b. c. c. phase which has arisen some technical interest as a possible solid electrolyte due to its high electrical conductivity. The interest in this part of the investigation has been focussed mainly on the properties of the mixtures above 520 °C. Later studies[11] have shown that a correct phase diagram is more complicated than Ref. [10] indicates. Thus it was considered meaningful (in the mixture containing 50 mole% Na_2SO_4) to give a thermal expansion coefficient for the b. c. c. phase (XI) only. The transition to the b. c. c. phase is accompanied by a considerable volume increase (of the order of 2 cm³/equivalent) and the high-temperature form has a high thermal expansivity. These facts may cause some technical problems.

The viscosity of the solid mixtures studied in the present work is very high (almost unmeasurable with conventional techniques[4, 20]). Our correction method for plasticity gives an opportunity to make a qualitative comparison between the different mixtures. No plasticity was detected in any low-temperature form. In $Li_2SO_4 - K_2SO_4$ the phase I + m showed the most pronounced plasticity and in $Li_2SO_4 - Na_2SO_4$ the phase XI.

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[20] Development work of a very high viscosity viscometer is in progress in this laboratory.