liche Abtragung und Ionisierung des Probenmaterials über den gesamten Beschußquerschnitt – ca. 1 mm² Halbwertsbreite – gegeben. Das hat zur Folge, daß Inhomogenitäten der Probensubstanz wesentlich geringeren Einfluß haben als bei der Hochfrequenzfunkenionenquelle, bei der viel kleinere von Funken zu Funken wechselnde Emissionszentren gebildet werden.

Die kontinuierliche Materialabtragung bietet weiterhin die Möglichkeit, Analysen in Abhängigkeit von der Beschußzeit und damit der Schichttiefe durchzuführen. So wurde zum Beispiel vom Verfasser die Diffusionsfront von Gallium in Silicium bestimmt.

Schluß

Die vorliegende Arbeit stellt den Versuch einer systematischen Untersuchung der SI-Ausbeute reiner Targets und einiger Metalle in Abhängigkeit von ihrer Konzentration in einer Eisenmatrix durch Argonionenbeschuß dar. Der Einfluß der Ionisierungsenergie auf die SI-Ausbeute der einzelnen Targetelemente wird gezeigt.

Die Anwendung der Ionenbeschuß-Ionenquelle in der qualitativen Festkörperanalyse ist bereits von mehreren Autoren beschrieben worden. Herzog [8] berichtet außerdem über die Isotopenverhältnismessung von $^7Li/^6Li$ am Holbrook Meteoriten und über die quantitative Analyse von Bor in Silicium.

Zur quantitativen Analyse beliebiger Probensubstanzen müssen die SI-Ausbeuten der noch nicht gemessenen Elemente bestimmt und die möglichen Einflüsse von Matrixeffekten untersucht werden. Messungen mit dieser Zielsetzung sollen am hiesigen Institut angeschlossen werden.

Ich danke Herrn Prof. Dr. R. Kollath für die Ermöglichung dieser Arbeit sowie der Deutschen Forschungsgemeinschaft und der Allgemeinen Elektricitäts-Gesellschaft für die leihweise Überlassung verschiedener Meßgeräte.

The Electrical Conductivity of Pure Molten Alkali Sulphates and Molten Equimolar Alkali Sulphate Mixtures

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The electrical conductivity of pure Na_2SO_4, Rb_2SO_4 and Cs_2SO_4 and of the nine equimolar mixtures $LiNaSO_4$, $LiRbSO_4$, $LiCsSO_4$, $NaKSO_4$, $NaRbSO_4$, $NaCsSO_4$, $KRbSO_4$, $KCsSO_4$ and $RbCsSO_4$ has been measured up to 1145 °C. From the measurements we have estimated the number of cations taking part in cooperative motions in these salts. The relation between the Tobolsky parameter and the conductivities is discussed.

For mixtures of Li_2SO_4 and Ag_2SO_4, two salts with a common anion and cations of very different mass, the electrical conductivity can be written [1]

$$\Lambda = \Lambda_1 x^k + \Lambda_2 (1 - x^k) \qquad (1)$$

where x is the mole fraction of the salt with the lighter cation and Λ_1 and Λ_2 are the conductivities of the light and heavy salts. The parameter k was interpreted to be the number of cations taking part in a cooperative motion of ions [1].

In mixtures, where the cations differ considerably in size, we may modify Eq. (1) by taking into account that the mobility of the ions depends on the free volume v_f of the salt.

A relation between Λ and v_f has been given by Cohen and Turnbull [2]

$$\Lambda = A T^{1/2} \exp(-B/v_f) \qquad (2)$$

where T is the temperature in °K and A and B positive constantes.

A change Δv_f of the free volume gives

$$\Delta\Lambda/\Lambda = B \cdot \Delta v_f / v_f^2 \qquad (3)$$

and Eq. (1) can be written

$$\Lambda = \Lambda_1 \left(1 + \frac{\Delta v_f(1)}{v_f^2(1)}\right) x^k + \Lambda_2 \left(1 + \frac{\Delta v_f(2)}{v_f^2(2)}\right)(1 - x^k). \qquad (4)$$

[1] A. Kvist, Z. Naturforschg. **22 a**, 208 [1967].

[2] M. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 [1959].

t °C	$\varkappa$ Ω^{-1} cm^{-1}
Na_2SO_4	
958.8	2.498
935.0	2.422
927.5	2.400
916.0	2.361
Rb_2SO_4	
1122.0	1.485
1096.2	1.449
1091.5	1.439
1085.2	1.429
1084.0	1.430
1080.2	1.422
1078.8	1.417
1067.0	1.401
Cs_2SO_4	
1081.5	1.196
1064.5	1.173
1063.0	1.177
1044.0	1.145
1038.8	1.146
1013.5	1.113
$LiNaSO_4$ (molten)	
848.0	2.568
828.2	2.471
801.8	2.364
773.2	2.234
750.5	2.125
723.5	1.995
685.6	1.810
660.2	1.684
655.0	1.656
630.2	1.533
(solid)	
599.0	1.238
592.8	1.175
568.2	1.026
545.8	0.8970
$LiRbSO_4$	
938.5	1.320
924.2	1.287
901.5	1.232
878.8	1.173
856.6	1.117
813.2	1.063
812.5	1.012
794.2	0.9644
785.0	0.9292
769.5	0.8946

t °C	$\varkappa$ Ω^{-1} cm^{-1}
$LiCsSO_4$	
1003.0	1.1910
993.0	1.1750
982.2	1.1468
968.0	1.1184
952.5	1.0893
930.8	1.0443
890.2	0.9631
876.2	0.9298
853.8	0.8808
832.2	0.8375
808.8	0.7876
791.0	0.7479
771.4	0.7105
$NaKSO_4$	
920.2	1.698
909.5	1.666
$NaRbSO_4$	
987.8	1.405
968.5	1.383
926.5	1.304
910.5	1.272
890.8	1.231
868.5	1.182
840.8	1.121
$NaCsSO_4$	
905.8	1.0525
882.8	1.0131
868.2	0.9758
847.8	0.9373
820.2	0.8811
803.5	0.8461
784.2	0.8072
743.0	0.7201
736.8	0.7061
719.2	0.6671
698.8	0.6264
682.5	0.5910
$KRbSO_4$	
1109.0	1.669
1087.5	1.630
1064.0	1.592
$KCsSO_4$	
1002.0	1.290
969.8	1.233
959.8	1.213
942.2	1.191
$RbCsSO_4$	
1145.2	1.293
1135.2	1.279
1115.5	1.257
1100.0	1.241
1084.2	1.219
1077.2	1.212
1059.0	1.188
1055.8	1.179

$\Delta v(i)/v(i)$ is the relative difference in free volume between the pure salt with the conductivity Λ_i and the mixture.

In order to test Eq. (4) and to estimate k, we have measured the electrical conductivities of some pure alkali sulphates and alkali sulphate mixtures.

All salts were reagent grade and were used without further purification. The experimental technique is described elsewhere in detail [1].

The obtained conductivities are tabulated in Table 1. The results of pure sodium sulphate are about five percent higher than those obtained by ARNDT [3]. The conductivities of pure Li_2SO_4 (l. c. [4]), K_2SO_4 (l. c. [5]) and Ag_2SO_4 (l. c. [1]) have recently been reported by the author.

It has been found that the systems $Li_2SO_4 - Ag_2SO_4$ (l. c. [1]) and $Li_2SO_4 - K_2SO_4$ (l. c. [6]) exhibit volumetric additivity and we have therefore assumed that this is the case in all the investigated sulphate mixtures. The molal conductivities in Table 2 have been calculated by using the densities of the pure salts [1, 7].

Salt	a	$-b$	s	Λ_{900} Ω^{-1} cm^{-2}	Range °C
Li_2SO_4	0.34166	65.0	0.4	242.5	860— 930
Na_2SO_4	0.25851	73.4	0.1	159.3	916— 960
K_2SO_4	0.23679	78.5	0.2	134.6	1068—1086
Rb_2SO_4	0.20317	70.1	0.2	112.8	1067—1122
Cs_2SO_4	0.18051	51.2	0.4	111.3	1013—1082
Ag_2SO_4	0.19718	21.0	0.1	156.5	670— 750
$LiNaSO_4$	0.31101	105.9	0.4	174.0	860— 848
$LiKSO_4$	—	—	—	122.6	—
$LiRbSO_4$	0.21343	96.5	0.3	95.6	769— 938
$LiCsSO_4$	0.19673	93.1	0.4	84.0	771—1003
$NaKSO_4$	0.30841	133.6	0.2	144.0	909— 920
$NaRbSO_4$	0.19261	67.9	0.5	105.4	840— 988
$NaCsSO_4$	0.20168	85.2	0.2	96.3	682— 906
$KRbSO_4$	0.21313	70.2	0.2	121.6	1064—1109
$KCsSO_4$	0.20732	73.2	0.4	113.4	942—1002
$RbCsSO_4$	0.17322	50.3	0.3	105.6	1055—1145
$LiAgSO_4$	0.27760	77.8	0.4	172.0	580— 740

Table 2. The molar electrical conductivity described by the relation $\Lambda = a\,t + b$, where t is the temperature in °C. The densities were obtained from JAEGER and KAHN [7]. Λ_{900} of pure potassium sulphate has been extrapolated from previously published data [5].

Table 1. The specific electrical conductivity of molten Na_2SO_4, Rb_2SO_4, Cs_2SO_4 and some equimolar sulphate mixtures. The conductivities of the systems $Li_2SO_4 - Ag_2SO_4$ (l. c. [1]) and $Li_2SO_4 - K_2SO_4$ (l. c. [5]) have recently been published by the author. $LiNaSO_4$ forms a solid high temperature modification with a cubic (b.c.c.) lattice.

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[4] A. KVIST, Z. Naturforschg. **21 a**, 487 [1966].
[5] A. KVIST, Z. Naturforschg. **21 a**, 1221 [1966].
[6] D. JAMES and C. LIU, J. Chem. Eng. Data **8**, 469 [1963].
[7] F. JAEGER and J. KAHN, Koninkl. Ned. Akad. Wetenschap. Proc. **19**, 381 [1916].

Λ_{900} decreases with increasing PAULING radii of the cations

$$\Lambda(Li_2SO_4) > \Lambda(Na_2SO_4) > \Lambda(Ag_2SO_4) > \Lambda(K_2SO_4) > \Lambda(Rb_2SO_4) > \Lambda(Cs_2SO_4).$$

As might be expected we also find

$$\Lambda(LiNaSO_4) > \Lambda(LiAgSO_4) > \Lambda(LiKSO_4) > \Lambda(LiRbSO_4) > \Lambda(LiCsSO_4).$$

But if we look at the mixtures containing caesium sulphate

$$\Lambda(KCsSO_4) > \Lambda(NaCsSO_4) > \Lambda(LiCsSO_4).$$

Table 3 shows that the free volume of the pure univalent sulphates increases with increasing radius of the cation and the mobility of i. e. a potassium ion in $(Li, K)_2SO_4$ should then decrease with increasing concentration of lithium sulphate. This is in agreement with observations made by LJUBIMOV and LUNDÉN [8].

Salt	Cation radius Å	v_f (cm³/mole) 800 °C	900 °C	1000 °C
Li_2SO_4	0.60	18.9	19.9	21.1
Na_2SO_4	0.95	28.9	30.4	32.1
K_2SO_4	1.33	39.7	42.1	44.5
Rb_2SO_4	1.48	47.9	50.4	53.1
Cs_2SO_4	1.69	55.7	57.6	60.0
Ag_2SO_4	1.26	22.3	23.9	25.6

Table 3. The free volume of the pure sulphates. The radius of the sulphate ion was taken as 2.4 Å and the volume of the cations was calculated by using PAULING radii.

When the difference in radii between the two cations is big, the conductivity of the equimolar mixture is even lower than of both the pure salts. This is the case for five of the eleven mixtures in Table 2.

The constant B has been calculated from Eq. (2) and it is seen in Table 4 that B/v_f falls between 0.4 and 1.6. For the pure alkali sulphates B/v_f is about 0.7.

We have in Eq. (4) used a mean value of B/v_f, which is about one, and Eq. (4) can thus for 1:1 mixtures be written

$$\Lambda = \Lambda_1 \left(1 + \frac{\Delta v_f(1)}{v_f(1)}\right) x^k + \Lambda_2 \left(1 + \frac{\Delta v_f(2)}{v_f(2)}\right) (1 - x^k). \quad (5)$$

Salt	B	B/v_f 800 °C	900 °C	1000 °C
Li_2SO_4	14.09	0.75	0.71	0.67
Na_2SO_4	19.39	0.67	0.64	0.60
K_2SO_4	28.79	0.73	0.68	0.65
Rb_2SO_4	36.20	0.76	0.72	0.68
Cs_2SO_4	40.78	0.73	0.71	0.68
Ag_2SO_4	10.68	0.48	0.45	0.42
$LiRbSO_4$	36.61	1.10	1.04	0.99
$LiCsSO_4$	53.14	1.42	1.37	1.32
$NaKSO_4$	31.49	0.92	0.89	0.82
$NaRbSO_4$	32.72	0.85	0.81	0.77
$NaCsSO_4$	68.31	1.61	1.55	1.48
$KCsSO_4$	42.92	0.90	0.86	0.82

Table 4. The constant B and B/v_f for the pure sulphates and some of the investigated mixtures, calculated from Eq. (2). For the mixtures v_f was taken to be the arithmetic mean of the corresponding two values in Table 3.

The k-values estimated from Eq. (5) are tabulated in Table 5. k is generally about four and as might be expected k decreases with increasing temperature. An interesting consequence of this is that the relative mobility of the cations should increase with increasing temperature. k increases somewhat with decreasing values of B.

Salt	k 800 °C	900 °C	1000 °C
$LiKSO_4$	—	3.2	—
$LiRbSO_4$	4.1	3.7	3.5
$LiCsSO_4$	5.1	4.4	3.9
$NaCsSO_4$	3.8	3.2	2.9
$LiAgSO_4$	2.5	2.1	—

Table 5. The number of ions taking part in a cooperative motion estimated from Eq. (5).

In a previous paper [9], we have calculated k from conductivity measurements of lithium sulphate with small quantities of potassium sulphate and from electromigration experiments. We then obtained $k = 2.7$ at 890 °C, and this value is in satisfactory agreement with the value $k = 3.2$ obtained here. In that paper we also pointed out that it was probable that k increases with increasing radius of the impurity cation in molten lithium sulphate and this hypothesis is supported by this investigation.

It has often been proposed that the electrostatic forces between the cations and anions are very important for the transport properties in molten salt mixtures, but it seems then difficult to understand for instance why the electrical conductivity of pure

[8] V. LJUBIMOV and A. LUNDÉN, Z. Naturforschg. **21 a**, 15 [1966].

[9] A. KVIST, Z. Naturforschg. **21 a**, 1601 [1966].

lithium sulphate is so much higher than in the other sulphates. It is also difficulty to explain the decrease in conductivity of molten lithium sulphate when impurity cations are added [9].

The concentration region, where a is small has little interest in this investigation, since the term a^k in Eq. (5) is very small.

WARD and JANZ [10] have proposed that in a binary mixture the difference between the "ideal" conductivity,

$$\Lambda_{\text{ideal}} = a\,\Lambda_1 + (1-a)\,\Lambda_2\,,$$

and the measured one, is a function of the TOBOLSKY parameter Θ, a quantity which has been found very useful in the theory relating viscosity and surface tension of molten salts [11–12]. Θ is defined from

$$\Theta = [\,(d_1 - d_2)/(d_1 + d_2)\,]^2,$$

where d_i is the sum of the diameters of the cation and the anion. DE NOOIJER [13] has plotted $\Lambda_{\text{ideal}} - \Lambda$ as a function of Θ for univalent nitrate mixtures and he found that it is possible to draw a straight line through these points.

Also the results for molten sulphates give an approximately straight line (Fig. 1). It is, however, seen in Table 2 that the conductivity of an equimolar mixture is almost the same as the conductivity of the

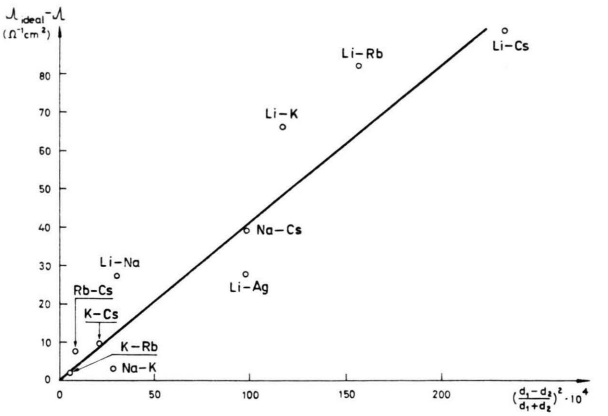

Fig. 1. The difference between the "ideal" electrical conductivity and the measured one as a function of the TOBOLSKY parameter.

pure component with the lowest conductivity and this is the case also in the nitrates investigated by DE NOOIJER [13]. If we then plot the difference in conductivity between the two pure salts as a function of Θ we also get a straight line. Since there is no reason why this quantity should be a function of Θ, we find it difficult to draw any conclusions from the fact that a straight line is obtained.

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