

In Abb. 4 ist der Verlauf der Thermokraft mit den der Arbeit von HOWARD und SONDHEIMER entnommenen Werten für δ (entsprechend dem jeweiligen Z) ebenfalls aufgetragen. Da der Verlauf der Thermokraft auf diese Weise wesentlich besser wiedergegeben wird, ist anzunehmen, daß Streuung am optischen Zweig der Gitterschwingungen in untersuchten Temperaturbereich vorherrscht. Zu ähnlichen Ergebnissen gelangte HUTSON⁴ bei der Untersuchung des Temperaturverlaufes der Beweglichkeit an ZnO-Einkristallen.

Zum Vergleich wurden in Abb. 4 die berechneten Kurven für die Thermokraft für drei verschiedene Werte der effektiven Masse aufgetragen; es ist zu ersehen, daß der Wert 0,07 beste Übereinstimmung von gemessenen und berechneten Werten bewirkt.

Der hier bestimmte Wert der effektiven Masse stimmt mit dem aus Untersuchungen der Infrarot-

reflexion von COLLINS und KLEINMANN⁹ gewonnenen Wert der Polaronenmasse $m^{(p)} = 0,06 m$ und dem von HUTSON⁵ aus dem Sättigungsverhalten des phonon-drag-Anteiles ermittelten Wert $m^{(1)} = 0,07 m$ (eine neuere Deutung dieses Versuchsergebnisses findet sich bei HUTSON¹⁰) gut überein. Hingegen bestehen Differenzen zu der von DIETZ¹¹ et al. aus der Temperaturabhängigkeit der Absorptionskante ermittelten effektiven Masse von 0,38 m und der von HUTSON⁴ aus HALL-Effektmessungen bestimmten Masse der Elektronen im Leitungsband $m^{(H)} = 0,5 m$ und der aus der Aktivierungsenergie der Donatoren abgeleiteten Masse von 0,27 m .

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¹⁰ A. R. HUTSON, J. Appl. Phys. **32** S, 2287 [1961].

¹¹ R. E. DIETZ, J. J. HOPFIELD u. D. G. THOMAS, J. Appl. Phys. **32** S, 2287 [1961].

The Electrical Conductivity of Molten Lithium Molybdate

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The electrical conductivity of Li_2MoO_4 has been measured on both sides of the melting point in order to see whether this salt has a high temperature modification with properties similar to $\alpha\text{-Li}_2\text{SO}_4$. This was found not to be the case. The temperature dependence of the conductivity was studied for the melt, giving

$$\kappa = -2.518 + 6.999 \cdot 10^{-3} t - 1.356 \cdot 10^{-6} t^2 \Omega^{-1} \text{ cm}^{-1} \quad (704-950^\circ \text{C}).$$

There is a discrepancy between our results and recent measurements by MORRIS and ROBINSON. Possible explanations are discussed.

Lithium molybdate might be expected to have a high temperature modification with structure and properties similar to $\alpha\text{-Li}_2\text{SO}_4$, i. e. characterized by a high cation mobility¹. In order to investigate if such a modification exists, we decided to measure the electrical conductivity on both sides of the melting point. When our series of measurements were nearly completed, a report appeared of conductivity measurements on molybdate melts by MORRIS and ROBINSON² (Abbreviated M. & R. in this paper). Since there was a discrepancy between their results

and ours, we made more measurements, which gave essentially the same results, and we tried to check all possible sources of error.

Commercial Li_2MoO_4 (Dr. Theodor Schuchart, München) was used without further purification. The conductivity cell and the experimental procedure has been described recently¹. The conductivity decreased rapidly as soon as the melt was cooled below the solidification point, i. e. it was evident that Li_2MoO_4 does not have any high temperature modification similar to $\alpha\text{-Li}_2\text{SO}_4$.

¹ A. KVIST and A. LUNDÉN, Z. Naturforschg. **20** a [1965], in press.

² K. B. MORRIS and P. L. ROBINSON, J. Phys. Chem. **68**, 1194 [1964].



Investigation	Eqn.	y	x	z	A	s_A	B	s_B	C	s_C	$\bar{x}$	$\bar{z}$	s
This	1	κ	$t \cdot 10^{-3}$	—	2.176	0.005	4.766	0.073	—	—	0.7936	—	0.022
	2	κ	$t \cdot 10^{-3}$	$t^2 \cdot 10^{-6}$	2.176	0.004	6.999	1.581	— 1.356	0.959	0.7936	0.6337	0.017
	3	$\ln \kappa$	$T^{-1} \cdot 10^3$	—	0.7685	0.0022	— 2.4982	0.0408	—	—	0.9405	—	0.026
	4	$\ln \kappa$	$T^{-1} \cdot 10^3$	$T^{-2} \cdot 10^6$	0.7685	0.0020	— 0.4130	1.1910	— 1.1312	0.6458	0.9405	0.8874	0.017
M. & R.	1'	κ	$t \cdot 10^{-3}$	—	5.199	0.048	18.682	1.010	—	—	0.8662	—	0.168
	2'	κ	$t \cdot 10^{-3}$	$t^2 \cdot 10^{-6}$	5.199	0.021	— 104.564	18.686	71.231	10.797	0.8662	0.7526	0.070
	3'	$\ln \kappa$	$T^{-1} \cdot 10^3$	—	1.6334	0.0080	— 4.6117	0.2150	—	—	0.8792	—	0.120
	4'	$\ln \kappa$	$T^{-1} \cdot 10^3$	$T^{-2} \cdot 10^6$	1.6334	0.0041	— 37.636	6.2135	18.7254	3.5226	0.8792	0.7744	0.073

Table 1. Temperature dependence of electrical conductivity expressed by means of four different equations for measurements by us and by MORRIS and ROBINSON². s_A , s_B , s_C are the standard deviations of the factors A , B , and C , respectively, and s is the standard deviation of the conductivity readings (l. c.¹).

For the molten salt five independent series of measurements were made, which were all used for computing the constants of linear or quadratic equations of the type¹

$$y = A + B(x - \bar{x}),$$

$$y = A + B(x - \bar{x}) + C(z - \bar{z}).$$

The results are summarized in Table 1, where the same equations also are used for the conductivity data reported by M. & R.³

The standard deviation s is found to be about the same whichever equation is used to express our results. It is, however, well known that a given set of empirical data often can be represented about equally well by a variety of equations⁴.

According to M. & R. the conductivity is by nearly a factor of two higher than found by us. Furthermore, the temperature dependence is different, M. & R. having found a much larger temperature gradient. If e. g. the ARRHENIUS eqns. (3) and (3') are considered, the "activation energy" $RB = 4.96$ kcal per equivalent found by us is in good agreement with what is commonly found for molten salts⁵ while the M. & R. data give $RB = 9.2$ kcal per equivalent. (M. & R. desisted from a rate theory interpretation of their results.) A comparison with our measurements at a common temperature of the two salts Li_2SO_4 and Li_2WO_4 (l. c.^{1,6}) shows that $\kappa_{\text{Li}_2\text{SO}_4} > \kappa_{\text{Li}_2\text{MoO}_4} > \kappa_{\text{Li}_2\text{WO}_4}$, which is to be expected. For both Li_2SO_4 and Li_2WO_4 our results are con-

sistent with other investigations. For the latter salt this investigation was made by MORRIS and ROBINSON⁷ with essentially the same technique as they used for Li_2MoO_4 .

There are four possible sources of the discrepancy: differences in the composition and purity of the salt used, changes in conductivity due to partial thermal decomposition, corrosion by the melt of the conductivity cells, and permeation of lithium ions through quartz. (It might not be possible to distinguish completely between corrosion and permeation). We checked the purity of our salt in several ways. Precipitation of Ag_2MoO_4 gave the expected amount of molybdate⁸. A spectrophotometric search for other alkali ions showed that neither Na nor K were present to more than a few tenths of a per cent, and aqueous solutions of our salt were neutral. The melting point of the salt was about 704 °C, i. e. in agreement with literature values. All these checks were made both on virgin salt and on salt that had been used in our experiments, giving the same results in each case. Furthermore, the five series of measurements were deliberately extended over different temperature ranges (highest temperature varied between 740 °C and 950 °C) and periods of time (up to six days) but they all coincided regarding conductivity as well as freezing point. Thus it is evident that our salt was completely stable in spite of the fact that our measurements were made in air, while M. & R. had an argon atmosphere in their cells.

³ The reason for computing four different equations is that eqns. (1) and (2) are suitable for interpolating conductivity data, the ARRHENIUS eqn. (3) is associated with the rate theory of transport, and eqn. (4) can be used to obtain the "activation energy" at an arbitrary temperature, while (3) gives the "activation energy" averaged over the whole temperature range.

⁴ A. HALD, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 568.

⁵ G. J. JANZ and R. D. REEVES, Adv. Electrochem. and Electrochem. Eng. V. (Ed. P. DELAHAY and C. W. TOBIAS), in press.

⁶ A. KVIST and A. LUNDÉN, unpublished.

⁷ K. B. MORRIS and P. L. ROBINSON, J. Chem. Eng. Data **9**, 444 [1964].

⁸ Standard Methods of Chemical Analysis, (Ed. N. H. FURMAN), 6th Ed. Van Nostrand, New York 1962, Vol. I, p. 675.

M. & R. used capillary cells made of quartz, while we had Alsint cells¹. M. & R. report that their cells were corroded by the melt and were discarded after some time. In some preliminary experiments we tried Vycor cells, but we found that they were corroded so rapidly by the Li_2MoO_4 melt that they cracked after 2 hours, while the lifetime of a cell containing molten Li_2WO_4 was 12 hours⁹. In comparison the corrosion by Li_2SO_4 is small. Apparently high conductivity readings might be due either to a widening of the capillary bore by corrosion, or to permeation of the quartz by lithium ions. The rates of both these phenomena are likely to increase rapidly with temperature. This would cause a high apparent tem-

perature gradient for the measured conductivity, and would explain why M. & R. found an unusually large temperature dependence. Widening of the bore would result in a time dependent "conductivity"¹⁰, while permeation is more difficult to detect with certainty. Corrosion observations for halide melts indicate that a certain migration of lithium ions might occur at elevated temperatures in Vycor and some ceramics^{11, 12}. Summarizing we find that permeation or corrosion phenomena are the most likely explanation of the observed discrepancy.

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⁹ On the other hand, M. & R. (private communication) find that tungstate melts are more corrosive than molybdate melts. The disagreement between their and our corrosion observations might be due to several reasons such as: differences in purity or composition of the salts, or to the fact that they used quartz and we Vycor for the cells.

¹⁰ M. & R. checked the calibration of each cell after a complete set of measurements and discarded those cells where there was a change in cell constant. They doubt that corrosion influenced their data (private communication).

¹¹ A. LUNDÉN, unpublished, see also A. LUNDÉN, Corrosion Sci. **1**, 62 [1961].

¹² The migration of lithium ions through quartz under the influence of a high electric field has been studied by J. PAULY, C. R. Acad. Sci., Paris **252**, 2407 [1961].

Die Atomverteilungskurven für festes und flüssiges Aluminium nach Untersuchungen an SAP

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Es wurde die Atomverteilungskurve für festes und für flüssiges Aluminium in der Nähe der Schmelztemperatur bestimmt. Die Untersuchungen wurden an Sinteraluminium (SAP) durchgeführt.

Die für die feste Phase ermittelte Wahrscheinlichkeitskurve stimmt bis 20 Å zufriedenstellend mit der für ein Al-Gitter errechneten Kurve überein. Das mittlere Schwankungsquadrat beträgt für benachbarte Atome etwa 0,05 Å², für entferntere Atome etwa 0,08 Å² und ist damit kleiner, als nach der DEBYESchen Theorie abgeschätzt wird.

In der Schmelze kann man für die ermittelten 8,3 Atome der ersten Koordinationsschale einen definierten mittleren Abstand angeben, der 2 bis 3% kleiner ist als in der festen Phase. In der Größe der thermischen Schwankungen ist kein Unterschied festzustellen.

Weiterhin wird gezeigt, daß man auch den Atomen im unsymmetrischen Teil des ersten Maximums der Schmelze einen definierten mittleren Abstand vom Bezugsatom zuordnen kann.

In einer vorhergehenden Arbeit¹ wurde die an Hand von RÖNTGEN-Interferenzaufnahmen ermittelte Atomverteilungskurve von flüssigem Kupfer mit den für das hexagonale und das kubische Gitter bei der Schmelztemperatur berechneten Kurven verglichen. Die Berechnung basiert auf Abschätzungen der thermischen Relativbewegung entfernter Atome und der

Korrelation in der Bewegung benachbarter Atome. Um beurteilen zu können, inwieweit diese Abschätzungen zutreffen, wurde versucht, die Atomverteilungskurve für die feste Phase in der Nachbarschaft des Schmelzpunktes nach der gleichen röntgenographischen Methode experimentell zu ermitteln wie für die flüssige Phase.

Als Versuchsstoff wählten wir Sinter-Aluminium, das in der metallischen Matrix dispergierte Alu-

¹ H. RUPPERSBERG, Soc. fr. Métall. Journ. Automne, Paris 1963; Mem. Sci. Rev. Met. **61**, 709 [1964].