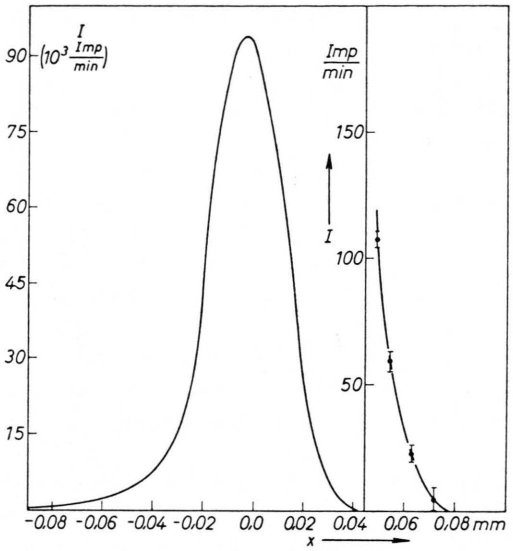

Abb. 10. Blindstreukurve und Primärstrahlprofil der RÖNTGEN-Kleinwinkel-Kamera bei einer Eintrittsspaltweite von $d = 8$ μm.

weiten betrugen $d_1 = 0{,}06$ mm und $d_2 = 8$ μm, die Zählrohrspaltweiten $z_1 = 0{,}15$ mm und $z_2 = 0{,}03$ mm. Die Impulsraten im Primärstrahl bei geöffnetem Zählrohrspalt betrugen $7{,}4 \cdot 10^6$ Imp./min und $1{,}9 \cdot 10^5$ Imp./min. Bei beiden Messungen wurde der in Abb. 2 dargestellte Reflektor eingesetzt. Die Verwendung eines kürzeren Reflektors im zweiten Fall bringt keine Verbesserung der Monochromasie, da für kleine Divergenzen des Primärstrahls der Verlauf der Monochromatorfunktion nur durch den Verlauf des Reflexionskoeffizienten des Reflektormaterials bestimmt ist. Den Kurven kann entnommen werden, welche minimale Streukraft mit der Kamera noch nachgewiesen werden kann.

Unser besonderer Dank gilt unserem verehrten Lehrer, Herrn Prof. Dr. W. SCHÜTZ, für das Interesse und die Förderung, die er der Arbeit entgegengebracht hat. Herrn Dr. D. UNANGST danken wir für Diskussionen und für seine Hinweise beim Aufbau der Kleinwinkelkamera.

Isotope Effect at the Transition Point Studied by Zone Refining of Solid Lithium Sulfate

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The technique of zone refining has been applied at the transition point between α- and β-Li_2SO_4. The light lithium isotope is enriched in the direction of zone travel. The equilibrium distribution coefficient, k_0, is 0.996 for the two isotopic lithium sulfates. It is estimated that the transition point of $^6Li_2SO_4$ is about 0.7 °C lower than that of $^7Li_2SO_4$.

Zone melting has in a few years developed into a common method of purification of solids, and has for many applications proved to be superior to other separation methods [1]. The basic conditions for zone refining are that the equilibrium distribution coefficient, k_0, differs from unity, and that the effective diffusion coefficient, D, differs considerably between the two phases. In principle, the technique should be applicable also at the transition between two solid phases if these two requirements are fulfilled [1]. However, as a rule the change in diffusion coefficient at a solid-solid transition is moderate and far less than required for zone refining. A further restriction is that the rate of zone travel should be less than D/l, where l is the zone length, which means that, anyhow, the travel rate will be too slow for practical applications in most solids [2]. However, a few salts are known to have high-temperature modifications, where D is of the order of 10^{-5} cm² s^{-1}. This is the case for lithium sulfate [3], and we have recently demonstrated, that zone refining can be performed

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[1] W. G. PFANN, Zone Melting, Wiley & Sons, New York 1958.

[2] For molten zones the travel rate is not restricted by l but by the diffusion layer thickness δ. Since $\delta \ll l$ due to convection in the melt, higher travel rates are possible in melts than for solid zoning [1].

[3] A. LUNDÉN, Z. Naturforschg. **17 a**, 142 [1962].

at the transition point of a binary mixture of lithium and silver sulfates [4]. Thus, zone refining of pure lithium sulfate should give information on a possible slight difference between the transition points of $^6Li_2SO_4$ and $^7Li_2SO_4$.

A slight isotope separation has been obtained by zone melting of lithium metal [5], for which an isotope shift of 0.23 degr. has been reported for the melting point [6]. A slight separation of boron isotopes has been obtained by zone melting of the oxide [7], while zone melting of ice has given a considerable separation of hydrogen isotopes [8–10].

From the established theory for zone refining [1] we shall quote here only the facts that are essential for the interpretation of our experiments. The distribution coefficient is equal to the ratio C_L/C_H, where C denotes solute concentrations ($^6Li_2SO_4$ in our case) and the subscripts L and H denote low and high temperature phases respectively. The effective distribution coefficient k is always less than the equilibrium distribution coefficient k_0, since

$$k = \frac{k_0}{k_0 + (1-k_0)\, e^{-f\delta/D}} \tag{1}$$

where f is the growth rate, D the diffusivity in the zone, and δ is the diffusion layer thickness. After passage of one molten zone through a charge of uniform initial concentration, C_0, the solute concentration, C, at the distance x from the starting end is given by READ's equation

$$C/C_0 = 1 - (1-k)\exp(-k\,x/l) \tag{2}$$

where l is the zone length. After n passes the concentration at $x=0$, $C_n(0)$, is given by REISS' equation

$$\frac{C_0}{C_n(0)} = 1 + n(k-1) - \sum_{s=1}^{n-1} \frac{(n-s)\,(k-1)\, s^{s-2}\, k^{s-1}\, e^{-sk}}{(s-1)\,!} . \tag{3}$$

Eqn. (2) is not valid for the last zone length where normal "freezing" occurs. In this zone the distribution follows

$$C_n(x) = C_n(L-l)\;[(L-x)/l]^{k-1} \tag{4}$$

where L is the length of the ingot and $C_n(L-l)$ is the concentration at the distance l from the end.

The general procedure of our experiment is to measure the isotope distribution along the sample after one or more passes and to calculate k by means of the eqns (2) – (4). Thereafter k_0 can be estimated according to eqn (1) provided that δ/D is known. The experimental method [1] to determine this ratio is hardly practicable in our case. For solid zoning $\delta = l$, and the problem is now to determine l with sufficient accuracy. Regarding D, a crude determination of the cation self diffusion coefficient in Li_2SO_4 exists [3], from which we estimate that $D = 3 \cdot 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$ at the transition point.

Inside a tube of Vycor glass a column was built up of slabs of lithium sulfate with ceramic rods as end pieces. The column was held together with a spring to allow for the volume expansion at the phase transition. The column was placed horizontally inside a furnace, where the heating was concentrated to a short coil made of a spiral of "Kanthal A" wire. (A spiral winded with a diameter of 5 mm was bent to form a loop of 25 mm diameter.) By means of a screw the furnace was driven at a slow speed along the Vycor tube.

The heating power was supplied from a voltage stabilizer, and three thermocouples (two in fixed positions in the moving furnace and one inside the salt column) were connected to a recorder so that the temperature could be checked during the whole experiment, which could take a couple of weeks. Since temperature fluctuations of a few degrees are unavoidable, the maximum temperature was chosen about 12° higher than the transition point of pure lithium sulfate (575 °C), which gives a zone length of about 8 mm. If several zone passes are planned, the total sample length should be at least five times the zone length, but for single pass experiments it is sufficient that $L > l$.

Three experiments were performed, see Table 1. Before the last experiment the whole ingot was heated to above the transition point for some hours in order to remove grain boundaries and ensure complete homogenity, while for the first two experiments, the zone refining was done directly on the

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Experiment	1	2	3
Number of passes n	10	1	1
Growth rate f mm/hour	2.3	0.43	0.43
Zone length, l mm	10	7	10
Total length, L mm	41	22	17
First sample $(Q_b - 1) \cdot 10^4$	55 ± 16	14 ± 17	32 ± 15
Last sample $(1 - Q_e) \cdot 10^4$	58 ± 16	80 ± 17	62 ± 15
$(1 - k_b) \cdot 10^4$	12 ± 3	14 ± 17	30 ± 15
$(1 - k_e) \cdot 10^4$	21 ± 5	24 ± 5	21 ± 5
$(1 - k_{ob}) \cdot 10^4$ for $(\delta/D)_{exp}$	100	18	45
$(1 - k_{oe}) \cdot 10^4$ for $(\delta/D)_{exp}$	174	32	31
$(1 - k_{ob}) \cdot 10^4$ for $(\delta/D)_{adj}$	43	17	38
$(1 - k_{oe}) \cdot 10^4$ for $(\delta/D)_{adj}$	75	28	27

Table 1. Results of zone refining at transition point of lithium sulfate. $Q = ({}_7C/{}_6C)/({}_7C_0/{}_6C_0)$ = isotope separation factor [12], where ${}_6C$ and ${}_7C$ are the concentrations of the two isotopes, and the subscript o denotes the initial concentration. k=effective distribution coefficient [12], k_0=equilibrium distribution coefficient, the subscripts b and e correspond to samples at the beginning and end of the ingot. $(\delta/D)_{exp}$ ratio between the experimental values for the diffusion layer thickness and the self-diffusion coefficient. $(\delta/D)_{adj} = 0.6(\delta/D)_{exp}$. The errors quoted for Q and k correspond to the standard deviations of the measured isotope abundance ratios.

column of salt slabs. These slabs seemed to have sintered together to form a homogeneous column after one pass. After quenching, the columns were divided into samples of a length of about one mm. The samples were converted into lithium nitrate, and the ^{7}Li/^{6}Li isotope abundance ratio was measured with a mass spectrometer. Since only a small isotope separation was expected, the samples were measured in carefully chosen sequences, and the separation factors were calculated as described elsewhere [11]. It was found that the light isotope was enriched in the direction of zone travel, i. e. that the transition point is lower for $^6Li_2SO_4$ than for $^7Li_2SO_4$, and by definition $k<1$. For experiment no 2 "humps" in the isotope abundance ratio were noticed at the position where the boundary between two salt slabs had been. (Although the surface of the column was homogeneous, the position of the boundary could be traced in the interior.) It is thus obvious that the first zone pass causes the slabs to sinter together, but that transport of lithium ions through the "boundary" does not occur with full efficiency during this pass. The question then arises if the ion transport is slightly restricted also at the grain boundaries originally present within the salt slabs. For this reason experiment 3 is considered more reliable than no. 2.

The errors quoted in Table 1 for Q and k correspond to a standard deviation of 0.026 for nearly normal isotope abundance ratios when our mass spectrometer is in its best condition [11–13]. It is obvious that much larger errors than the quoted one can be introduced into the calculated k_0. The importance of the exponent $f\delta/D$ of eqn (1) increases strongly with increasing rate f. This is shown in Table 1 where k_0 is given both for the "experimental" $f\delta/D$, i. e. $\delta = l$ and $D = 3 \times 10^{-5}$ cm^2 s^{-1}, and for an "adjusted" exponential obtained either by assuming that the actual zone length was only 60% of the l quoted in Table 1, or that $D = 5 \times 10^{-5}$ cm^2 s^{-1}. The effect of this adjustment is drastic for the ten-pass experiment but moderate for the one-pass experiments, and it is seen that the deviations between the three experiments now become resonable. The uncertainty in δ/D is large enough to account for "adjustments" like this. The temperature distribution along the column is such that the gradient is steep (~ 14 degr./mm) at a distance of $4-5$ mm from the maximum, which means that the actual zone length hardly can be much larger than quoted in Table 1, but that l might well be somewhat smaller, if the heater is not adjusted properly. Regarding D, the measurement was crude, and we have now extrapolated 25° below the lowest measuring point [3], which means that the used D-value might well be off by a factor of two. Thus we find it plausible that the equilibrium distribution coefficient for the two isotope lithium sulfates is 0.996.

The equilibrium distribution coefficient k_0 can be used to estimate the difference ΔT between the transition points of $^6Li_2SO_4$ and $^7Li_2SO_4$ by means of the following formula, which is strictly valid for dilute solutions [1]:

$$\Delta T = N_2 R T^2 (1 - k_0)/\Delta H \qquad (5)$$

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[11] A. Lundén, Chalmers Tekn. Högskol. Handl. No. 289, Göteborg 1964.

[12] For isotope separation experiments the results are usually expressed by means of the separation factor Q, while the distribution coefficient k is used in the theory of zone refining.

[13] A few measurements of isotope abundance ratios were discarded because they differed significantly from the other measurements for the experiment in question.

where ΔH is the heat of transition, N_2 is the mole fraction of solute (^{6}Li), and R is the gas constant. According to Voskresenskaya and Banashek the heat of transition is 6.5 kcal/mole, which is in fair agreement with other measurements [14, 15]. Thus we find that ΔT is about 0.7°. Zone refining should also be applicable for estimating isotope shifts in the melting points, and work is now in progress with several lithium salts.

The equilibrium distribution coefficient k_0 is close to unity, which is to be expected at elevated temperatures for isotope effects due to differences in zeropoint-energy. Thus, our estimation of k_0 confirms Klemm's interpretation of the isotope effect in electromigration as being due to a kinetic effect [16].

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Ein Verfahren zur getrennten Untersuchung der einzelnen Mineralbestandteile von Steinmeteoriten mittels spezifischer Lösungsmittel

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Different chemical solvents are used to dissolve the diverse mineral fractions of stone meteorites for measurements of their rare gas content. In this procedure the meteoritic minerals are dissolved step by step. The main advantage of the method is that the whole meteorite sample is used for the analyses and no restrictions due to grain size occure.

As an example, rare gas measurements on the meteorite Mocs are described using the technique. The quality of the separation of the main mineral fraction is shown by chemical analyses.

Bei unseren Untersuchungen über den Edelgasgehalt der Steinmeteorite tauchte das Problem auf, die Edelgase der einzelnen Hauptminerale getrennt zu messen. Wie bereits an anderer Stelle ausgeführt wurde [1], sind die gebräuchlichen Methoden zur Isolierung von Mineralen für diesen Zweck nicht anwendbar, da dabei Zwischenfraktionen anfallen. Für unsere Versuche aber ist es wichtig, daß die Gesamtprobe erhalten bleibt, ohne daß eine Fraktionierung in der Korngröße eintritt. Es war daher notwendig ein Verfahren zu finden, das es erlaubt, ausgehend von einer relativ kleinen Einwaage, die Hauptminerale möglichst rein und quantitativ zu erfassen. Dies gelingt, wenn man nacheinander verschiedene Lösungsmittel einwirken läßt, die jeweils nur ein bestimmtes Mineral bevorzugt lösen. Durch Anpassung der Einwirkungsdauer der Reagenzien kann man eine sehr gute Trennung der einzelnen Phasen erreichen.

Auswahl der Lösungsflüssigkeiten

Die gepulverte Probe wird mit angesäuertem Wasser ($p_{\mathrm{H}} = 4$) ausgelaugt. Hierbei gehen eventuell in Spuren vorhandener Lawrencit ($FeCl_2$) und Oldhamit (CaS) in Lösung. Zum Lösen der Metallphase standen mehrere Verfahren zur Auswahl. Die oft angewandte Methode nach Wilner und Merck [2], die Quecksilber-II-chlorid zum Lösen des Nickeleisens verwendet, schien für unsere Zwecke nicht sehr günstig, da mit dem Rückstand sehr viele Quecksilbersalze anfallen. Eisen-III-chlorid [3] wieder hatte den Nachteil, daß es praktisch unmöglich war, die Lösungsflüssigkeit quantitativ in den Lösungskolben zu bringen, wodurch wieder Schwierigkeiten bei der Bestimmung des in Lösung gegangenen Eisens auftraten. Außerdem ging im allgemeinen etwas mehr Silikat in Lösung als bei der später verwendeten $CuCl_2$-Lösung. Eisen-III-chlorid hat jedoch

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