LETTER TO THE EDITOR

The diffusion of ^{6}Li and ^{7}Li and the isotope effect in liquid lithium

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Abstract. Absolute values of the diffusivities of ^{6}Li in isotopically enriched ^{6}Li melts and of ^{7}Li in natural liquid lithium have been measured by means of the pulsed-field-gradient nuclear magnetic resonance technique (PFG NMR) between 454 K and 580 K using sample sizes and geometries that did not require any corrections for systematic errors. The diffusivities of ^{6}Li and ^{7}Li in ^{6}Li/^{7}Li isotopic alloys decreased significantly with increasing ^{7}Li concentration. This result (which is thought to be of general significance for self-diffusion in liquid metals) constitutes clear evidence for the collective nature of self-diffusion in liquid metals. The melting-point ratio of the self-diffusivities of ^{6}Li and of ^{7}Li, $D^6/D^7 = 1.25$, is significantly greater than the square root of the inverse mass ratio, $(m^7/m^6)^{1/2} \cong 1.08$. This result is incompatible with any classical theory but agrees with a quantum mechanical calculation by Omini.

The fact that lithium has two stable isotopes, ^{6}Li and ^{7}Li, with a rather large mass ratio $((m^7/m^6)^{1/2} \cong 1.08)$ makes it suitable for the study of isotope effects in mass transport. Of particular interest are such measurements on *liquid* lithium, since the literature contains several reports of very large mass dependences of kinetic properties of Li melts. For example, for the ratio of the shear viscosities of the separated isotopes ^{7}Li and ^{6}Li at the melting points Ban and coworkers [1] reported $\eta^7/\eta^6 = 1.44$. In their investigation of the mutual diffusion in both nearly pure ^{6}Li and nearly pure ^{7}Li Löwenberg and Lodding [2] found the ratio† $D^{7/6.070}/D^{6/6.945} = 1.30 \pm 0.08$ at the melting point. Direct measurements of the self-diffusivities of liquid ^{6}Li or ^{7}Li by means of pulsed-field-gradient nuclear magnetic resonance (PFG NMR) by Murday and Cotts [3] gave $D^{6/6.010}/D^{7/6.999} = 1.18 \pm 0.07$.

The results just mentioned are clearly incompatible with theories of diffusion based on classical mechanics, which predict the square root of the inverse mass ratio as an upper limit for the ratios of kinetic coefficients. (In the case of tracer self-diffusivities this upper limit can be reached only if no other atoms participate in the diffusive jumps.) They are to be contrasted with the result $D^{6/6.007}/D^{7/6.926} = 1.09 \pm 0.06$ of Krüger *et al* [4]. A quantum mechanical calculation by Omini [5] based on pseudo-potential theory gave for the ratio between the self-diffusivities of ^{6}Li and ^{7}Li the value $D^{6/6}/D^{7/7} = 1.25$, which within the experimental uncertainties is compatible with the result of Murday and Cotts [3].

† We denote the diffusion of the isotope with mass number n in a matrix with average mass number m by $D^{n/m}$.

In view of the unclear situation we have attempted to determine the diffusivities of ^{6}Li and ^{7}Li in liquid lithium by means of the PFG NMR technique with very high accuracy and without the need for corrections for systematic errors. The present investigation goes beyond the earlier work by the same technique not only with regard to accuracy but also since it includes the dependence of the diffusivities of ^{6}Li and ^{7}Li on temperature and isotopic composition.

Table 1. Isotopic composition of the samples.

	Mole fractions x		Matrix mass number
Sample	^{7}Li: x_7	^{6}Li: $x_6 = (1 - x_7)$	$m = (6x_6 + 7x_7)$
I	0.0132	0.9868	6.013
II	0.9258	0.0742	6.926
III	0.16	0.84	6.16
IV	0.45	0.55	6.45

Table 1 gives the isotopic composition of the four samples investigated in the present work. Sample I consisted of enriched of 99.9% purity ^{6}Li purchased from Oak Ridge National Laboratory, sample II of high-purity (less than 1 wt ppm O, N, C, Pb) natural lithium supplied by the Institut für Festkörperforschung, University of Vienna. Samples III and IV were prepared by mixing enriched ^{6}Li with molten natural lithium and mechanical stirring. The entire sample preparation was carried out in a glove box under helium atmosphere. The melted metal was transferred by He-gas pressure into Al_2O_3 ceramic capillary tubes of 10 mm length and an inner diameter of 300 μm. Bundles of about 60 capillaries filled in this way were sealed in an Al_2O_3 container under He gas.

The NMR signals of ^{6}Li and ^{7}Li were observed by means of a home-built Fourier-transform spectrometer using phase-alternating pulse schemes and quadrature detection. All measurements were performed at a spin-precession frequency of 52 MHz, corresponding to magnetic fields of 8.30 T and 3.14 T for ^{6}Li and ^{7}Li, respectively. The sample temperatures were monitored with two Pt–PtRh thermocouples and maintained by means of a digital PID controller combined with ohmic heating of the sample. The temperature drift during a measurement run was less than ± 0.2%. The tracer diffusivities D^6 and D^7 of ^{6}Li and ^{7}Li were determined up to 580 K† by means of the pulsed-field-gradient nuclear magnetic resonance spin-echo technique [6] from the echo attenuation as a function of the applied magnetic field gradient g. The gradient currents were recorded at a shunt resistor in series with the load, thus allowing us to take into account the actual shape of the gradient pulses [7]. Non-uniform background magnetic field gradients arising from inhomogeneous local fields due to contributions from the electron magnetic susceptibility of our cylindrical samples were negligibly small. In order to avoid echo instabilities produced by gradients associated with eddy currents, a stationary background gradient g_0 was applied [8]. For typical values of the background gradient g_0 and of the duration δ, separation Δ, and magnitude g_m of the two gradient pulses required to achieve complete echo suppression see table 2.

If we take $t_D = (\Delta - \delta/3)$ as effective diffusion time during a PFG NMR experiment, the RMS displacement in one dimension of a spin carrier, $(2Dt_D)^{1/2}$, is about 10 μm near the

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† Samples that were held several hours above 600 K showed a significant chemical reaction of the hot lithium melt with the Al_2O_3 capillary tubes. The diffusion coefficient decreased irreversibly, so that after cooling the diffusivities near the melting point could not be reproduced. For the diffusion measurements below 600 K there was good reproducibility of all diffusion data even after several temperature cycles.

Table 2. Parameters of the PFG NMR spin-echo sequences.

	Typical times		Field gradients	
Isotope	δ (ms)	Δ (ms)	g_m (T m^{-1})	g_0 (T m^{-1})
^{6}Li	0.2–0.5	3.3–3.6	20	0.080
^{7}Li	0.2–0.5	2.3–2.6	14	0.040

melting temperature $T_m = 454$ K. Alignment of the sample capillary tubes along the axis of the field gradient and of the RF field perpendicular to it ensured that the diffusion path in the direction of the magnetic field gradient was not constrained by boundaries acting as barriers or traps. The use of cylinder-shaped samples thus constitudes a substantial improvement over the droplet dispersions employed in the earlier NMR work [3, 4], which required corrections not only for inhomogeneous magnetic fields but also for the limitation of the diffusion by boundaries.
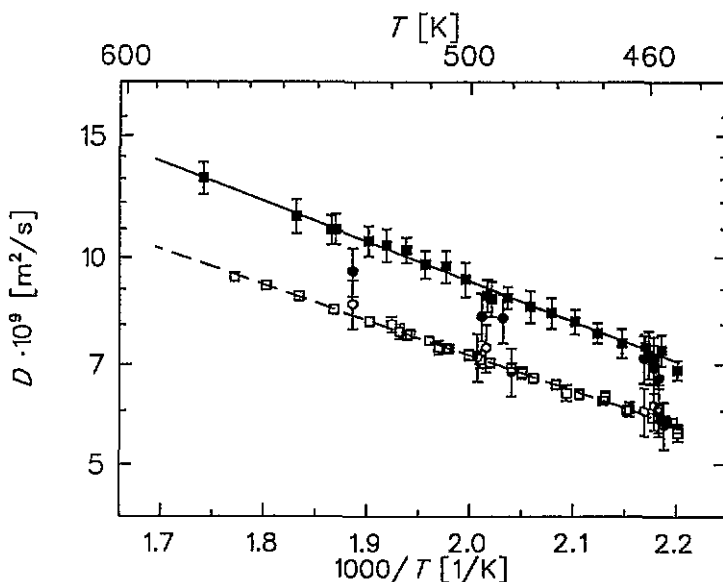

Figure 1. Arrhenius plot of self-diffusivities of liquid lithium. The square symbols show the results of the present PFG NMR measurements; the round symbols are data of Murday and Cotts [3]. Empty squares represent diffusion of ^{7}Li in natural lithium (sample II) and full squares that of ^{6}Li in enriched ^{6}Li (sample I). The solid line corresponds to $D^{6/6.013} = 1.3 \times 10^{-7} \exp(-115 \text{ meV}/k_B T)$ m^2 s^{-1}, the dashed line to $D^{7/6.926} = 7.6 \times 10^{-8} \exp(-102 \text{ meV}/k_B T)$ m^2 s^{-1}.

Figure 1 shows Arrhenius plots of the tracer diffusivities $D^{6/6.013}$ of ^{6}Li in enriched liquid ^{6}Li (sample I), and $D^{7/6.926}$ of ^{7}Li in natural lithium (sample II). The error bars denote 95% confidence limits. Also included in figure 1 are diffusivities obtained by Murday and Cotts [3] ($D^{6/6.007}$ and $D^{7/6.999}$) at isotopic compositions that differ slightly from ours.
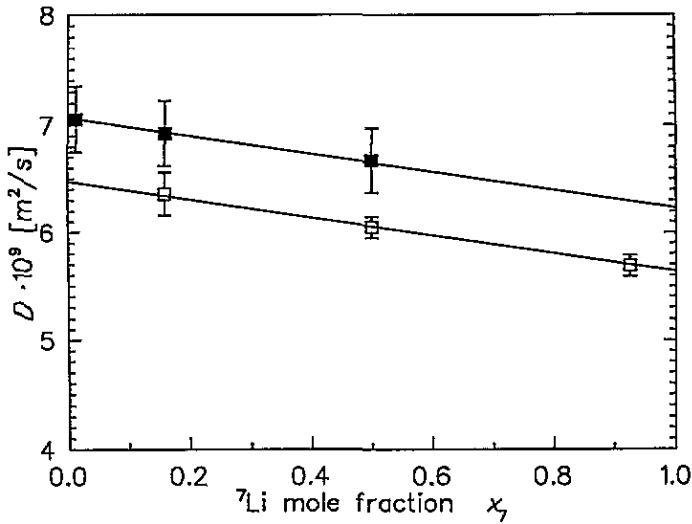
Figure 2. Diffusivities of ^{6}Li (full squares) and ^{7}Li (empty squares) at 454 K in liquid lithium of various isotopic compositions.

Least-squares fits of our data to†

$$D^{n/m} = D_0^{n/m} \exp(-H^{n/m}/k_B T) \tag{1}$$

yield

$$D_0^{6/6.013} = (1.3 \pm 0.2) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$$
$$H^{6/6.013} = (115 \pm 10) \text{ meV} \tag{1a}$$

and

$$D_0^{7/6.926} = (7.6 \pm 0.5) \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$$
$$H^{7/6.926} = (102 \pm 5) \text{ meV}. \tag{1b}$$

The measurements on samples III and IV were confined to temperatures near the melting point. The results for the diffusivities at 454 K are listed in table 3.

Table 3. Diffusivities of ^{6}Li and ^{7}Li at 454 K in various isotopic alloys with ^{7}Li mole fractions x_7. $E^{6/7} = [(D^6/D^7) - 1]/[(m^7/m^6)^{1/2} - 1]$ is the the isotope effect parameter.

x_7	0^a	0.013	0.160	0.450	0.926	1^a
$D^6 \times 10^9$ (m^2 s^{-1})	7.07 ± 0.3	7.05 ± 0.3	6.92 ± 0.3	6.67 ± 0.3	—	6.23 ± 0.3
$D^7 \times 10^9$ (m^2 s^{-1})	6.48 ± 0.1	—	6.36 ± 0.2	6.05 ± 0.1	5.69 ± 0.1	5.64 ± 0.1
$E^{6/7}$	1.14 ± 0.8	—	1.10 ± 1.0	1.28 ± 0.8	—	1.31 ± 0.9

^{a} Extrapolated values.

† An Arrhenius law for the temperature dependence of the diffusivity D in liquid alkali metals is not necessarily the correct physical representation as discussed elsewhere [9], but in the narrow temperature range here an Arrhenius law fit represents the diffusion data quite well. We are therefore justified in using it as an interpolation formula for comparison with literature data.

Figure 2 shows the diffusivities of ^{6}Li and ^{7}Li in the different isotopic lithium alloys at 454 K as a function of the ^{7}Li mole fractions x_7. From this graph we may extrapolate self-diffusivities for ^{6}Li in ^{6}Li ($x_7 = 0$) and ^{7}Li in ^{7}Li ($x_7 = 1$) (see table 3).

The present work demonstrates that measurements by the PFG NMR technique are well suited to study the dependence of the self-diffusivity of liquid lithium on the atomic mass. For technical reasons the study of the temperature dependence of the self-diffusivity was restricted to an interval extending only over about 120 K above the melting temperature, so that in the present work a reliable distinction between different temperature laws could not be made. For completeness we record that fits to a power law† $D \sim T^n$ gave

$$n = 2.37 \pm 0.06 \text{ for the diffusivity of } ^7\text{Li in natural lithium and}$$

$$n = 2.68 \pm 0.20 \text{ for the diffusivity of } ^6\text{Li in enriched } ^6\text{Li.}$$

Figure 2 shows that within the experimental error the ratio of the diffusivities $D^{6/m}$ of ^{6}Li and $D^{7/m}$ of ^{7}Li in liquid lithium is independent of the isotopic composition of the Li matrix. This ratio corresponds to a weighted average isotope effect parameter

$$\langle E^{6/7} \rangle = \left\langle \frac{(D^{6/m}/D^{7/m}) - 1}{(m^7/m^6)^{1/2} - 1} \right\rangle = 1.2 \pm 0.8. \tag{2}$$

On the other hand, the individual diffusivities $D^{6/m}$ and $D^{7/m}$ are clearly dependent on the isotopic composition of the matrix. From this we conclude that in Li melts, and presumably in liquid metals in general, diffusion must be a collective phenomenon which includes the diffusing particle (the tracer) as well as the surrounding particles. In setting up a theoretical framework for diffusion in liquid metals this has to be taken into account, independent of the further treatment of the problem, whether classical or by quantum mechanics. According to the present data the variation of the diffusivities with the isotopic composition is well described by a linear dependence on the mole fraction.

The ratio of the self-diffusivities of ^{6}Li and ^{7}Li near the melting point (deduced from the extrapolations $x_7 \to 0$ and $x_7 \to 1$) is

$$D^{6/6}/D^{7/7} = 1.25 \pm 0.08. \tag{3}$$

Equation (3) agrees (within the error bars) with the result of Murday and Cotts [3]. It is clearly incompatible with classical pictures, since these predict $D^{6/6}/D^{7/7} = (m^7/m^6)^{1/2} \cong 1.08$. Equation (3) is fully compatible with the prediction of Omini [5] based on a quantum mechanical calculation (using pseudo-potential theory) of the mean free path of Li atoms in liquid Li (cf. section 1). For the isotope effect parameter (equation (2)) classical statistical mechanics predicts the upper limit 1.00. Since the dependence of the diffusivities on the isotopic composition indicates a collective character of the diffusion, the isotope effect parameter $E^{6/7}$ in ^{6}Li/^{7}Li isotopic alloys should be distinctly smaller than this upper limit. The experimental result given in equation (2) is therefore in serious conflict with any classical model on self-diffusion in melts. We conclude that only a quantum mechanical description can give the right physical picture of the diffusion process in liquid lithium.

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† A power law with exponent $n = 2$ has been advocated in the literature (cf. [9] for further discussions).

References

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