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Diffusion of ^{23}Na and ^{39}K in the eutectic melt $Na_{0.32}K_{0.68}$

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The diffusivities of ^{23}Na and ^{39}K in the eutectic melt $Na_{0.32}K_{0.68}$ have been measured by means of pulsed-field-gradient nuclear magnetic resonance (PFG-NMR) between the melting temperature ($T_m \cong 260$ K) and 640 K. A very high accuracy could be achieved without the need for corrections for systematic errors caused by gravity-induced convections. Within the considered temperature ranges, the diffusivities of both sodium and potassium are well represented by single Arrhenius laws. The corresponding parameters are $H_a = 89$ meV and $D_0 = 8.6 \times 10^{-8}$ m^2 s^{-1} for sodium and $H_a = 79$ meV and $D_0 = 4.1 \times 10^{-8}$ m^2 s^{-1} for potassium. The ratio of the diffusivities of sodium and potassium, $D^{Na}/D^{K} \geqslant 1.34$, is discussed in terms of classical and quantum mechanical diffusion mechanisms. The present data are analyzed together with the results of previous PFG-NMR studies of the self-diffusion in liquid Na and in ^{6}Li/^{7}Li isotopic alloys. Generally, the diffusivity decreases with increasing average mass of the matrix atoms, which constitutes evidence for the collective nature of diffusion in liquid alkali metals.

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I. INTRODUCTION

Reliable and accurate measurements of diffusion coefficients in metallic melts are demanding and difficult.[1] A fundamental experimental problem is that even a small amount of convection may seriously interfere with the diffusivity determinations based on measurements of concentration profiles. Strong efforts have been made to either correct systematic errors caused by convection or develop techniques to minimize this effect (see, e.g., Shimoji and Itami,[1] Gerl and Bruson,[2] and Frohberg[3]).

The diffusivities measured in liquid Sn, Pb, Sb, In, and Zn (Refs. 3–5) under so-called microgravity conditions in space were significantly lower [10% in the case of liquid Zn at 823 K (Ref. 3)] than the best values furnished by ground-based experiments, indicating that these were indeed perturbed by gravity-induced convection. Fortunately, there are two experimental techniques for the determination of diffusivities in melts that are simpler and cheaper than microgravity experiments but should be about as insensitive against gravity-induced convections as these. They are quasielastic neutron scattering[1] (QENS) and nuclear magnetic resonance using pulsed magnetic field gradients[6,7] (PFG-NMR). While the QENS technique has been applied to quite a number of liquid metals (for reviews, see Refs. 1 and 8), the application of the PFG-NMR technique to liquid metals has so far been restricted to Li (Refs. 9–13) and Na (Refs. 13–15). It has been found that the diffusivities of ^{6}Li and ^{7}Li in ^{6}Li/^{7}Li isotopic alloys decrease significantly with increasing ^{7}Li concentration.[12,13] This result constitutes clear evidence for the collective nature of self-diffusion in liquid lithium. Furthermore, 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, $(7/6)^{1/2} \cong 1.08$, indicating a quantum mechanical diffusion mechanism.[12,13]

It is still an open question whether the collective and nonclassical nature of self-diffusion in lithium melts is a general feature for the diffusion in liquid metals. In order to gain new insights, further experimental work on the diffusion of liquid metals is required, in particular on the dependence of D on the masses of the diffusing (“tracer”) and matrix atoms. Owing to the lack of suitable isotopes, in no other pure metal can the mass dependence of D be studied over such a wide range as in lithium. The eutectic melt $Na_{0.32}K_{0.68}$, however, is also capable of providing information on that matter. An advantage of the Na-K system is the low melting temperature ($T_m \cong 260$ K) at the eutectic point (32 at. % Na and 68 at. % K; see Fig. 1 and Ref. 16). In this system the isotopes ^{23}Na (natural abundance: 100%, nuclear spin $I = 3/2$, and gyromagnetic ratio $\gamma/2\pi = 11.26$ MHz/T) and ^{39}K (93.1%, $I = 3/2$, and $\gamma/2\pi = 1.99$ MHz/T) are well suited for NMR measurements. The objective of the present work was to determine the absolute values of the diffusivities of ^{23}Na and ^{39}K in the eutectic melt $Na_{0.32}K_{0.68}$ by means of the PFG-NMR technique with high accuracy and without the need for corrections for systematic errors. The present results are compared with the self-diffusivity in liquid sodium, which has been measured previously by the same technique.[13,15] This allows us to consider the changes in the diffusivities with both the mass of the diffusing atoms and the average

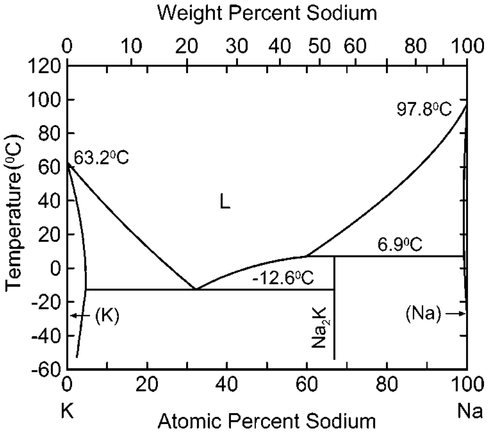

FIG. 1. Phase diagram of the binary sodium-potassium system (Ref. 16).

mass of the matrix atoms over a range that goes far beyond that of earlier studies.

II. EXPERIMENTS

The entire preparation of the $Na_{0.32}K_{0.68}$ sample was carried out in a glovebox with helium atmosphere. Bringing into contact appropriate amounts of pure sodium and potassium in a stainless steel container initiates the melting process at room temperature. Mechanical stirring ensured homogeneity of the resulting eutectic melt. Sodium and potassium are by far less reactive than lithium so that special alkali-resistant quartz glass[17] could be used as sample container at temperatures up to about 650 K. The eutectic melt was transferred by He-gas pressure into quartz glass capillaries. The length of the capillaries was 10 mm and their inside diameter was about 300 μm. A bundle of nearly 450 capillaries filled in this way was sealed in a quartz tube of 9 mm inside diameter under helium gas.

The diffusivities of ^{23}Na and ^{39}K were measured by PFG-NMR using the two-pulse spin-echo sequence introduced by Stejskal and Tanner.[7] The PFG-NMR spectrometer is a homebuilt device with phase-alternating pulse schemes and quadrature detection. A gradient coil of anti-Helmholtz type was mounted in the 89-mm room-temperature bore of a superconducting magnet with $B=5.23$ T, corresponding to spin-precession frequencies of 59.0 MHz and 10.4 MHz for ^{23}Na and ^{39}K, respectively. In addition to the pulsed magnetic field gradients, which reached up to 25 T/m (corresponding to a current of 60 A through the gradient coil), a small time-independent field gradient G_0 was applied for echo stabilization.[18] Typical values for the separation of the two rf pulses τ, the duration of the gradient pulses δ, and for the stationary background gradient G_0 were in the ranges $\tau=2.5$–4.0 ms, $\delta=0.2$–1.5 ms, and $G_0=0.04$–0.12 T/m. The diffusion coefficients D were determined from the variation of the spin-echo amplitude,

$$M(G)=M(0)\exp\left\{-D\gamma^2\left[\int_0^{2\tau}\left(\int_0^{t'}G(t'')dt''\right)^2 dt'\right]\right\}, \tag{1}$$

with the amplitude of the applied field–gradient pulses G at constant τ and δ. Deviations from the rectangular shape of the gradient pulses were taken into account by measuring the time dependence of the current through the gradient coil using a fast 12-bit transient recorder and evaluating the double integral in Eq. (1) numerically.

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 was less than $\pm 0.3\%$.

III. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the diffusivities of ^{23}Na and ^{39}K, D^{Na} and D^{K}, measured in $Na_{0.32}K_{0.68}$ by PFG-NMR. Due to the lower NMR sensitivity, the measurements of D^{K} have been restricted to the temperature range 298–402 K, whereas D^{Na} has been determined between a melting temperature of about 260 K and 640 K. A straightforward approach to analyze diffusion data is to fit an Arrhenius law

$$D=D_0\exp(-H_a/k_BT) \tag{2}$$

to the experimental results. Within the entire temperature ranges, the temperature dependences of both D^{Na} and D^{K} are indeed well represented by single Arrhenius laws. The solid lines in Fig. 2 are obtained by fitting Eq. (2) to the diffusivities. The corresponding fitting parameters are given in Table I together with the diffusivities at the melting temperature $D(T_m)$.

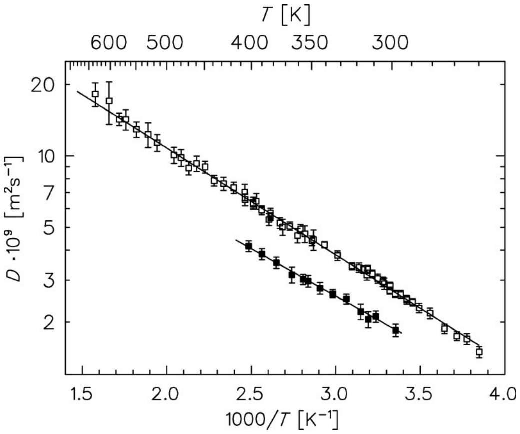

FIG. 2. Temperature dependence of the diffusivities of Na (open squares) and K (solid squares) in the eutectic melt $Na_{0.32}K_{0.68}$. The solid lines are obtained by fitting Arrhenius expressions to the diffusion coefficients. The corresponding diffusion parameters are given in Table I.

The ratio of the diffusivities of sodium and potassium at the melting point is

$$D^{\mathrm{Na}}(T_m)/D^{\mathrm{K}}(T_m)=1.34\pm 0.05. \tag{3}$$

This ratio increases with increasing temperature, and $D^{\mathrm{Na}}/D^{\mathrm{K}}=1.54$ is obtained at 373 K. Using the concepts developed for isotropic crystalline material, the ratio $D^{\mathrm{Na}}/D^{\mathrm{K}}=(m_{\mathrm{K}}/m_{\mathrm{Na}})^{1/2}\cong 1.30$ is expected for classical ‘‘over-barrier’’ jumps of ^{23}Na and ^{39}K.[19] This relation implies that ^{23}Na and ^{39}K are essentially two ‘‘isotopes’’ of an alkali metal with a unique potential curve for both types of atoms, and it is further assumed that no other atoms participate in the diffusive jumps. A more adequate description of liquid metals is based on either a model for amorphous materials or on a model employing gas concepts. For binary Na-K alloys, where the situation is even more complex than in a simple metal, only one theoretical approach to diffusion has been reported so far: In the so-called linear trajectory approximation an expression of the diffusivity D^i of species i has been derived as a function of the mass m_i and the rigid sphere diameter σ_i.[20] For the diffusivities in $Na_{0.30}K_{0.70}$ at 373 K, the absolute values $D^{\mathrm{Na}}=5.270\times 10^{-9}$ m^2 s^{-1} and $D^{\mathrm{K}}=3.618\times 10^{-9}$ m^2 s^{-1} are calculated in Ref. 20. These data are in surprisingly good agreement with our experimental

TABLE I. Diffusion parameters of ^{6}Li, ^{7}Li, ^{23}Na, and ^{39}K in melts of alkali metals (cf. Fig. 3). The activation enthalpies H_a and preexponential factors D_0 are obtained by fitting Arrhenius expressions to the diffusivities measured by PFG-NMR within the indicated temperature ranges. Estimated uncertainties are typically ±3% in H_a and ±20% in D_0.

Isotope	Sample	T range [K]	D_0 [10^{-9} m^2 s^{-1}]	H_a [meV]	T_m [K]	$D(T_m)$ [10^{-9} m^2 s^{-1}]
^{6}Li	^{6}Li enriched ^{6}Li$_{0.987}$^{7}Li$_{0.013}$	454 – 580	133	115	454	7.1
^{7}Li	nat. Li ^{6}Li$_{0.074}$^{7}Li$_{0.926}$	454 – 580	76	101	454	5.7
^{23}Na	nat. Na pure ^{23}Na	371 – 673	87	101	371	3.7
^{23}Na	eutectic melt Na$_{0.32}$K$_{0.68}$	260 – 640	86	89	260	1.6
^{39}K	eutectic melt Na$_{0.32}$K$_{0.68}$	298 – 402	41	79	260	1.2 [a]

[a] The diffusivity of ^{39}K at the melting temperature T_m of Na$_{0.32}$K$_{0.68}$ has been extrapolated from the measured data.

results $D^{\mathrm{Na}}(373\ \mathrm{K}) = 5.4\times10^{-9}\ \mathrm{m^2\,s^{-1}}$ and $D^{\mathrm{K}}(373\ \mathrm{K}) = 3.5\times10^{-9}\ \mathrm{m^2\,s^{-1}}$ in Na$_{0.32}$K$_{0.68}$. Furthermore, the ratio of the diffusivities at 373 K calculated in Ref. 20, $D^{\mathrm{Na}}/D^{\mathrm{K}} \approx (m_{\mathrm{K}}\sigma_{\mathrm{K}}/m_{\mathrm{Na}}\sigma_{\mathrm{Na}})^{1/2} \cong 1.45$, is only slightly smaller than the experimental result $D^{\mathrm{Na}}(373\ \mathrm{K})/D^{\mathrm{K}}(373\ \mathrm{K}) = 1.54$.

The above agreement may point to a classical diffusion mechanism in liquid Na$_{0.32}$K$_{0.68}$, with negligible contributions from quantum diffusion. However, if diffusion in this system is a collective phenomenon, the masses of ^{23}Na and ^{39}K have to be replaced by *reduced* masses.[19] As pointed out below, evidence for a collective mechanism of diffusion has, indeed, been found in Na$_{0.32}$K$_{0.68}$. In this case, the ratio $D^{\mathrm{Na}}/D^{\mathrm{K}}$ expected for a classical diffusion mechanism should be significantly smaller than 1.45, while the experimental data yield even a slightly higher ratio at 373 K. Thus, one may think of quantum mechanical diffusion mechanisms as in lithium. The Na$^+$ and K$^+$ ions in the metallic system Na$_{0.32}$K$_{0.68}$ have the same net charge but, besides the different masses, they have different numbers of filled electron shells. Ignoring the possibility that this may also affect the diffusivities introduces some uncertainty in the present consideration. This is unlike the situation in lithium, where isotopes of the same type of atom have been compared.[12,13] Moreover, quantum effects are expected to be less important for heavier atoms like sodium and potassium than for lithium. Thus, a final conclusion about the role of quantum mechanical effects for diffusion in liquid Na$_{0.32}$K$_{0.68}$ requires a quantum theory of binary metallic melts, which does to our knowledge not yet exist.

Evidence for a collective mechanism of diffusion is obtained by comparing the present results with the self-diffusivities in sodium[13,15] and in two lithium systems with different isotopic compositions,[12,13] which have been measured previously by the same technique. The data of the different samples are plotted in Fig. 3 on an inverse temperature scale normalized by the corresponding melting temperature. The solid lines in Fig. 3 represent Arrhenius laws [Eq. (2)] with the fitting parameters given in Table I. As discussed elsewhere,[13,15] more sophisticated models of self-diffusion in liquid metals (e.g., random-barrier model,[21] significant-structure theory[22]) yield for the temperature dependence of the diffusivities at higher temperatures slight deviations from single Arrhenius laws. But for comparison of the data the use of Arrhenius expressions is justified. As a general trend, the diffusivity at the melting point decreases with increasing mass of the diffusing atoms and for identical diffusing atoms with increasing mass of the matrix atoms. The melting-point diffusivity of sodium in Na$_{0.32}$K$_{0.68}$ is, for example, 1.34 times that of potassium in the same sample [cf. Eq. (3)], but it is only 0.43 times the melting-point diffusivity in pure sodium. This constitutes evidence that in liquid metals in

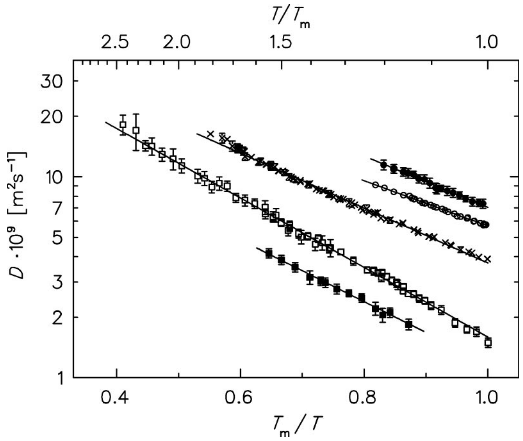

FIG. 3. Diffusivities of ^{6}Li, ^{7}Li, ^{23}Na, and ^{39}K in melts of alkali metals. Solid and open circles: ^{6}Li in ^{6}Li-enriched lithium and ^{7}Li in natural lithium (Refs. 12 and 13). Crosses: self-diffusivity in sodium (Refs. 13 and 15). Solid and open squares: K and Na in the eutectic melt Na$_{0.32}$K$_{0.68}$. The temperature scale is normalized by the melting temperatures, and the solid lines represent Arrhenius laws with the parameters given in Table I.

general (as already proposed[12,13]) diffusion near T_m is a collective mechanism which includes the diffusing particle as well as a substantial number of surrounding particles. A concise physical picture for this phenomenon has not yet been developed but it is intuitively clear that it must be related to the correlation effects mentioned in Ref. 13 and their increasing importance as T approaches T_m.

IV. SUMMARY AND CONCLUSIONS

The diffusivities D^{Na} and D^{K} of ^{23}Na and ^{39}K in the eutectic melt $Na_{0.32}K_{0.68}$ have been measured with very high accuracy by means of pulsed-field-gradient NMR. Owing to the rather short measuring times in the range of milliseconds effects of gravity-induced convection are negligible in the PFG-NMR experiments. Within the entire temperature range (260–640 K for sodium and 298–402 K for potassium) the temperature dependence of D follows a single Arrhenius behavior with an activation enthalpy of 89 meV for Na and 79 meV for K. A comparison of the present data with the self-diffusivity in sodium[13,15] indicates a collective diffusion mechanism, which includes the diffusing particle as well as the surrounding particles. This is in accordance with the observations in ^{6}Li/^{7}Li isotopic alloys,[12,13] suggesting that the collective nature of diffusion is a general feature of liquid alkali metals. In setting up a theoretical framework for diffusion in liquid metals this has to be taken into account. The ratio of the diffusivities of sodium and potassium in liquid $Na_{0.32}K_{0.68}$ is $D^{Na}/D^{K}=1.34$ at the melting point ($T_m \cong 260$ K), and it increases with increasing temperature. A definitive distinction between classical and quantum mechanical diffusion processes in liquid $Na_{0.32}K_{0.68}$ is not yet possible and it requires a quantum theory of diffusion in binary metallic melts.

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