Quasielastic neutron scattering and diffusion in liquid lithium and lithium–hydrogen melt

Quasielastic neutron scattering and diffusion in liquid lithium and lithium–hydrogen melt

N M Blagoveshchenskii[1], V A Morozov[1], A G Novikov[1], M A Pashnev[1], V V Savostin[1], A L Shimkevich[2] and O V Sobolev[3]

[1] State Scientific Center of Russian Federation—Institute for Physics and Power Engineering named after A I Leipunskii, 249033, Obninsk, Kaluga region, Bondarenko Square, 1, Russia
[2] Russian Scientific Center 'Kurchatov Institute', Akademika Kurchatova Square, 1, 123182, Moscow, Russia
[3] LGIT, University of Grenoble and CNRS, BP 53, Maison des Géosciences—Domaine Universitaire, 38041 Grenoble Cedex 9, France

E-mail: novikov@ippe.ru

Abstract
Neutron quasielastic scattering experiments on liquid lithium (at 500 and 830 K) and a lithium–hydrogen melt (99 at.% Li^7 and 1 at.% H at 830 K) have been performed. The characteristics of the diffusion mobility for lithium and hydrogen atoms have been extracted from the experimental results and analyzed with the use of phenomenological and theoretical models. The self-diffusion coefficient in liquid lithium obtained for both temperatures is in agreement with values in the literature. The mechanism of hydrogen diffusion mobility in liquid lithium is discussed. It has been concluded that the hydrogen in the liquid lithium exists and diffuses in the form of the hydride LiH.

1. Introduction

The presented work is aimed at providing information on diffusion mobility in pure liquid lithium and a lithium–hydrogen melt. There are no doubts about the practical importance of such investigations from the point of view of nuclear power engineering [1] and thermonuclear problems [2].

The experimental neutron scattering results on liquid lithium ($T = 500$ and 830 K) and lithium–hydrogen melt ($T = 830$, hydrogen concentration $\sim$ 1 at.%) were obtained with the DIN-2PI time-of-flight spectrometer (IBR-2 pulsed reactor, Frank Laboratory of neutron physics, JINR, Dubna) [3]. The experimental conditions were optimized for the measurement and analysis of the quasielastic scattering, which contains information on the characteristics of the diffusion in the studied liquid. The initial neutron energy was taken to be $E_0 = 3.67$ meV ($\Delta E_0 \sim 0.17$ meV), the sample container (cylindrical layer with thickness of 7 mm and height of 100 mm) was made from niobium foil of 0.3 mm thickness

(by electron welding). Thus, the coherent elastic scattering effects on the container in the region of the neutron wavevector transfer $Q < 3$ Å^{-1} were practically excluded.

The neutron scattering spectra were obtained in the Q-region 0.2 Å^{-1} < 2 Å^{-1}. Based on the Lovesey model [4], it was assumed that coherent effects on liquid lithium in this Q region are negligible. After corrections for neutron flux attenuation in the sample and container, detector efficiency and multiple scattering (estimated as less then 3% of common scattering for $Q \sim 2$ Å^{-1}), the quasielastic scattering spectra were transformed into the energy scale and Q-constant representation. Examples of the incoherent quasielastic scattering peaks for a number of Q are shown in figure 1.

2. Liquid lithium ($T = 500$ and 830 K)

The quasielastic scattering results for pure lithium were analyzed under the assumption that the natural form of the incoherent quasielastic scattering peaks can be described by
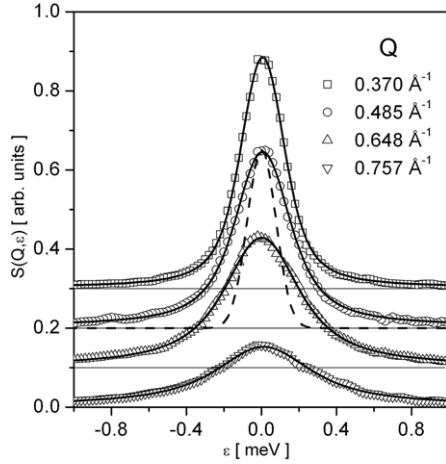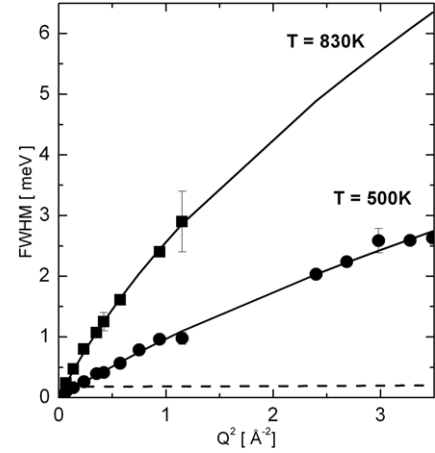
Figure 1. Experimental peaks of incoherent quasielastic scattering on liquid lithium and their description by the Lorentzian curves for different Q values and $T = 500$ K. The dashed line represents the resolution function of the spectrometer.

the single Lorentzian curve:

$$S(Q, \varepsilon) = \left(\frac{A \exp(-Q^2 \langle u^2 \rangle)}{2\pi} \frac{\Delta E(Q)}{\varepsilon^2 + 0.25 \, \Delta E^2(Q)} \right.$$
$$\left. + (a + b\varepsilon) \right) \otimes R(Q, \varepsilon), \qquad (1)$$

where A is the thermal factor (in our conditions it does not influence the shape of the quasielastic scattering peaks), $\varepsilon = E - E_0$ is the change of neutron energy due to a scattering event, $\exp(-Q^2 \langle u^2 \rangle)$ is the Debye–Waller factor (D–W) and $\langle u^2 \rangle$ is the mean square amplitude (MSA) of a particle vibration in the force field of neighbors. MSA can be determined experimentally from the Q-dependence of the integral intensity of incoherent quasielastic scattering. But, due to some experimental circumstances, we could not get this value from the quasielastic scattering results presented here with satisfactory accuracy. To pass over these difficulties we used MSA values calculated in our previous paper [5] using the frequency distribution spectra of the liquid lithium obtained from the inelastic neutron scattering experiment. This value demonstrates a linear temperature dependence and equal $\langle u^2 \rangle \approx 0.04 \text{ Å}^2$ at $T = 500$ K and $\langle u^2 \rangle \approx 0.06 \text{ Å}^2$ at $T = 830$ K [5]. The second term in the brackets takes into account the effects of inelastic scattering (for $S(Q < 2 \text{ Å}^{-1}, 0)$ less then 5%). The sum of two terms in (1) is convoluted with the spectrometer resolution function $R(Q, \varepsilon)$, measured on the special vanadium sample.

The full widths at half-maximum (FWHM) of the quasielastic scattering as a function of Q, obtained for two temperatures, are presented in figure 2. The analysis of these results was performed in two steps. In the fist step the experimental points of figure 2 were described by the phenomenological model [6], which assumes a mixed character of the diffusion mobility in liquid. It also assumes a combination of two mechanisms: jump diffusion (with parameter τ_0 the residence time of a particle around the temporary equilibrium position) and continuous diffusion

Figure 2. The FWHM of the incoherent quasielastic peaks of the liquid lithium for two temperatures. The solid lines represent the optimal description of the set of experimental points by the model (2) with the parameters: $\tau_0 = 0.6 \pm 0.1$ ps, $D_0 = 3.4 \pm 0.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D = 8.0 \pm 0.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ($T = 500$ K) and $\tau_0 = 0.32 \pm 0.1$ ps, $D_0 = 7.6 \pm 0.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D = 25.5 \pm 0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ($T = 830$ K). The dashed line shows the FWHM of the spectrometer resolution function.
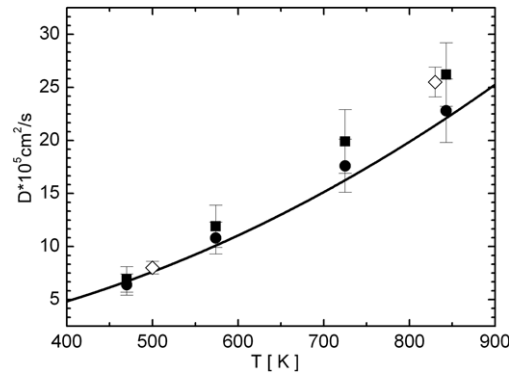
Figure 3. Temperature dependence of the self-diffusion coefficient in liquid lithium: the data of the present study (rhombs) and the neutron scattering results of [7] (black circles and squares). The line represents model calculations [8].

(with parameter D_0 the coefficient of continuous diffusion of a particle together with its surroundings). The quasielastic peak is supposed to be the Lorentzian with FWHM:

$$\Delta E(Q^2) = \frac{\hbar}{\tau_0} \left[1 + D_0 Q^2 \tau_0 - \frac{\exp(-Q^2 \langle u^2 \rangle)}{1 + (D - D_0) Q^2 \tau_0} \right], \quad (2)$$

where D is the total coefficient of diffusion. The model parameters derived by optimal fitting of the experimental points by expression (2) are given in figure 2 as well. The values of the self-diffusion coefficients for both temperatures are in good agreement with known data (figure 3).

The second step in the analysis of the experimental results consists in the comparison of these data with the predictions of the mode coupling theory (MCT). As was repeatedly underlined in the literature (see, for instance, [9, 10]), the main features of the diffusion dynamics of the liquid particles

Table 1. Coefficients of equations (7) and (8) for liquid lithium.

500 K				830 K			
a(7)	b(7)	c(8)	d(8)	a(7)	b(7)	c(8)	d(8)
Calc (Å)	Calc (Å)	Exp (Å^2)	Exp (Å^2)	Calc (Å)	Calc (Å)	Exp (Å^2)	Exp (Å^2)
0.038	0.075	0.13	0.10	0.075	0.15	0.30	0.29
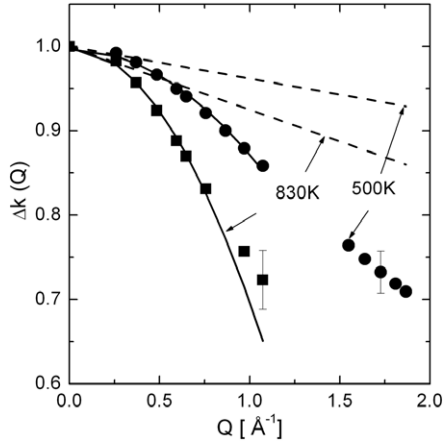
Figure 4. The reduced natural widths of the incoherent quasielastic peaks of liquid lithium for two temperatures. The lines represent the calculations with (7) (dashed lines) and (8) (solid lines).
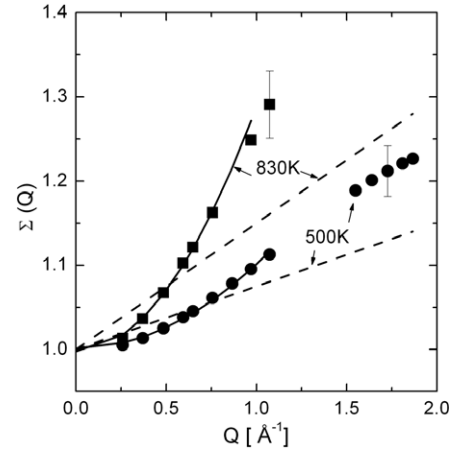
Figure 5. The reduced amplitudes of the incoherent quasielastic peaks of liquid lithium for two temperatures. The lines represent the calculations with (7) (dashed lines) and (8) (solid lines).

are reflected (embodied) in two characteristics of incoherent quasielastic scattering:

reduced FWHM of the quasielastic peak

$$\Delta k(Q) = \Delta E/2\hbar D Q^2, \qquad (3)$$

and reduced amplitude of the quasielastic peak

$$\Sigma(Q) = S(Q, 0)2\hbar D Q^2. \qquad (4)$$

We found the amplitude of the quasielastic peak from the expression

$$S(Q, 0) = P(Q)/\Delta E, \qquad (5)$$

where $P(Q)$ is the area of the quasielastic peak, which is supposed to be equal to the D–W factor we found earlier [5]. So, the reduced amplitude of the quasielastic peak takes the form:

$$\Sigma(Q) = S(Q, 0)/2\hbar D Q^2 = P(Q)/\Delta k(Q). \qquad (6)$$

Our experimental $\Delta k(Q)$ and $\Sigma(Q)$ of liquid lithium for two temperatures are shown in figures 3 and 4, respectively.

The MCT was applied for the estimation of the $\Delta k(Q)$ and $\Sigma(Q)$ deviation from the hydrodynamic behavior (continuous diffusion) [9, 10]. One of the MCT versions is based on the assumption that the slowing down of the particle diffusion mobility compared to the hydrodynamic predictions (Fick's law) takes place due to the interaction of the particle diffusion motions with the shear modes of the surroundings [11].

According to the predictions of this MCT version, the real deviations of the $\Delta k(Q)$ and $\Sigma(Q)$ depend on Q linearly:

$$\Delta k(Q) = 1 - aQ \qquad \Sigma(Q) = 1 + bQ. \qquad (7)$$

The calculations based on the MCT version, which assumes the diffusion of the tagged particle to be influenced by the wider excitation spectrum of the surroundings, result in a quadratic Q-dependence of $\Delta k(Q)$ and $\Sigma(Q)$ deviations from the hydrodynamics [12]:

$$\Delta k(Q) = 1 - cQ^2; \qquad \Sigma(Q) = 1 + dQ^2. \qquad (8)$$

The comparison of our experimental results with calculations by expressions (7) and (8) are shown in figures 4 and 5. The values of the corresponding coefficients used are given in table 1. The coefficients a and b were calculated using expressions taken from [13]. We did not find explicit expressions for c and d, thus, the values, given for them in table 1, are empirical ones, obtained by fitting the experimental points with expression (8).

From figures 4 and 5 it is seen that our experimental $\Delta k(Q)$ and $\Sigma(Q)$ in the small Q region follow expression (8) and the deviations from Fick's law increase with the temperature elevation.

Our results of figures 4 and 5 are obtained in the restricted region of Q (for $T = 500$ K $Q < 2$ Å^{-1}). Nevertheless, it is seen that for larger Q the results demonstrate some flattening tending to a minimum (for $\Delta k(Q)$) and a maximum (for $\Sigma(Q)$) which correspond to the position of the main peak of the structure factor. It is understood usually to be the reflection of the space dependence of the diffusion processes [8].
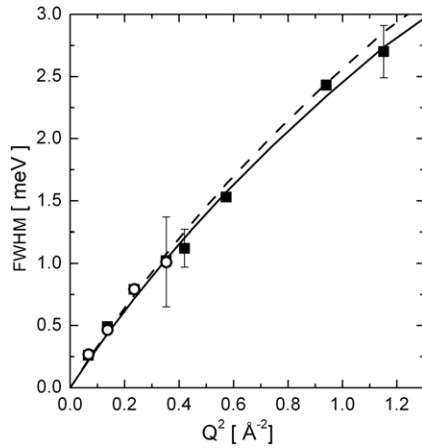
Figure 6. The FWHM of the incoherent quasielastic peaks on the lithium–hydrogen melt (squares) and the hydrogen admixture (open circles). The solid line represents the optimal description of the set of experimental points using the model (2): $\tau_0 = 0.37 \pm 0.1$ ps, $D_0 = 7.7 \times 10^{-5}$ cm^2 s^{-1}, $D = 24.8 \pm 1.5 \times 10^{-5}$ cm^2 s^{-1}. The dashed line corresponds to the model (2) description for pure lithium.

3. Lithium–hydrogen melt ($T = 830$ K, hydrogen concentration ~ 1 at.%)

The small concentration of hydrogen compensated by the remarkable difference in the incoherent scattering cross section of the melt components: for Li $\sigma_{\text{incoh}} \sim 0.7b$, for H $\sigma_{\text{incoh}} \sim 80b$ (for the low initial neutron energy $E_0 \sim 3$ meV we used). Thus, the contributions of both components in the common scattering intensity are almost equal.

Along with the analysis of the experimental data on the lithium–hydrogen melt, expression (1) was used with an additional Lorentzian which hypothetically should account for scattering on the hydrogen. However, the FWHMs of both components were found to be identical within the error bars. Moreover, the FWHMs obtained by fitting the lithium–hydrogen melt data with the single Lorentzian function, coincide with those obtained for pure lithium (figure 6). We also used another method for extraction of the hydrogen component: after proper relative normalization, the scattering intensities on the melt and pure lithium were subtracted from each other. Again, the FWHM of this component was found to be equal to the FWHM for pure lithium (figure 6, empty points). Similar diffusion characteristics of pure lithium and lithium–hydrogen melt give rise to the assumption that under our experimental conditions hydrogen exists and diffuses in the lithium–hydrogen melt in the form of lithium hydride LiH. When applying expression (2) to describe the experimental points of figure 6, we obtain the diffusion coefficient $D_{\text{LiH}} = 24.8 \pm 1.5 \times 10^{-5}$ cm^2 s^{-1}. In the limits of the experimental errors this value agrees with that for pure lithium, thereby being slightly less than the latter, possibly because of small differences in the mass.

In conclusion it should be mentioned that our results for the diffusion mobility of hydrogen in liquid lithium are in good agreement with those obtained for a tritium–lithium system [14].

4. Conclusion

From the inelastic neutron scattering spectra of liquid lithium ($T = 500$ and 830 K) and a lithium–hydrogen melt ($T = 830$ K, hydrogen concentration ~ 1 at.%), the incoherent quasielastic component was extracted. The FWHM and amplitudes of the quasielastic peaks were analyzed and the diffusion mobility characteristics of lithium and hydrogen atoms were revealed. We found out that:

- The self-diffusion coefficients in pure lithium obtained in our experiment for both temperatures agree with the data existing in the literature.
- In pure lithium the Q dependence of the reduced FWHM and amplitude of the incoherent quasielastic peaks in the small Q region deviates from the hydrodynamic predictions in the parabolic form, coinciding with the results of some MCT versions.
- The FWHMs of the quasielastic peaks in pure lithium and the lithium–hydrogen melt are very close and give rise to the assumption that the hydrogen in the liquid lithium exists and diffuses in the hydride LiH form.

References

[1] Subbotin V I, Arnoldov M N, Ivanovskii M N, Mosin A A and Torbov A A 1999 *Lithium* (Moscow: IsdAt) (in Russian)
[2] Mihailov V N, Evtiuhin V A, Lublinckii I E, Vertkov A V and Chumanov A N 1999 *Lithium in Thermonuclear and Cosmic Energetic of XXI Age* (Moscow: Energoatomizdat) (in Russian)
[3] Sikolenko V (ed) 1997 *User Guide. Neutron Experimental Facilities for Condensed Matter Investigation at JINR* (Dubna: JINR Press) p 25
[4] Lovesey S 1971 *J. Phys. C: Solid State Phys.* **4** 3057
[5] Blagoveshchenskii N M, Morozov V A, Novikov A G, Pashnev M A, Savostin V V and Shimkevich A L 2007 *Crystallogr. Rep.* **52** 460
[6] Oskotskii V 1967 *Sov. Solid State Phys.* **9** 550
[7] Canales M, Gonzalez D, Gonzalez L, Alemany M and Gallego L 2000 *Phys. Rev.* **62** 12095
[8] Ohse R W (ed) 1985 *Handbook of Thermodynamic and Transport Properties of Alkali Metals* (Oxford: Blackwell)
[9] Boon J and Yip S 1980 *Molecular Hydrodynamics* (New York: McCraw-Hill)
[10] Scopigno T and Ruocco G 2005 *Rev. Mod. Phys.* **77** 881
[11] de Schepper I and Ernst M 1979 *Physica* A **98** 189
[12] Wahnstrom G and Sjogren L 1982 *J. Phys. C: Solid State Phys.* **15** 401
[13] Morkel Ch, Gronemeyyer C and Glaser W 1989 *Springer Proc. in Physics* vol 40 (Berlin: Springer) p 41
[14] Moriyama H, Iwasaki K and Ito Y 1992 *J. Nucl. Mater.* **191–194** 190