

Investigation of diffusion processes in liquid sodium and sodium-hydrogen melt by quasielastic neutron scattering

N. M. Blagoveshchenskii¹⁾, A. G. Novikov, A. V. Puchkov, V. V. Savostin, M. S. Shamaev, I. I. Zasorin

Leypunsky Institute for Physics and Power Engineering, 249033 Obninsk, Russia

Submitted 11 November 2013

The quasielastic neutron scattering experiments on liquid sodium (at $T = 378, 573,$ and 693 K) and sodium-hydrogen melt ($T = 693$ K, hydrogen concentration $\sim 0.4\%$ at.) were performed with the DIN-2PI time-of-flight spectrometer. The characteristics of the diffusion mobility for particles comprising the liquids studied are extracted from the experimental results and analyzed with the help of the phenomenological and “relaxing cage” models. The self-diffusion coefficient in liquid sodium obtained for all temperatures is in the agreement with the values known from literature. The diffusion mobility in pure sodium and in sodium-hydrogen melt were found to be coinciding; it leads to the conclusion that in our experimental conditions hydrogen exists and diffuses in melt in the form of hydride NaH.

DOI: 10.7868/S0370274X13240156

1. Introduction. The behavior of impurities in liquid sodium coolant of nuclear power reactors leads to serious problems during their exploitation and attracts the attention of operators and elaborators of these installations [1], including active investigations by experiments and calculations. So, there are no doubts in practical importance of such extended studies from the point of view of nuclear power engineering [2].

It seems useful to invoke for the investigations of these problems the neutron scattering methods which are able to provide a lot of interesting information on the microscopic level. But the majority of the impurities existing in liquid sodium coolant are of too low solubilities to be felt in the neutron scattering experiments. The only substance which supposed to be applied in such kinds of experiments is hydrogen due to its high scattering cross section.

It should be remembered that liquid sodium attracted the attention of inelastic neutron scattering experiment as a simple metallic liquid since the origination of this method (see ref. [1] in [3]). The numerous works of the last decades including neutron scattering experiments, molecular dynamics simulations and theoretical calculations (see review paper [4] and references therein) opened the ways for the deep understanding of the microdynamical processes in this liquid. In particular, the measurements of quasielastic neutron scattering on liquid sodium performed in the very wide temperature region revealed the microscopic nature of the temperature dependence for the diffusion mobility of its

particles [5, 6]. As to behaviour of impurities in liquid sodium, we do not know such kinds of experiments with application of neutron scattering methods.

So, in this paper we present our first experimental results on the quasielastic neutron scattering by the sodium – hydrogen melt. In so doing, the pure sodium serves as the reference system.

2. Experiment. The experimental results of incoherent quasielastic neutron scattering on liquid sodium ($T = 378, 573,$ and 693 K) and sodium-hydrogen melt ($T = 693$ K, hydrogen concentration $\sim 0.4\%$ at.) were obtained with the DIN-2PI spectrometer (IBR-2 pulsed reactor, Frank Laboratory of Neutron Physics, JINR, Dubna) [7]. The conditions of the experiment were chosen with the aim to facilitate the measurements and analysis of the incoherent quasielastic scattering region that in its turn, opens the possibility to get the information about the characteristics of diffusion and relaxation processes in the liquids under study. The initial neutron energy was chosen $E_0 = 3.0$ meV with the resolution in the elastic peak $\Delta E_0 \sim 0.15$ meV. The sample, a cylindrical layer with the thickness of 6 mm and the outer diameter 60 mm, was held in aluminum container of 2 mm wall thickness. Using the aluminum container restricted the allowable level of the sample temperature (keeping in mind the addition pressure of hydrogen to be expected in the sample volume) it should be not more than ~ 700 K and according to hydrogen solubility in liquid sodium it corresponds to the hydrogen concentration about 0.4% at. [1].

To diminish the influence of the coherent effects, the spectra of incoherent quasielastic scattering were con-

¹⁾e-mail: blag@ippe.ru

sidered only in the region of the neutron wave vector transfer $Q < 1.5 \text{ \AA}^{-1}$ for $T = 378 \text{ K}$ and $Q < 1.0 \text{ \AA}^{-1}$ for $T = 693 \text{ K}$ (structure factor of liquid sodium and its temperature dependence see in [8]). Basing on the Lovesey model [9], it was estimated that the coherent effects on liquid lithium in this Q -region are negligible. After evaluation and introduction of all the required corrections (neutron flux attenuation in the sample substance and the container, effects of the container, detector efficiency, multiple scattering estimated as less than 2% of common quasielastic scattering for $Q \sim 2 \text{ \AA}^{-1}$), the quasielastic scattering spectra were transformed into the equidistant energy scale and Q -constant representation.

3. Data analysis. The neutron spectra in the region of incoherent quasielastic scattering for pure sodium were analyzed under assumption that the natural form of incoherent quasielastic scattering peaks can be described by a single Lorentzian curve:

$$S(Q, \varepsilon) = \left\{ A^* B / 2\pi^* \Delta E(Q) \left[\varepsilon^2 + \frac{1}{4} \Delta(Q)^2 \right]^{-1} + (a + b\varepsilon) \right\} \otimes R(Q, \varepsilon), \quad (1)$$

where A is a thermal factor (in our conditions it does not influence the shape of quasielastic scattering peaks), $B = \exp(-Q^2 \langle u^2 \rangle)$ is Debye–Waller factor, $\langle u^2 \rangle$ is a mean-square amplitude of particle vibrations in the force field of neighbors. Amplitude $\langle u^2 \rangle$ was calculated with the help of the liquid sodium frequency distribution spectra, obtained in our experiments. It was calculated as

$$\langle u^2 \rangle = \frac{\hbar}{M} \int_0^\infty \frac{g(\omega)}{\omega} \text{cth} \left(\frac{\hbar\omega}{kT} \right) d\omega,$$

where $g(\omega)$ – the frequency spectrum of liquid sodium, we get from our experimental data unpublished till now. For $T = 378 \text{ K}$ $\langle u^2 \rangle = 0.18 \text{ \AA}^2$. The second term in (1) takes into account the small effects of coherent (with the use of Lovesey model [9]) and inelastic incoherent scattering. The sum of two terms in (1) finally was convoluted with the spectrometer resolution function $R(Q, \varepsilon)$, measured on the special vanadium sample. The examples of the incoherent quasielastic scattering peaks for three temperatures at $Q = 0.44 \text{ \AA}^{-1}$ are shown in Fig. 1. The Q -dependence of the full intrinsic widths at the half-maximum (FWHM, $\Delta E(Q)$) of the incoherent quasielastic scattering peaks, we got from our experimental data for three temperatures, is presented in Fig. 2.

4. Results and discussion. *4.1. Pure sodium.* The analysis of these results was performed by two ways.

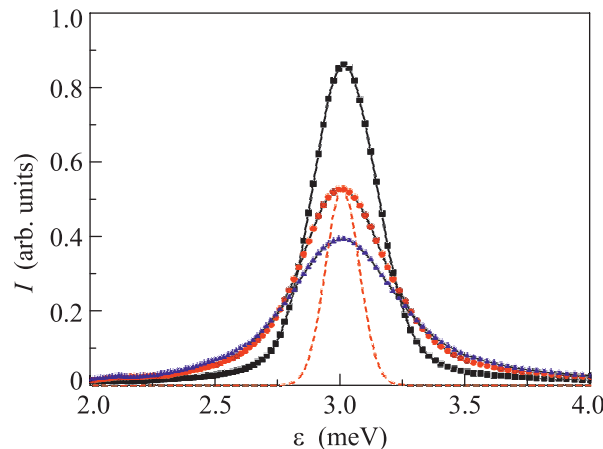


Fig. 1. Experimental peaks of incoherent quasielastic scattering on liquid sodium at $T = 378 \text{ K}$ (squares), 573 K (circles), and 693 K (triangles) for $Q = 0.44 \text{ \AA}^{-1}$. The dashed curve shows the spectrometer resolution function

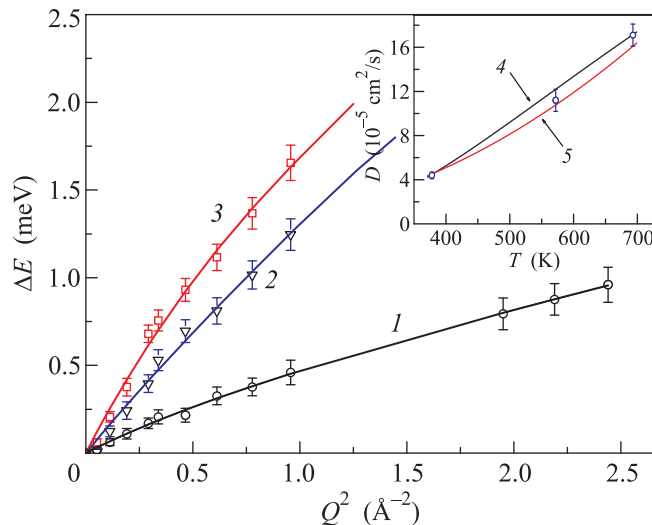


Fig. 2. Intrinsic FWHM of incoherent quasielastic peaks $\Delta E(Q^2)$ of liquid sodium for three temperatures $T = 378 \text{ K}$ (1), 573 K (2) and 693 K (3). The solid lines are the optimal description of the set of experimental points by the model (2) with parameters: $T = 378 \text{ K}$: $D = (4.4 \pm 0.5) \cdot 10^{-5} \text{ cm}^2/\text{s}$, $D_0 = (2.1 \pm 0.5) \cdot 10^{-5} \text{ cm}^2/\text{s}$, $\tau_0 = (3.4 \pm 2.0) \cdot 10^{-12} \text{ s}$, $T = 693 \text{ K}$: $D = (17.1 \pm 1.0) \cdot 10^{-5} \text{ cm}^2/\text{s}$, $D_0 = (6.9 \pm 0.5) \cdot 10^{-5} \text{ cm}^2/\text{s}$, $\tau_0 = (1.0 \pm 0.4) \cdot 10^{-12} \text{ s}$. Inset: temperature dependence of selfdiffusion coefficient for liquid sodium: circle – our results; 4 – calculation with activation model [8]; 5 – calculation with power model [11]

At the first way the experimental points of Fig. 2 were described by the phenomenological model [10], which supposes the mixed character of diffusion mobility in the liquid. It includes two mechanisms: jump diffusion (with parameter τ_0 , the residence time of a particle in the tem-

porary equilibrium position) and continuous diffusion (with parameter D_0 , coefficient of continuous diffusion of a particle together with surrounding). The quasielastic peak is supposed to be a Lorentzian with FWHM:

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

Here D is a total coefficient of self-diffusion. Optimal fitting of the experimental points by expression (2) is shown in Fig. 2, the corresponding parameters of the model are given below this figure. The values of self-diffusion coefficients for the temperatures investigated are in a satisfactory agreement with the known data [8, 11] (inset of Fig. 2).

As the second way of the analysis of our experimental results, the application of so called the “relaxing cage model” [12–14] was applied. According to this model the diffusion event in the liquid can be realized only under the condition if the nearest surrounding of atom is decayed or transformed in essential way. This kind of relaxation is usually understood as slow, or α -relaxation. In the frames of this approach the intermediate scattering function $I(Q, t)$ can be written in the *stretched exponent* form describing its possible non-exponential decay:

$$I(Q, t) = \text{KWW}(t) = \exp[-(t/\tau_W)^\beta], \quad (3)$$

and incoherent dynamical structure factor:

$$S_{QE}(Q, \varepsilon) = \frac{1}{\pi\hbar} \int_0^\infty \exp[-(t/\tau_W)^\beta] \cos(\varepsilon^* t/\hbar) dt. \quad (4)$$

The parameters τ_W (α -relaxation time), β (form parameter) and mean relaxation time

$$\langle \tau_W \rangle = \int_0^\infty dt \text{KWW}(t) = \frac{\tau_W}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (5)$$

depend on Q . The latter can be expressed by the power function:

$$\langle \tau_W \rangle = \tau_0 (Q/Q_0)^{-\gamma}. \quad (6)$$

In the case of simple (continuous) diffusion $\gamma = 2$ and under departure from the hydrodynamic limit γ turns out to be different than 2. The results of our experimental data analysis with application of the “relaxing cage” model are depicted on Figs. 3 and 4.

It seems to be interesting to compare the mean relaxation time of surrounding for given particle $\langle \tau_W \rangle$ with its residence time τ_0 which was estimated in our former analysis (inset of Fig. 4). It is seen these two times

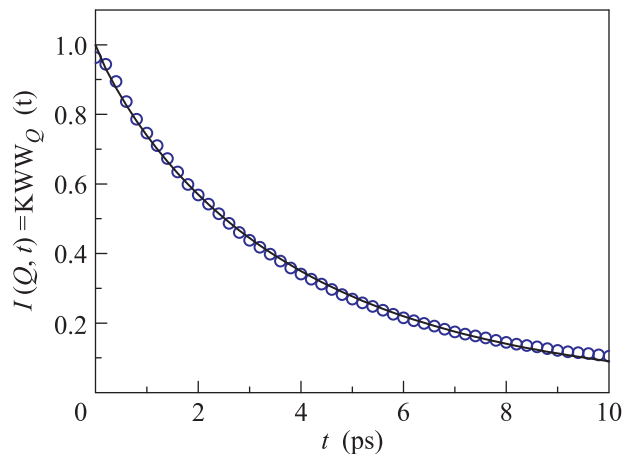


Fig. 3. Intermediate scattering function $I(Q, t)$ for liquid sodium, $T = 378$ K and $Q = 0.78 \text{ \AA}^{-1}$. Full line – description of $I(Q, t)$ by KWW-function (3) and (4) with $\langle \tau_W \rangle = (3.79 \pm 0.04)$ ps, $\beta = 0.90 \pm 0.01$

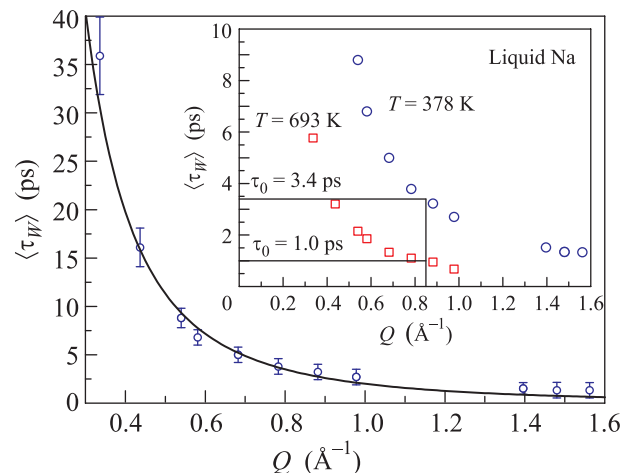


Fig. 4. Typical Q -dependence of mean relaxation time $\langle \tau_W \rangle$ for liquid sodium at 378 K and its description by Exp. (6): $\tau_0 = 2 \pm 0.2$ ps, $\gamma = 2.5 \pm 0.2$. Inset: $\langle \tau_W \rangle(Q)$ for $T = 378$ and 693 K together with corresponding residence time $\tau_0(T)$ obtained from phenomenological model, showing that α -relaxation in liquid sodium takes place for second neighbors

are near each other at $Q \sim (0.8-0.9) \text{ \AA}^{-1}$, that in the direct (coordinate) space corresponds to the distances $R \sim (7-8) \text{ \AA}$ and exceeds remarkably the average interparticle distance in the liquid sodium for $T = 378$ K ($R_0 \sim 3.72 \text{ \AA}$). So, we have ground to suppose that the residence time of the particle τ_0 in the terms of “relaxing cage” model corresponds to the decay time of the near surrounding on the level of the *second neighbors*.

4.2. *Sodium-hydrogen melt.* Fig. 5 demonstrates the comparison of the experimental quasielastic scattering spectra on pure liquid sodium and sodium-hydrogen

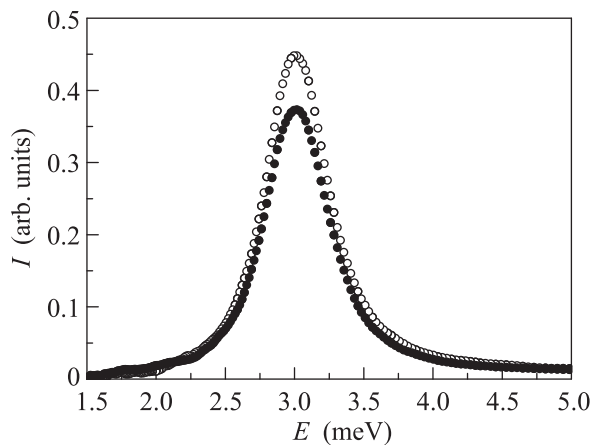


Fig. 5. Comparison of experimental quasielastic incoherent scattering spectra for pure sodium (full symbols) and sodium-hydrogen melt (open symbols); $T = 693$ K, $Q = 0.44 \text{ \AA}^{-1}$

melt. It is obvious the additional intensity, associated with the presence of hydrogen. The rough estimations with the use of this figure reveal the hydrogen concentration $C \sim 0.4\%$ at., which is about that, determined in the process of sample filling with melt. In the course of the experimental data analysis on sodium-hydrogen melt the expression (1) was used supplemented with an additional Lorentzian which was supposed to account for scattering on the hydrogen admixture. But the second component of the incoherent quasielastic spectrum with the FWHM, remarkably different from the first one was not revealed. Furthermore, the FWHM's of the single Lorentzians in the melt was found to coincide with ones obtained for pure sodium (see Fig. 6). The coincidence of the diffusion mobility in pure sodium and sodium-hydrogen melt allows us to suppose that in our experimental conditions hydrogen exists and diffuses in the sodium-hydrogen melt in the form of sodium hydride, NaH. The diffusion coefficient for sodium hydride we get from Fig. 6 applying the phenomenological model (2) within the limits of experimental errors agrees with that for pure sodium and is equal $D_{\text{NaH}} = (17.1 \pm 1.0) \cdot 10^{-5} \text{ cm}^2/\text{s}$. The similar conclusions about the hydrogen diffusion were obtained formerly on potassium-hydrogen [15] and lithium-hydrogen melts [16]. The possible explanation of this phenomena can be found in the comparison of energy dissociations of hydride molecule and diffusion activation energy for liquid alkalis, latter being much less than former one (for NaH $E_{\text{dis}} \sim 56 \text{ kcal/m}$ [17] and $E_{\text{dif}} \sim 10 \text{ kcal/m}$ [8]). So, from the energetic point of view for hydride molecule it is more profitable to diffuse as a whole, than to be dissociated with the subsequent separated diffu-

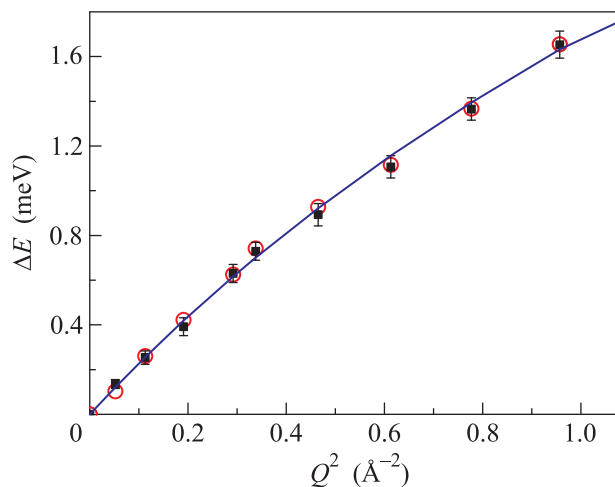


Fig. 6. Comparison of the $\Delta E(Q^2)$ dependence for pure sodium (open symbols), and that of sodium-hydrogen melt (full symbols), $T = 693$ K. Full line – description of experimental points by Exp. (2). No deviations between the data sets within experimental errors are detected

sion. One can easily show that the rotational diffusion of the molecule NaH in the liquid Na is negligible. Moreover, the account of complex diffusion of the ellipsoid molecule NaH is equal to the self-diffusion of the atom Na: the effective radius of ellipsoid NaH is equal to the atom Na radius, while masses of NaH and Na are equal to it other with a good accuracy.

5. Conclusion. From the inelastic neutron scattering spectra for liquid sodium ($T = 378, 573,$ and 693 K) and sodium-hydrogen melt ($T = 693$ K, hydrogen concentration $\sim 0.4\%$ at.) the incoherent quasielastic component was extracted. The FWHM of the incoherent quasielastic peaks were analyzed with applications of two models: phenomenological one (model of mixed diffusion) and model of “relaxing cage”. In the frame of the mixed diffusion model self-diffusion coefficients, residence times of particle and coefficients of collective diffusion of particle together with surrounding were extracted. The self-diffusion coefficients of pure sodium and their temperature dependence are in agreement with the calculations and experimental data available in literature. In the frame of the “relaxing cage” model the relaxation time of surrounding of given particle (τ_W) (α -relaxation) and its Q -dependence were estimated and compared with residence time τ_0 . It was found that the residence time of the particle in the terms of “relaxing cage” model corresponds to the decay time of the near surrounding on the level of the *second neighbors*. It was revealed that diffusion processes in pure sodium and sodium-hydrogen melt approach the continuous diffusion particularly for high temperatures. The diffusion

mobility in pure sodium and in sodium-hydrogen melt was found to be coinciding. It leads to the conclusion that in our experimental conditions hydrogen exists and diffuses in melt in the form of hydride, NaH. The coefficient of diffusion for NaH in liquid Na ($T = 693$ K) was found to be $D_{\text{NaH}} = (17.1 \pm 1.0) \cdot 10^{-5} \text{ cm}^2/\text{s}$.

This work was supported by the RFBR (grant # 11-08-00520-a) and Rosatom (contract No D.4f.43.90.13.1042).

1. F. A. Kozlov, L. G. Volchkov, E. K. Kuznetsov, and V. V. Matyukhin, *Liquid metal coolants*, M., Energoatomizdat (1983), 127 p. (in Russian).
2. V. I. Subbotin, M. N. Arnoldov, F. A. Kozlov, and A. L. Shimkevich, *Atomnaja energija* **92**, 31 (2002).
3. A. Stangl, Chr. Morkel, U. Balucani, and A. Torcini, *J. Non-Cryst. Solids*. **205–207**, 402 (1996).
4. W.-C. Pilgrim and Chr. Morkel, *J. Phys.: Condens. Matter*. **18**, R585 (2006).
5. C. Morkel and W.-C. Pilgrim, *J. Non-Cryst. Solids*. **312–314**, 128 (2002).
6. W.-C. Pilgrim and Ch. Morkel, *Z. Phys. Chem.* **217**, 957 (2003).
7. *User Guide. Neutron Experimental Facilities for Condensed Matter Investigations at FLNP (JINR)*, ed by V. Sikolenko, Dubna, JINR Press (1997), p. 25.
8. *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, Oxford, ed by R. W. Ohse, Blackwell (1985), 985 p.
9. S. Lovesey, *J. Phys. C* **4**, 3057 (1971).
10. V. S. Oskotskii, *Sov. Solid State Phys.* **5**, 1082 (1963).
11. J.-F. Wax, R. Albaki, and J.-L. Bretonnet, *Phys. Rev. B* **65**, 014301 (2001).
12. S.-H. Chen, C. Liao, F. Sciortino, P. Gallo, and P. Tartaglia, *Phys. Rev. E* **59**, 6708 (1999).
13. V. Grupi, D. Majolino, P. Migliardo, and V. Venuti, *J. Phys. Chem. B* **106**, 10884 (2002).
14. F. Demmel and C. Morkel, *Phys. Rev. B* **85**, 051204 (2012).
15. U. Freudenberg and W. Glaser, *J. Phys. F* **15**, 1253 (1985).
16. O. V. Sobolev, N. M. Blagoveshchenskii, V. A. Morozov, A. G. Novikov, M. A. Pashnev, V. V. Savostin, and A. L. Shimkevich, *J. Phys.: Cond. Matter*. **20**, 104211 (2008).
17. C. Wolvertom and V. Ozolins, *Phys. Rev. B* **69**, 144109 (2004).