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1990 J. Phys.: Condens. Matter 2 5825

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Pulsed neutron diffraction study on a molten NaOD structure using a nickel metal cell

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Received 3 August 1989, in final form 6 March 1990

Abstract. A nickel metal cell has been used in the neutron diffraction measurements of highly corrosive molten NaOD. The scattering intensities originating from the nickel metal cell could be satisfactorily subtracted from those from the cell and the melt.

With respect to the intraionic O–D correlation, the result obtained from real space is consistent with that from reciprocal space. The correlations for O–D and Na–O have been observed at 98 pm and 242 pm, respectively, while the Na–D correlation has not been observed as an isolated peak.

1. Introduction

Alkali metal hydroxides consist of a spherical alkali metal ion and a linear diatomic hydroxide ion and they are classified as simple salts. The information on these structures in the molten state should be useful for an understanding of ionic melts. No structural investigation by x-ray or neutron diffraction, however, has been performed for the melt, presumably because it is highly corrosive towards most of the conventional materials used in the cells. Neutron diffraction is superior to x-ray diffraction for condensed matters consisting of light atoms such as deuterium and lithium. In particular, pulsed neutron diffraction combined with a time-of-flight (TOF) method can cover a region of high momentum transfer, which is particularly suitable for the accurate determination of intraionic distances.

It is important to select a suitable material as a cell for the neutron diffraction measurement of such corrosive melts. So far, a Ti–Zr alloy, quartz glass, and vanadium metal have been used for measurements of common materials because of their favourable characteristics as cell materials in neutron diffraction. Their corrosion resistance is not, however, enough against molten alkali hydroxides. In the present work, a nickel metal cell was selected because of its high corrosion resistance against hydroxide melts. Nickel metal shows, however, an intense Bragg pattern for neutron diffraction due to

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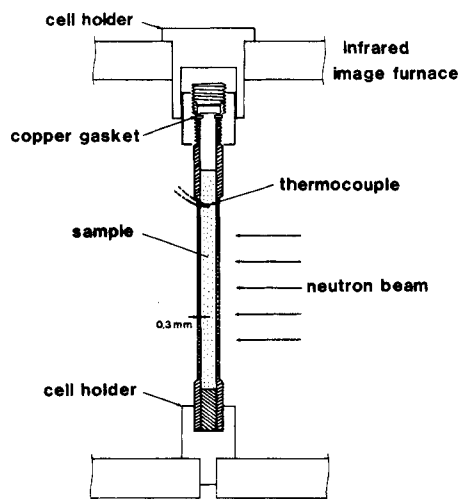


Figure 1. Set-up of the sample cell.

the large coherent cross section ($13.3 \times 10^{-24} \text{ cm}^2$) and the polycrystalline structure. We first examined whether the intense pattern by the nickel cell could be sufficiently corrected; the neutron diffraction measurement was performed for vanadium metal using a conventional quartz cell as well as the nickel cell.

The measurement on molten NaOD was carried out with the cell at 773 K to obtain the structure factor for the melt. The NaOH crystal [1] forms a layer structure in which five Na^+ and five OH^- ions coordinate pyramidally to each other. The orientation of all the OH^- ions is perpendicular to the layer, with the constituent oxygen atoms pointing to the cations. This structure would be due mainly to the anisotropic interaction of the OH^- ion with the cation; large anisotropy in LiOH is inferred from an *ab initio* MO calculation [2]. In molten NaOH, large anisotropy is also expected for the distribution of a Na^+ ion with reference to the nearest OH^- ion, even if the structure should be obscured to some extent by the thermal motion in the liquid state.

In the present paper we will show full applicability of a nickel metal cell to neutron diffraction measurements of molten hydroxides and give a brief discussion on the structure of molten NaOD.

2. Experimental methods

The cell was made of 99% pure nickel metal. The set-up is shown in figure 1. The inner diameter of the cell was 8 mm. The part to be irradiated by the neutron beam was machined uniformly to be as thin as 0.30 mm. The bottom of the cell was sealed with a Ni rod by means of electron beam welding.

Pulsed neutron diffraction was performed by using the TOF method with the high intensity total scattering spectrometer (HIT) equipped with a pulsed spallation neutron source [3] at the National Laboratory for High Energy Physics (KEK), Tsukuba. A series of neutron diffraction experiments performed in the present work are tabulated in table 1. Firstly, the nickel cell containing a vanadium rod 50 mm long and 8 mm in diameter was fixed precisely at a given position in an infrared image furnace in the vacuum chamber of the spectrometer. Then the vacant nickel cell was measured similarly. For

Table 1. A series of neutron diffraction experiments for a NaOD melt. (RT stands for room temperature.)

Measurement	Temperature
Check on full correction of the diffraction peaks from a nickel cell	
Nickel cell containing a vanadium rod	RT
Nickel cell	RT
Silica cell containing a vanadium rod	RT
Silica cell	RT
Vanadium rod	RT
Background	RT
Measurements of a NaOD melt	
Nickel cell containing NaOD	773 K
Nickel cell	773 K
Vanadium rod	RT
Background	RT

comparison, measurements using a quartz glass cell were taken in the same way as above described. Scattering intensities from the vanadium rod as well as background intensities were measured for normalisation. All the measurements above mentioned were taken at room temperature.

The scattered neutrons were detected by ^3He detectors at the scattering angles 2θ of 8° , 13° , 23° , 32° , 42° , 90° and 150° , which were connected with 2048-channel time analysers through amplifiers and discriminators. The data were recorded on a hard disk using a computer-controlled data-acquisition system, and were then processed by use of a HITAC M-680 computer at KEK. A more detailed description of the instrument is given in [3].

The observed intensities for the vanadium-containing cell were corrected for the cell, background, absorption [4], and multiple [5] and incoherent scatterings. Since the coherent scattering length of vanadium is negligibly small (-0.03824×10^{-12} cm), a vanadium rod was used for the purpose of checking the correction of the scattering intensities from the Ni cell; the normalised intensities should be unity for all Q .

The NaOD sample was used instead of NaOH to avoid large incoherent scattering by H atoms. It was prepared from the commercially available aqueous solution (CEA; 98.5 mol% D). After drying, it was dissolved into heavy water of high purity (Wako Pure Chem. Ind. Ltd., Osaka; 99.75 mol% D) and again dehydrated under a stream of dried nitrogen at 800 K for several hours [6]. The purity of the sample was about 99.5 mol% D. Then, the melt was poured into the nickel cell. After being allowed to cool, the nickel cell was evacuated and sealed with a copper gasket. All the procedures were done in a stainless steel dry box filled with dried nitrogen.

A thermocouple was located on the surface of the cell just above the part to be irradiated. A preliminary measurement for the empty cell indicated that the temperature at the location of the thermocouple was 17 K lower than that at the centre of the cell in the vertical and horizontal directions. Thus, in the case of the cell containing the melt, the temperature was expected to read nearly that of the melt owing to the high thermal conductivity of the cell and the good convection of the melt.

The scattering intensities were observed at 773 K for the cell filled both with and without the sample. The observed intensities for the sample were corrected for the

nickel metal cell, background, absorption, and multiple and incoherent scatterings. The coherent scattering intensities $I(Q)$ were normalised using the scattering intensities from the vanadium rod. The coherent scattering from the vanadium metal was neglected since the Bragg peaks of the vanadium metal were not detectable with the resolution for this angle. The scattering lengths for thermal neutrons were taken from the literature [7]. The data obtained at $2\theta = 32^\circ$ were used for further analyses because the correction for the inelastic scattering from light atoms is relatively small. The Placzek correction was made for the self-term of all the constituent atoms according to the Powles method [8]. With respect to the interference term for the intraionic O–D correlation, the results obtained with and without the correction were compared. Using the 32° detector a structure factor was obtainable for $Q = 0.006\text{--}0.22\text{ pm}^{-1}$. This range is sufficient to determine the intraionic correlation accurately. The resolution $\Delta Q/Q = 0.017$ for the whole range at $2\theta = 32^\circ$ and is sufficient for the evaluation of inter- and intra-ionic correlations.

The structure factor $S(Q)$ in the Faber–Ziman form [9] is obtained from the definition of

$$S(Q) = \left\{ I(Q) - \left[\sum (x_i b_i^2) - \left(\sum x_i b_i \right)^2 \right] \right\} / \left(\sum x_i b_i \right)^2 \quad (1)$$

where b_i is the coherent scattering length of the i th nuclear species ($b_{\text{Na}} = 0.3630$, $b_{\text{O}} = 0.5805$ and $b_{\text{D}} = 0.6674 \times 10^{-12}\text{ cm}$ [7]) and x_i the atomic fraction. The neutron weighted radial distribution function $G^n(r)$ is derived by numerical Fourier transformation of the structure function $Qi(Q)$ ($= Q[S(Q) - 1]$)

$$G^n(r) = 1 + (1/2\pi^2 r \rho_0) \int_0^{Q_{\text{max}}} Qi(Q) \sin(rQ) dQ \quad (2)$$

where ρ_0 is the average number density of atoms, and Q_{max} is a cut-off value of Q , i.e. 0.22 pm^{-1} , for the Fourier transformation.

The intraionic structure function $Qi_{\text{intra}}(Q)$ was evaluated by the optimisation of the experimental $Qi(Q)$ in the Q range of $0.13\text{--}0.22\text{ pm}^{-1}$ using the Debye equation [10].

$$Qi_{\text{intra}}(Q) = 2n_{\text{OD}}x_{\text{O}}b_{\text{O}}b_{\text{D}} \sin(Qr_{\text{OD}}) \exp(-l_{\text{OD}}^2 Q^2/2) / \left[r_{\text{OD}} \left(\sum x_i b_i \right)^2 \right] \quad (3)$$

where we have three parameters to be optimised; n_{OD} is the intraionic coordination number of D atoms about an O atom, and l_{OD}^2 is the mean squared displacement of the intraionic equilibrium distance r_{OD} . In this case, n_{OD} should be unity.

Since the intraionic O–D correlation shows a sharp and isolated peak in the $G^n(r)$ as will be shown in figure 5, the n_{OD} can be also evaluated from an integration of $G^n(r)$ [11],

$$n_{\text{OD}} = \left(\sum x_i b_i \right)^2 \int_{r_0}^{r_{\text{max}}} 4\pi r^2 \rho_0 G^n(r) dr / x_{\text{O}} b_{\text{O}} b_{\text{D}} \quad (4)$$

where r_0 and r_{max} are the distances at the nearest approach and at the peak of the $rG^n(r)$, respectively.

3. Results and discussion

Figure 2 shows the relative scattering intensities $I^{\text{obs}}(\lambda)$, plotted versus neutron wavelength λ , from the nickel cell containing the vanadium rod and the empty cell. The corrected and normalised intensity $I_{\text{V}}(Q)$ for the vanadium metal obtained at $2\theta = 23^\circ$

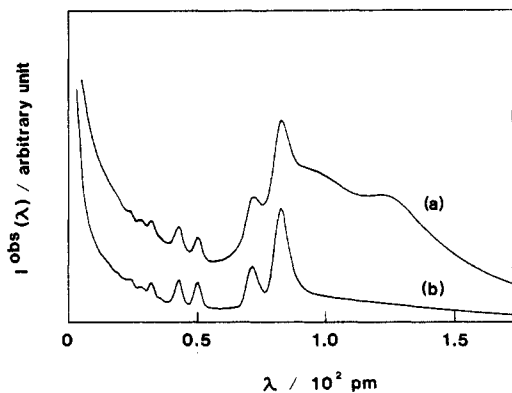


Figure 2. Relative scattering intensities $I^{\text{obs}}(\lambda)$ from the nickel metal cell containing a vanadium rod (a) and the empty cell (b) at $2\theta = 23^\circ$.

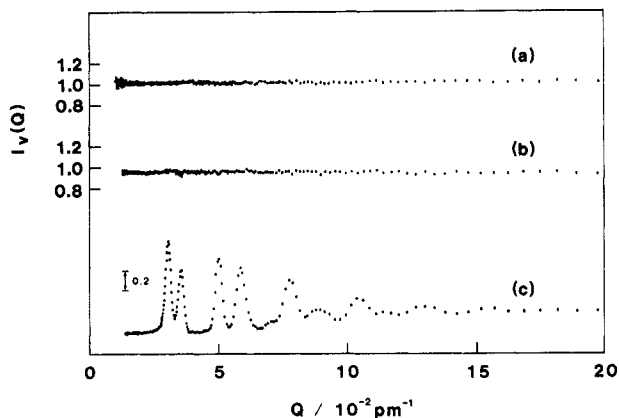


Figure 3. Corrected and normalised intensities $I_V(Q)$ of the vanadium rod set in the quartz glass (a) and nickel metal (b) cells and the diffraction pattern (c) of the nickel metal cell at $2\theta = 23^\circ$.

using the nickel metal cell is shown in figure 3(b) in comparison with the result obtained with the conventional silica glass cell (figure 3(a)). Both values of $I_V(Q)$ should be unity for all Q . The scattering intensities from the nickel metal cell are also presented in figure 3(c) on the same scale. The error in the cell correction was within the statistical error of the experiment. It is clear from the figure that the scattering from the nickel metal cell is successfully subtracted for all Q . The difference of 1 mm in the horizontal positions between the empty cell and the vanadium-containing cell corresponds to a maximum of 0.4% in the error of magnitude of the wave number vector Q at 0.05 pm^{-1} and $2\theta = 23^\circ$. The difference may affect the resultant structure factor as residues of the sharp Bragg peaks remain with nickel metal although this is not a serious problem in the case of the haloes produced by silica glass. Therefore, the nickel cell had to be located much more precisely than in the case of a silica cell. The quality of the resultant normalised intensities is comparable to that from the quartz glass cell, while both of them involve some noise because the accumulated counts were about one-twentieth as small as those of usual experiments. Thus, the nickel cell is fully applicable to neutron diffraction measurements

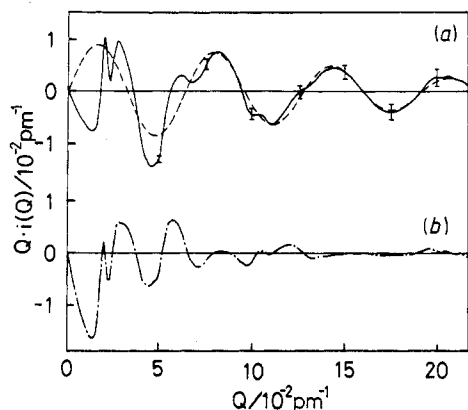


Figure 4. Structure function $Qi(Q)$ for molten NaOD at 773 K obtained at $2\theta = 32^\circ$ by applying the nickel metal cell. (a) —: experimental one; ---: $Qi_{\text{intra}}(Q)$ derived from the Debye equation and (b) - · -; residue after subtracting the intra-ionic part of the curve from the experimental one.

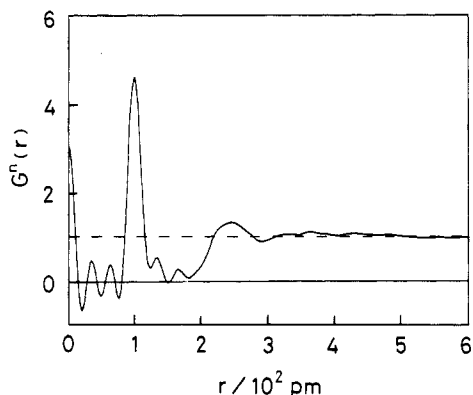


Figure 5. Radial distribution function $G^n(r)$ obtained at $2\theta = 32^\circ$ for molten NaOD at 773 K.

Table 2. Comparison of parameters obtained both from reciprocal space and from real space with respect to the intraionic O–D correlation in molten NaOD. Γ is the FWHM of the intraionic O–D peak. The symbols A and B represent the results without and with, respectively, the Placzek correction for the interference term.

Parameters	Reciprocal space		Real space A
	A	B	
r_{OD} (pm ⁻¹)	98 ± 1	98 ± 1	97
l_{OD} (pm ⁻¹)	7.7 ± 0.5	7.7 ± 0.5	—
Γ (pm ⁻¹)	18^\dagger	—	20
n_{OD}	0.99 ± 0.10	0.99 ± 0.10	0.95

[†] See the text.

of molten alkali hydroxides and the other highly corrosive melts in spite of the large Bragg peaks.

Figure 4(a) shows the total structure function obtained at $2\theta = 32^\circ$ for molten NaOD at 773 K. The estimated statistical error of the data is shown by the error bars in the figure. A double peak is found around $Q = 0.03 \text{ pm}^{-1}$ and the $Qi(Q)$ oscillates nearly sinusoidally at $Q > 0.13 \text{ pm}^{-1}$. At large Q the intraionic O–D correlation is expected to dominate the structure function. Thus, $Qi_{\text{intra}}(Q)$ of the Debye equation for the intraionic O–D correlation is fitted to the experimental one in the range $Q = 0.13\text{--}0.22 \text{ pm}^{-1}$ by a least squares method. The optimised parameters are given in table 2. At $2\theta = 32^\circ$, the difference between these structural parameters with and without the Placzek correction for the interference term was negligibly small. The intraionic structure function thus obtained is also shown in figure 4(a). The optimisation is excellent. The residual curve after subtracting the intra-ionic component from the $Qi(Q)$ must be attributed to the

Table 3. Comparison of parameters for the intraionic O–D (or O–H) correlation of NaOD and D₂O in various states and of the isolated OH[−] ion.

	State	r_{OD} (pm ^{−1})	l_{OD} (pm ^{−1})	Method†	Reference
NaOD	solid	98	—	N	[1]
	liquid	98	7.7	N	this work
OH [−]	isolated	97‡	—	MO	[2]
	isolated	96‡	—	I	[13]
D ₂ O	solid	101	—	N	[14]
	liquid	93	—	N	[15]
	liquid	98	—	N	[16]
	liquid	95	14.2	E	[17]
	vapour	97	5.6	E	[18]

† The symbols N, I, E and MO represent neutron diffraction, infrared spectroscopy, electron diffraction and MO calculation, respectively.

‡ The distance between O and H.

interionic correlation and is plotted in figure 4(b); the function decays to zero at Q greater than 0.13 pm^{−1}.

The $G^n(r)$ calculated from (2) is shown in figure 5; this figure is obtained without any window function in the Fourier transformation. The first intense peak at 97 pm is assignable to the intraionic O–D correlation. The noise at small r may be caused by the truncation of the Fourier transformation at a finite value. The distance of the peak is practically invariant whether the Riemann window [12] is used or not in the Fourier transformation. Thus, the obtained value of the intraionic O–D distance is not influenced by the Fourier noise. The coordination number n_{OD} obtained from the integration of the isolated first peak of $G^n(r)$, i.e. (4), is 0.95. The full width at half maximum (FWHM), Γ , for the peak is 20 pm, which agrees well with the optimised value to the $Qi(Q)$ curve (18 pm = $4[(l_{OD}^2/2) \ln 2]^{1/2}$).

The parameters (n_{OD} , r_{OD} and Γ) thus obtained in two ways, i.e. from real space and from reciprocal space, are consistent with each other as expected. This shows that both the Fourier transformation and the optimisation to the Debye equation have been successfully carried out.

In table 3 the comparison of the intraionic structure of OH[−] or OD[−] ions is presented for molten, crystalline and isolated plasma states. The O–D bond length in D₂O is also given in the table. The intraionic O–D distances are almost the same while the distance in liquid D₂O reported in (15) is a little shorter. The distance and the coordination number for an intraionic O–D pair obtained in the present work are very reasonable.

An apparently single peak is observed at 242 pm in figure 5. This may be assigned to the correlation between O and Na since the distance is nearly equal to the sum of the effective ionic radii [19] of Na⁺ (102 pm) and OH[−] (135 pm) in the crystalline state, although the concept of ionic radius for polyatomic ions is not unanimously accepted. The peak may include not only the Na–O correlation but also the D–D and Na–D correlations. The Na–D correlation is not observed as an isolated peak. The broad peak at large r (= 300–500 pm) may originate from the correlations for such pairs as Na–Na and O–O.

4. Conclusions

It is shown that a nickel metal cell is fully applicable to neutron diffraction measurement of liquids in respect of the correction of scattering from the cell. The cell can be employed for molten hydroxides such as NaOH without any problems with material corrosion. The present result suggests that even metal cells having Bragg patterns can generally be applied to neutron diffraction.

The most probable distances of the intraionic O–D and Na–O correlations are observed at 98 pm and 242 pm, respectively, while the Na–D correlation is not observed as an isolated peak.

Based on the experimentally obtained $Q_i(Q)$ and $G^n(r)$, molecular dynamics simulation is now in progress to elucidate the structure of molten NaOD in more detail.

Acknowledgments

The expenses for this work were partly defrayed by the Grants-in-Aid for Scientific Research (Nos 63470008 and 63044044) from the Ministry of Education, Science and Culture, Japan. We thank the computer centres at the National Laboratory for High Energy Physics at Tsukuba for the use of the HITAC M-680 computers.

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