Structural study on molten MOD (M=^{7}Li, Na and K) by pulsed neutron diffraction

Structural study on molten MOD (M = ^{7}Li, Na and K) by pulsed neutron diffraction

Norikazu Ohtori†, Susumu Okazaki†, Osamu Odawara†,
Isao Okada†‖, Masakatsu Misawa‡ and Toshiharu Fukunaga§

† Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta,
Midori-ku, Yokohama 227, Japan
‡ National Laboratory for High Energy Physics, Oho, Tsukuba 305, Japan
§ Department of Crystalline Materials Science, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464, Japan

Abstract. The structure of molten MOD (M = ^{7}Li, Na and K) at 773 K has been investigated by neutron diffraction measurement using a nickel metal cell. The intraionic O–D bond lengths were 97, 98 and 98 pm and the most probable interionic M–O distances were 194, 242 and 279 pm for ^{7}LiOD, NaOD and KOD, respectively. The difference in the intraionic O–D distance among these melts was within the experimental error. The M–O distance depends linearly on the ionic radius of the cations; the OD$^-$ ion possesses an effective ionic radius of 139 pm in the melts. Long ranged oscillatory character was observed in the $G^n(r)$ for ^{7}LiOD but not for NaOD or KOD.

1. Introduction

Alkali metal hydroxides consist of spherical alkali metal ion and the simplest polyatomic ion, OH$^-$. The size of the hydroxide ion is as small as that of the F$^-$ ion and the centre of its negative charge is polarized to the oxygen side, so that it interacts anisotropically with the cation through the strong coulombic attraction [1]. According to the results of solid structure investigations [2], the LiOH crystal forms a layer structure in which four Li$^+$ ions coordinate squarely to an OH$^-$ ion only on its oxygen side and four OH$^-$ ions coordinate tetrahedrally to a Li$^+$ ion. The orientation of all the OH$^-$ ions is vertical to the layer, the oxygen side pointing to the cations. The NaOH crystal [3] also forms a layer structure, in which five Na$^+$ and five OH$^-$ ions coordinate pyramidally to each other. In the structural study of KOH crystal [4], it has been shown that each K atom is surrounded by a distorted octahedron of O atoms and *vice versa*. The hydrogen atoms in KOH have been shown to lie on or very near to the O–O axes.

 The purpose of the present study is to elucidate the structure of molten alkali hydroxides by means of neutron diffraction. In a previous study [5], neutron diffraction measurements were successfully carried out for highly corrosive NaOD melt using a nickel metal cell. The intraionic structure was evaluated with good accuracy and a peak, traceable mainly to the Na–O correlation, was observed at 242 pm in the radial distribution function. In the present study, neutron diffraction measurement has been performed for molten ^{7}LiOD and KOD as well as for the NaOD melt measured in the

‖ To whom any correspondence should be addressed.

previous study [5]. The cation dependence of the intraionic structure and the atom–atom distance has been examined.

2. Experimental details

The deuteroxide samples were used instead of hydroxides to avoid large incoherent scattering by the H atoms. The KOD sample was prepared from commercially available aqueous solution (CEA; 98.5 mol% D) and heavy water of high purity (Wako Pure Chemical Industries Ltd, Osaka; 99.75 mol% D) in a similar procedure to that for NaOD [5]. The purity of the prepared sample was about 99.5 mol% D.

Lithium-7 deuteroxide (^{7}LiOD) was prepared from ^{7}LiOH $\cdot$ H$_2$O (Tomiyama Chemical Co Ltd., Tokyo: 99.95 mol% ^{7}Li) and the heavy water. The ^{7}LiOH $\cdot$ H$_2$O was dehydrated at about 470 K for a few hours in a nickel crucible. The melt was decomposed to ^{7}Li$_2$O [6] by heating it to 950 K in an alumina crucible under vacuum (about 1600 Pa). The obtained ^{7}Li$_2$O was dissolved into D$_2$O in a stainless steel dry box filled with dried nitrogen gas. The Raman intensity ratio of the OH stretching mode at 3400 cm^{-1} to the OD stretching mode at 2500 cm^{-1} in the deuteroxide solution was less than 0.0025, which indicates that the H/D ratio was negligibly small. The solution was again dehydrated and heated at about 770 K for 3 h under a flow of dried nitrogen. Subsequently, the melt was poured into the nickel cell (inner diameter 8 mm). After cooling, the nickel cell was evacuated and sealed by a copper gasket.

Time of flight (TOF) pulsed neutron diffraction measurement was performed with the high intensity total scattering spectrometer (HIT) equipped with a pulsed spallation neutron source at the National Laboratory for High Energy Physics, Tsukuba. The scattering intensities were observed at 773 K only for the cell and then for the cell filled up with the sample. The observed intensities for the sample were corrected for the nickel metal cell, background, absorption [7], and multiple [8] and incoherent scatterings. The data at the scattering angle $2\theta = 32°$ were used for further analyses, since the inelastic scattering effect from light atoms is smaller with a decrease in the angle. The Placzek correction was made for the self term of all the constituent atoms according to the Powles method [9]. The interference term did not influence the results practically as described in the previous paper [5] at $2\theta = 32°$. The coherent scattering intensities $I(Q)$ were normalized by the use of the vanadium standard, where $\hbar Q$ denotes the momentum transfer. More details of the nickel cell and the instrument are given in [5] and [10].

The total structure factor $S(Q)$ in the Faber–Ziman form [11] is obtained from the definition

$$S(Q) = [I(Q) - \{\Sigma(x_i b_i^2) - (\Sigma x_i b_i)^2\}]/(\Sigma x_i b_i)^2 \tag{1}$$

where b_i is the coherent scattering length of the ith nuclear species and x_i the atomic fraction. The weights of the partial structure factors to the total one, $x_i x_j b_i b_j/(\Sigma x_i b_i)^2$, are shown in table 1. The neutron weighted radial distribution function $G^n(r)$ is derived by numerical Fourier transformation of the total structure function $Qi(Q)$ ($= Q(S(Q) - 1)$)

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

where ρ_0 is the average number density of atoms, and Q_{max} is a cut-off value of Q, i.e. 0.20 [12], 0.22 and 0.22 pm^{-1} for ^{7}LiOD, NaOD and KOD, respectively, for the Fourier transformation.

Table 1. The weight of the partial structure factor to the total one, $x_i x_j b_i b_j / (\Sigma x_i b_i)^2$, for alkali hydroxides. The letter 'M' denotes a metal atom.

System	M–M	M–O	M–D	O–O	O–D	D–D
^{7}LiOD	0.047	−0.122	−0.141	0.320	0.368	0.423
NaOD	0.051	0.081	0.093	0.130	0.149	0.172
KOD	0.053	0.082	0.095	0.129	0.148	0.170
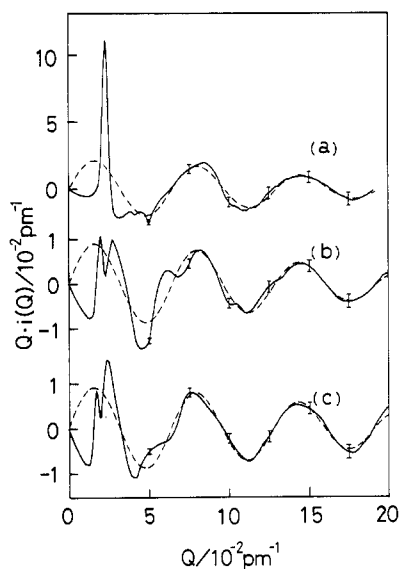
Figure 1. Structure function $Qi(Q)$ for molten alkali hydroxides at 773 K. (a), (b) and (c) refer to ^{7}LiOD, NaOD and KOD, respectively. ———: experimental results; – – –: $Qi_{\text{intra}}(Q)$ derived from the Debye equation.

The intraionic structure function $Qi_{\text{intra}}(Q)$ was evaluated by optimization of the experimenal $Qi(Q)$ in the Q range from 0.13 pm^{-1} to Q_{max} using the Debye equation [13];

$$Qi_{\text{intra}}(Q) = 2n_{\text{OD}} x_{\text{O}} b_{\text{O}} b_{\text{D}} \sin(Q r_{\text{OD}}) \exp(-l_{\text{OD}}^2 Q^2/2) / \{r_{\text{OD}}(\Sigma x_i b_i)^2\} \tag{3}$$

where there are three parameters to be optimized; n_{OD} is the intraionic coordination number of D atoms around an O atom, and l_{OD}^2 is the mean squared displacement of the intraionic equilibrium distance r_{OD}.

3. Results and discussion

Figure 1 shows the obtained total structure functions for molten MOD (M = ^{7}Li, Na and K) at 773 K. The estimated statistical error of the data is shown by the error bars in the figure. As seen from the figure, the first peak was single and intense for ^{7}LiOD, while the first peak splits into a doublet for NaOD and KOD. The difference could be caused by the negative scattering length of ^{7}Li. It was, however, revealed by molecular dynamics (MD) calculation for molten LiOH [14] that the first peak of ^{7}LiOD is mainly based on long ranged O–O correlation.

The $Qi(Q)$ points oscillate nearly sinusoidally at $Q > 0.13$ pm^{-1} in all the cases. At large Q, the intraionic O–D correlation is predominant in the $Qi(Q)$ points. In the

Table 2. Comparison of parameters obtained from reciprocal space for the intraionic O–D correlations and from real space for the M–O correlations in molten alkali hydroxides at 773 K. The values in parentheses denote the coordination numbers in the crystals.

System	r_{OD} (pm)	n_{OD}	l_{OD} (pm)	r_{MO} (pm)	r_M^a (pm) [16]
^{7}LiOD	97 ± 1	0.95 ± 0.10	8.2 ± 0.5	194 ± 10	59 (IV)
NaOD	98 ± 1	0.99 ± 0.10	7.7 ± 0.5	242 ± 5	102 (VI)
KOD	98 ± 1	1.02 ± 0.10	6.7 ± 0.5	279 ± 5	138 (VI)
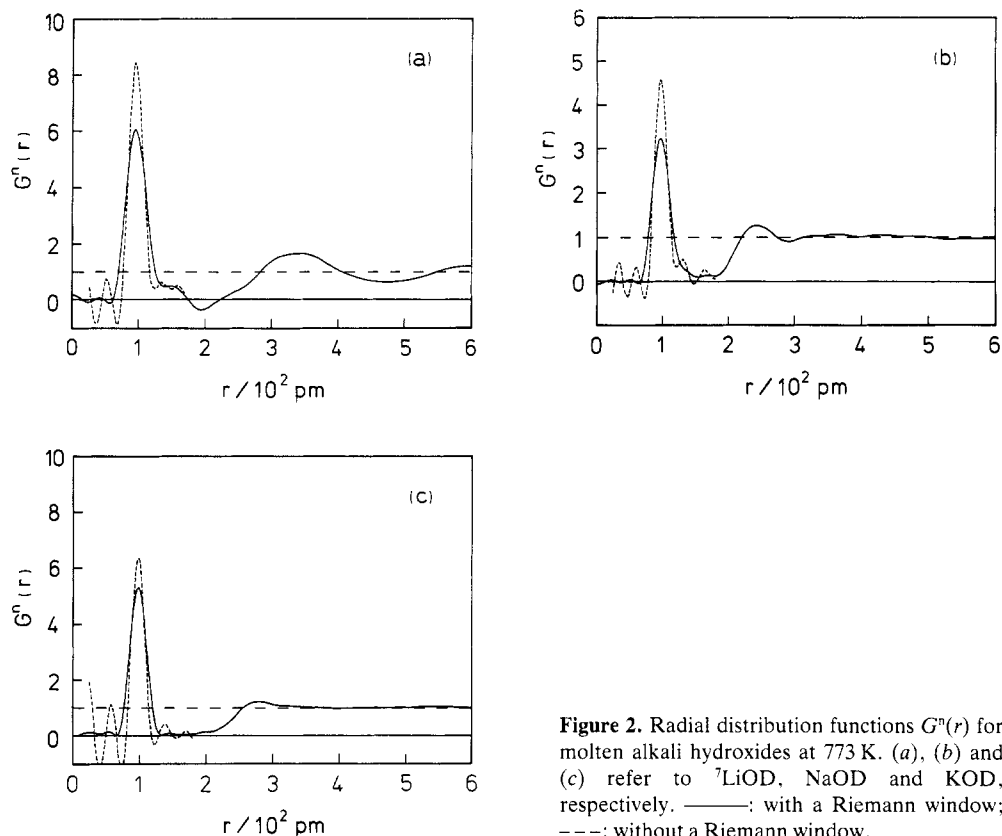
Figure 2. Radial distribution functions $G^n(r)$ for molten alkali hydroxides at 773 K. (a), (b) and (c) refer to ^{7}LiOD, NaOD and KOD, respectively. ———: with a Riemann window; – – –: without a Riemann window.

evaluation of the Debye equation, the value of n_{OD} changes within 10% at most according to the range of optimization. Table 2 shows the optimized parameters of r_{OD}, n_{OD} and l_{OD}. This result shows that the difference in the intraionic O–D distances among these melts was within the experimental error. The intraionic Debye structure functions obtained are also shown in figure 1. The n_{OD} values obtained from the Debye equation are reasonable and consistent with the values calculated from the integration of the intraionic O–D correlation in the following $G^n(r)$ values.

The total structure functions were Fourier transformed with and without a Riemann window [15]. The $G^n(r)$ of ^{7}LiOD, NaOD and KOD are presented in figures 2(a), 2(b) and 2(c), respectively. Each maximum peak at about 100 pm can clearly be assigned to the intraionic O–D correlation. The peaks at smaller r should be caused by the truncation
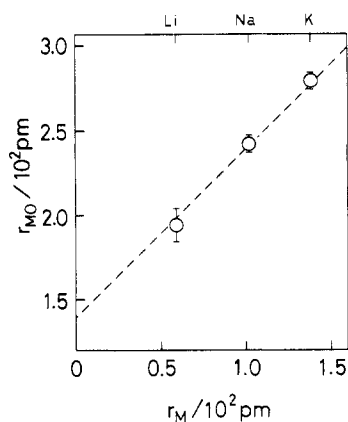
Figure 3. Plot of the M–O distance r_{MO} against the cation radius r_M. – – – is the best fit to the plot with a slope of unity; the intersection of the ordinate is 139 pm. As for the ionic radii, see also table 2.

of the Fourier transformation at a finite value. The $G^n(r)$ without the window function, however, may be preferable for the evaluation of this sharp and large peak of intraionic O–D correlation, since the window function more or less causes broadening of the peak. On the other hand, the position of small interionic peaks must be evaluated from $G^n(r)$ with the window function in order to avoid the uncertainty caused by the relatively large Fourier truncation ripple. In the case of $G^n(r)$ without the window function, from which the intraionic coordination numbers n_{OD} were calculated, only O–D intraionic peaks are shown in the figures.

The most probable Li–O distance was 194 pm, which could reasonably be assigned by taking account of the Li–O distance being 198 pm in the crystal [2]. This is also supported from the MD calculation [14]. According to analogous consideration, the peaks observed at 242 and 279 pm for NaOD and KOD are assigned mainly to the Na–O and K–O correlation, respectively. The coordination number could not definitely be determined because there exists some overlap of the other atom–atom correlations as well as the influence of the window function. The r_{MO} values are plotted in figure 3 against the ionic radii of cations r_M [16], which are presented in table 2. This plot approximately shows a straight line with a slope of unity. This suggests that the OD$^-$ ion has an effective ionic radius of 139 pm (the intersection of the ordinate in figure 3) against the cation in the melt. In the short ranged structure, the liquid may have a similarity with the crystal. The interionic distances of nearest-neighbour ions of an unlike sign can be determined by the cation size and the effective oxygen size in the melts. In this respect, it is interesting to investigate other oxy-anion systems such as nitrates and carbonates. On the other hand, no distinct M–D correlation is observed for all systems because of a great overlap of other atom–atom correlations. A very small negative peak or dent can be found at about 250 pm in $G^n(r)$ for the LiOD melt. However, this cannot be distinguished from the Fourier ripple and might not represent real correlation, although strong partial Li–D correlation was observed at this location by MD simulation [14].

The $G^n(r)$ for ^{7}LiOD shows oscillatory behaviour at $r > 300$ pm while such behaviour is not observed for NaOD or KOD. This is traceable to the single and intense peak at $Q = 0.023$ pm^{-1} in reciprocal space for ^{7}LiOD. According to the MD calculation for molten LiOH, the oscillatory behaviour in real space was also found and assigned to O–O correlation. For the present $G^n(r)$, there is a difference in the long-range correlation between ^{7}LiOD and the others.

There seems to exist a slight correlation around 150 pm in the $G^n(r)$ of the LiOD melt. This may represent D–D correlation, although large ghost peaks prevent further

analysis. In order to examine each correlation in more detail, an isotope substitution method is required from an experimental point of view. Further, computer simulation is a powerful tool for elucidating detailed structure of the liquids. The MD calculation for molten LiOH will be reported elsewhere [14].

4. Conclusions

Neutron diffraction measurements have been performed for molten MOD (M = ^{7}Li, Na and K) at 773 K using a nickel metal cell. From the $Qi(Q)$ values, the intraionic O–D bond lengths were determined to be 97, 98 and 98 pm for ^{7}LiOD, NaOD and KOD, respectively. The difference in the intraionic O–D distances among these melts was within the experimental error. The peaks in the M–O correlations were observed in the $G^n(r)$ values for ^{7}LiOD, NaOD and KOD at 194, 242 and 279 pm, respectively. The plot of the M–O distance against the ionic radii of the cation shows a good straight line with a slope of unity. This suggests that the OD$^-$ ion has an effective radius of 139 pm in the melts. The distances between adjacent ions of unlike sign can be determined from the radii of cation and the O atom size of the OD$^-$ ion.

Long-ranged oscillatory character was observed in the $G^n(r)$ for ^{7}LiOD but not for the NaOD or KOD melts.

Acknowledgments

References

[1] Okazaki S and Okada I 1989 *J. Chem. Phys.* **90** 5595
[2] Dachs H 1959 *Z. Kristallogr.* **112** 60
[3] Stehr H 1967 *Z. Kristallogr.* **125** 332
[4] Ibers J A, Kumamoto J and Snyder R G 1960 *J. Chem. Phys.* **33** 1164
[5] Ohtori N, Okazaki S, Odawara O, Okada I, Misawa M and Fukunaga T 1990 *J. Phys.: Condens. Matter* **2** 5825
[6] Blavo J 1963 *Inorganic Syntheses* vol 7, ed J Kleinberg (New York: McGraw-Hill) p 3
[7] Paalman H H and Pings C J 1962 *J. Appl. Phys.* **33** 2635
[8] Blech I A and Averbach B L 1965 *Phys. Rev.* A **137** 1113
[9] Powles J G 1979 *Mol. Phys.* **37** 623
[10] Misawa M, Fukunaga T, Yamaguchi T and Watanabe N 1986 *Proc. Ninth Meeting of Int. Collaboration on Advanced Neutron Source (ICANS-IX)* ed F Atchison and W Fischer (Villingen: Swiss Institute for Nuclear Research) p 539
[11] Faber T E and Ziman J M 1965 *Phil. Mag.* **11** 153
[12] The Q_{max} for ^{7}LiOD was limited by the accidental error originating from machine condition
[13] Debye P 1915 *Ann. Phys.* **46** 809
[14] Okazaki S, Ohtori N and Okada I 1990 *J. Chem. Phys.* **92** 7505
[15] Harris F J 1978 *Proc. IEEE* **66** 51
[16] Shannon R D 1976 *Acta Crystallogr.* A **32** 751