Structural Analysis of Molten Na_2BeF_4 by X-ray Diffraction †

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KEY WORDS: (Structural Analysis) (Molten Na_2BeF_4) (X-ray Diffraction)

In order to make clear the dynamical structure of molten fluoro-beryllates, the authors have measured the self-diffusion coefficients of cation and anion in molten XF-BeF_2 (X: Li, Na) mixtures.[1] The knowledge concerning the structure of these melts serves for the understanding of the diffusion behavior of each ion. Therefore, the structural analysis of molten Na_2BeF_4 with the X-ray diffraction was carried out. The short range configuration of the atoms in molten Na_2BeF_4, that is, the most possible positions of the nearest-neighbor sodium atoms around the BeF_4 tetrahedron were discussed from the observed scattering intensities.

Na_2BeF_4 sample was prepared from mixing weighted NaF and BeF_2, and then melting in a platinum crucible under He atmosphere. After holding for an hour at 700°C, the sample was cooled to the room temperature and then crushed. The used chemicals were analytical reagent grade NaF (prepared by Merk Co.) and BeF_2 (Rare Metallic Co., known impurities (in ppm): K + Na, 600; Ca, 10; Al, 20; Cr, 30; Fe, 10; Ni, 10).

The X-ray diffraction experiment was carried out using a θ-θ diffractometer with the parafocusing reflection geometry. The monochromatic MoKα radiation was obtained through the use of a curved graphite crystal mounted in the diffracted beam. Silt system of 1/2°-1/2° and 1°-1° were employed in the low ($3° \leqslant \theta \leqslant 10°$) and high angles ($8° \leqslant \theta \leqslant 50°$), respectively, where θ is the scattering angle. The scattering intensities were measured over the angular range $3° \leqslant \theta \leqslant 50°$ using the step-scanning techique, corresponding to the interval

$0.93\ \text{Å}^{-1} \leqslant S \leqslant 13.55\ \text{Å}^{-1}$ in the variable

$$S = 4\pi \sin\theta / \lambda, \tag{1}$$

where λ is the wavelength (0.7107 Å). Several runs were made in oder to accumulate 20000 counts per datum point in the low angles and 34000 in the high angles, respectively.

Na_2BeF_4 sample placed in a small electric furnace putting in an air-tight chamber with a window of Al foil (10 μm thickness) filled He gas. The temperature of the sample was controlled to 650 ± 10°C throughout the measurement.

The method on analysis was the same as described in the previous paper.[2] After the correction of background, polarization and Compton radiation, the observed scattering intensities were scaled to the independent scattering factor for the stoichiometric unit using the result of Krogh-Moe-Norman's method. The radial distribution function of electron density around the atom is given per molecule by the expression

$$\begin{aligned} D(r) &= 4\pi r^2 \sum_{i=1}^{m} \bar{K}_i g_i(r) \\ &= 4\pi r^2 g_o \sum_{i=1}^{m} \bar{K}_i + \sum_{i=1}^{m} (\bar{K}_i)^2 \, 2r/\pi \\ &\quad \int_0^{S_{max}} Si(S) \sin(Sr)\, dS, \end{aligned} \tag{2}$$

and

$$i(S) = I_{eu}^{coh}(S) / [\sum_{i=1}^{m} f_i(S)^2] - 1, \tag{3}$$

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† Received on March 31, 1979

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where m is the number of atoms in the stoichiometric unit, $\bar{K}_i$ the effective number of electrons in the atom i, $g_i(r)$ the effective electron density at distance r, g_o the average electron density, $f_i(S)$ the independent atomic scattering factor, $I_{eu}^{coh}(S)$ the total coherent scattering function and S_{max} the maximum value of S reached in the experiment. The average correlation function G(r) which is an alternate form of D(r) is expressed by

$$G(r) = 1 + \sum_{i=1}^{m} (\bar{K}_i)^2 / [\sum_{i=1}^{m} \bar{K}_i \pi^2 g_o r] \int_0^{S_{max}} Si(S) \sin(Sr)\, dS . \quad (4)$$

The constants used in these calculations are given in **Table 1.**

Table 1. Constants used in the calculation of the radial distribution function.

Na_2BeF_4	
temperature (°C)	650 ± 10
density (g/cm³)	2.093[3]
electron number	42
molar weight	88.997
effective	
electron number	
$\bar{K}_{Na}$	11.84
$\bar{K}_{Be}$	3.73
$\bar{K}_F$	8.65
S_{max} (Å^{-1})	13.55

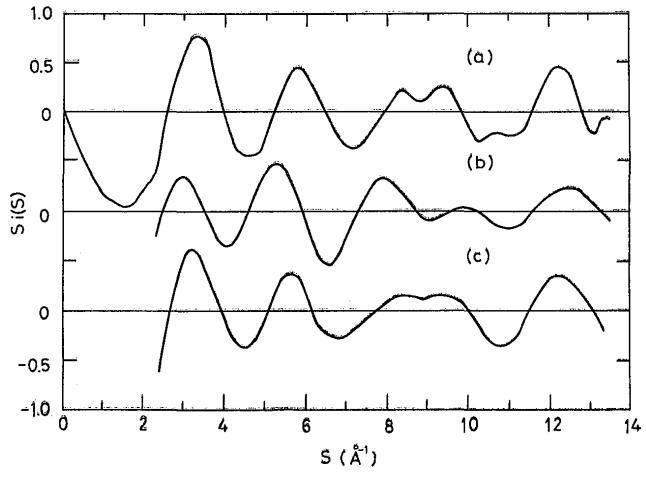

Figure 1. Observed and calculated reduced intensity functions Si(S) of molten Na_2BeF_4 at 650 ± 10°C. (a) observed, (b) isolated BeF_4 tetrahedron, (c) model.

The reduced intensity function Si(S) of molten Na_2BeF_4 is shown in **Figure 1(a).** The radial distribution function D(r), the function D(r)/r and the correlation function G(r) of molten Na_2BeF_4 are shown in **Figures 2** and **3**, respectively. The 1st peak at r = 1.65 Å of these functions corresponds to the Be-F interaction in the BeF_4 tetrahedron. In the crystalline from of Na_2BeF_4,[4] each beryllium atom is tetrahedrally surrounded by four fluorine atoms with the mean Be-F distance of 1.56 Å and F-F distance of 2.55 Å. The Be-F distance becomes slightly longer in the melt. The coodination number of the Be-F interaction can be calculated from the 1st peak of the function D(r)/r, assuming a Gaussian distribution peak.[5] The value was 4.02. The 2nd peak at r = 2.22 Å corresponds to the nearest-neighbor Na-F interaction ($r_{Na^+} + r_{F^-}$ = 2.28 Å, r_{Na^+}, r_{F^-}: he ionic radii of the Na^+ and F^-). The 3nd peak at r = 2.62 Å corresponds to the F-F distance of the BeF_4 tetrahedron. Separating the 2 and 3nd peaks of the function D(r)/r into the two Gaussian distribution peaks by the least square method, the coordination numbers of the nearest-neighbor fluorine atoms around the sodium and fluorine atom were 2.87 and 3.27, respectively. This coordination number of the F-F interaction indicates that the BeF_4 tetrahedra exist as

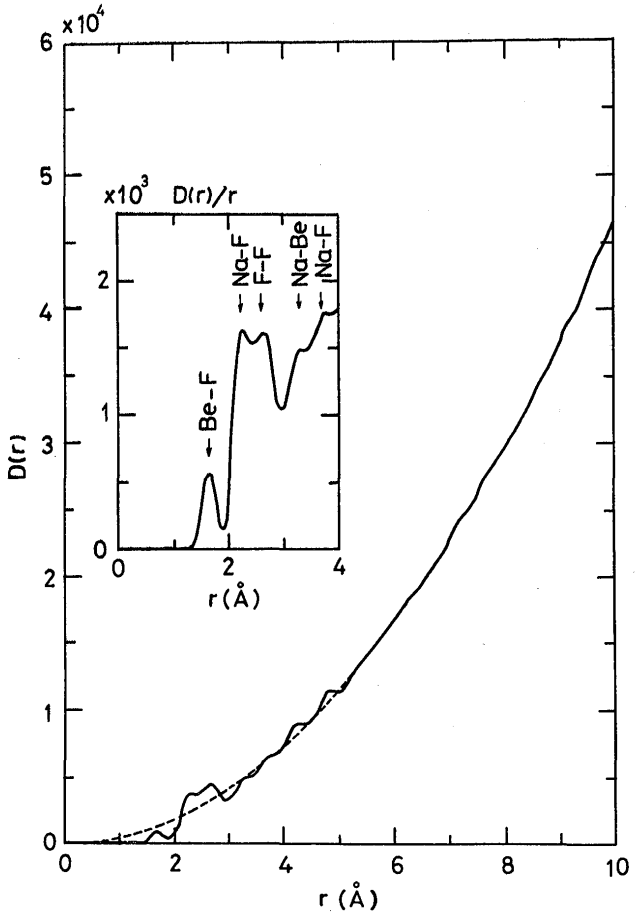

Figure 2. Radial distribution function D(r) and function D(r)/r of molten Na_2BeF_4 at 650 ± 10°C.

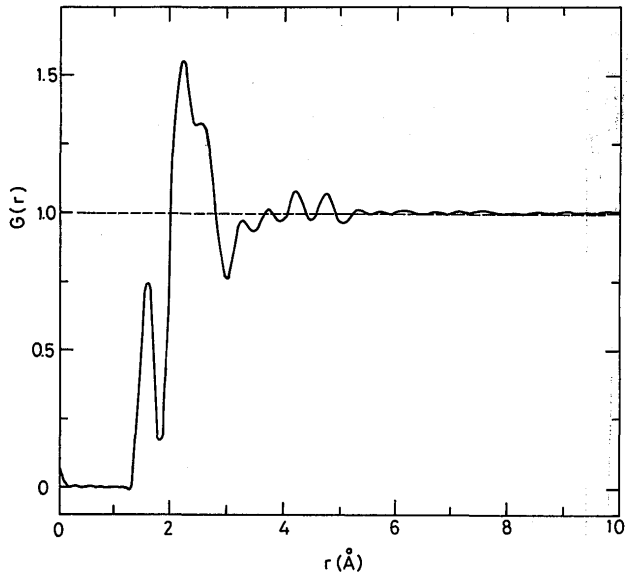

Figure 3. Average correlation function G(r) of molten Na_2BeF_4 at 650 ± 10°C.

the isolated form in molten Na_2BeF_4. The theoretical function Si(S) can be calculated from the Debye scattering equation[6] given by the expression.

$$Si(S)\left[\sum_{i=1}^{m} f_i(S)^2\right] = \sum_{i=1}^{m}\sum_{j} N_{ij} f_i(S) f_j(S)\left[\sin(Sr_{ij})/(Sr_{ij})\right] exp(-b_{ij}S^2), \quad (5)$$

where $f_i(S)$ and $f_j(S)$ are the independent atomic scattering factors of i and j atoms, respectively, r_{ij} the mean distance of the i-j interaction, b_{ij} the temperature factor that is a half of the mean square variation in r_{ij}. The calculated function Si(S) for the isolated BeF_4 tetrahedron using equation (5) is shown in **Figure 1(b)**. Comparing Figures 1(a) and (b), the maximum and minimum postions of molten Na_2BeF_4 below values of $S \leqslant 11 Å^{-1}$ slightly shift toward the higher and lower S region. This behavior results from the effect of the nearest-neighor sodium atoms around the BeF_4 tetrahedron. We can consider three typical configurations of the sodium atoms around the BeF_4 tetrahedron. One is a configuration that the sodium atom occupies the corner-site of the BeF_4 tetrahedron. Another is a configuration that the sodium atom occupies the edge-site. The other is a configuration that the sodium atom occupies the face-site. The function Si(S) calculated from the most possible configuration model by the method of trial and error is shown in **Figure 1 (c)**. The constants used in the calculation are given in **Table 2**. This structural model is as follow. There exist two sodium atoms around the BeF_4 tetrahedron, one of the two sodium atoms occupies the corner-site and the other occupies the edge-site. The schematic diagram of this structural model is shown in **Figure 4**. In this structural model, the coordination number of the nearest-neighbor Na-F interaction is 3.0. The value is almost equal to the coordination number calculated from the 2nd peak of the observed function D (r)/r.

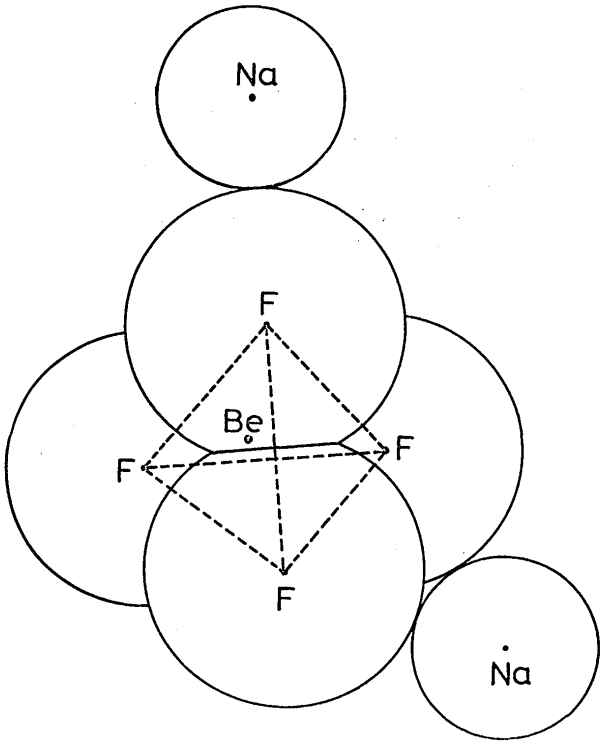

Figure 4. Schematic diagram of model.

Table 2. Constants used in the calculation of figure 1(c). Number of atoms j around any origin atom i, N_{ij}, atomic distance, r_{ij}, and associated rms displacement, $<\triangle r_{ij}^2>^{1/2}$.

i	j	N_{ij}	r_{ij} (Å)	$<\triangle r_{ij}^2>^{1/2}$ (Å)
Na	Na	2.0	——	——
Be	Be	1.0	——	——
F	F	4.0	——	——
Be	F	8.0	1.65	0.100
F	F	12.0	2.62	0.141
Na	Be	1.0	3.32	0.142
Na	Be	1.0	4.19	0.210
Na	F	3.0	2.22	0.110
Na	F	2.0	3.76	0.236
Na	F	3.0	4.64	0.285
Na	Na	2.0	5.37	0.437
∢ F-Be-F			105.1°	

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