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Structural Analysis of Molten Na_2BeF_4 by X-ray Diffraction †

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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 $\text{MoK}\alpha$ radiation was obtained through the use of a curved graphite crystal mounted in the diffracted beam. Silt system of $1/2^\circ$ - $1/2^\circ$ and 1° - 1° were employed in the low ($3^\circ \leq \theta \leq 10^\circ$) and high angles ($8^\circ \leq \theta \leq 50^\circ$), respectively, where θ is the scattering angle. The scattering intensities were measured over the angular range $3^\circ \leq \theta \leq 50^\circ$ using the step-scanning technique, corresponding to the interval

$0.93 \text{ \AA}^{-1} \leq S \leq 13.55 \text{ \AA}^{-1}$ in the variable

$$S = 4\pi \sin\theta / \lambda, \quad (1)$$

where λ is the wavelength (0.7107 \AA). Several runs were made in order 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 ($10 \mu\text{m}$ thickness) filled He gas. The temperature of the sample was controlled to $650 \pm 10^\circ\text{C}$ 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

$$\begin{aligned} D(r) &= 4\pi r^2 \sum_{i=1}^m \bar{K}_i g_i(r) \\ &= 4\pi r^2 g_0 \sum_{i=1}^m \bar{K}_i + \sum_{i=1}^m (\bar{K}_i)^2 2r / \pi \\ &\quad \int_0^{S_{\max}} Si(S) \sin(Sr) dS, \end{aligned} \quad (2)$$

and

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

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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_0 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

$$G(r) = 1 + \frac{\sum_{i=1}^m (\bar{K}_i)^2}{[\sum_{i=1}^m \bar{K}_i \pi^2 g_0 r]} \int_0^{S_{max}} Si(S) \sin(Sr) dS. \quad (4)$$

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

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

Na ₂ BeF ₄	
temperature (°C)	650 ± 10
density (g/cm ³)	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

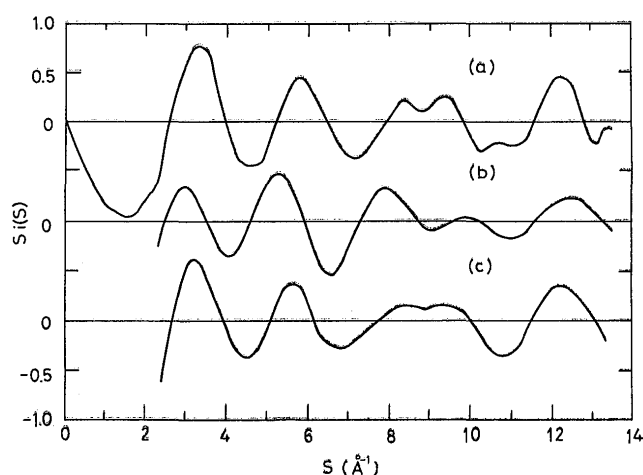


Figure 1. Observed and calculated reduced intensity functions $Si(S)$ of molten Na_2BeF_4 at $650 \pm 10^\circ C$. (a) observed, (b) isolated BeF_4 tetrahedron, (c) model.

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 $r = 1.65 \text{ \AA}$ of these functions corresponds to the Be-F interaction in the BeF_4 tetrahedron. In the crystalline form of Na_2BeF_4 ,⁴ each beryllium atom is tetrahedrally surrounded by four fluorine atoms with the mean Be-F distance of 1.56 \AA and F-F distance of 2.55 \AA . The Be-F distance becomes slightly longer in the melt. The coordination 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 $r = 2.22 \text{ \AA}$ corresponds to the nearest-neighbor Na-F interaction ($r_{Na^+} + r_{F^-} = 2.28 \text{ \AA}$, r_{Na^+} , r_{F^-} : the ionic radii of the Na^+ and F^-). The 3rd peak at $r = 2.62 \text{ \AA}$ corresponds to the F-F distance of the BeF_4 tetrahedron. Separating the 2 and 3rd 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

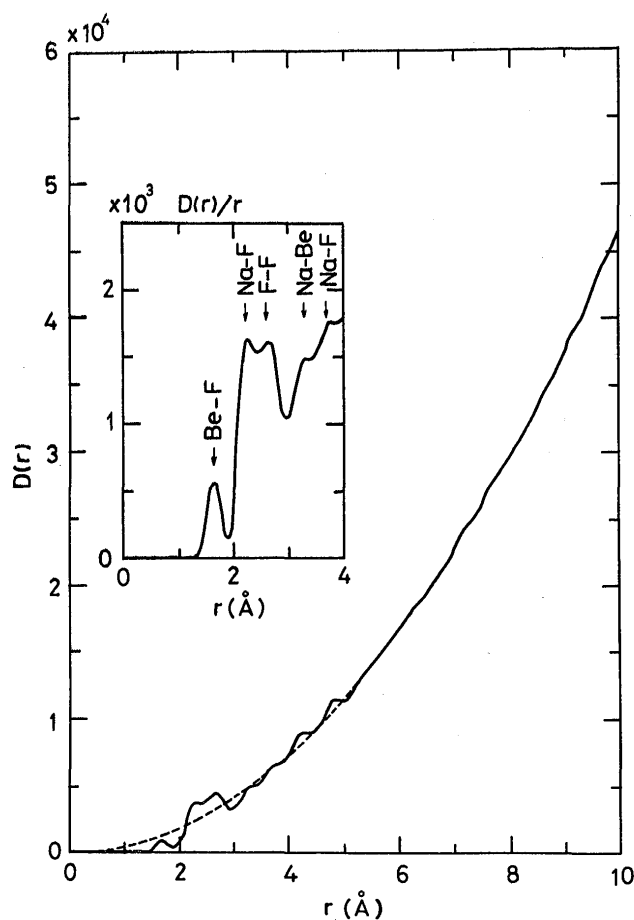


Figure 2. Radial distribution function $D(r)$ and function $D(r)/r$ of molten Na_2BeF_4 at $650 \pm 10^\circ C$.

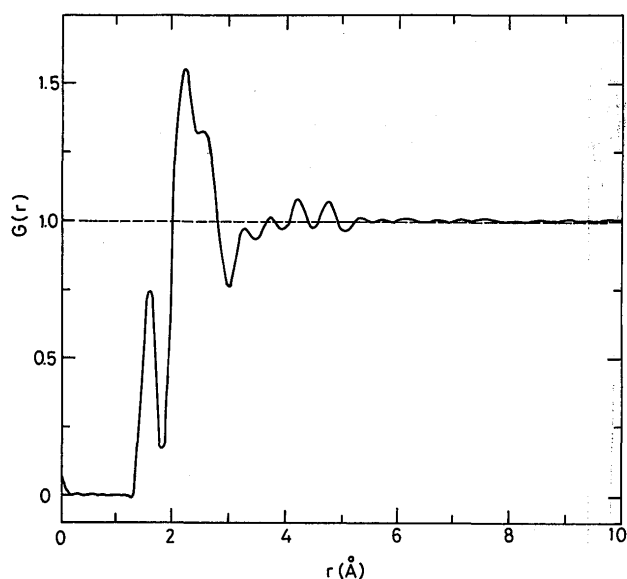


Figure 3. Average correlation function $G(r)$ of molten Na₂BeF₄ at $650 \pm 10^\circ\text{C}$.

the isolated form in molten Na₂BeF₄. The theoretical function $S_i(S)$ can be calculated from the Debye scattering equation⁶⁾ given by the expression.

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

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 $S_i(S)$ for the isolated BeF₄ tetrahedron using equation (5) is shown in Figure 1(b). Comparing Figures 1(a) and (b), the maximum and minimum positions of molten Na₂BeF₄ below values of $S \leq 11 \text{ \AA}^{-1}$ slightly shift toward the higher and lower S region. This behavior results from the effect of the nearest-neighbor sodium atoms around the BeF₄ tetrahedron. We can consider three typical configurations of the sodium atoms around the BeF₄ tetrahedron. One is a configuration that the sodium atom occupies the corner-site of the BeF₄ 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 $S_i(S)$ 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 BeF₄

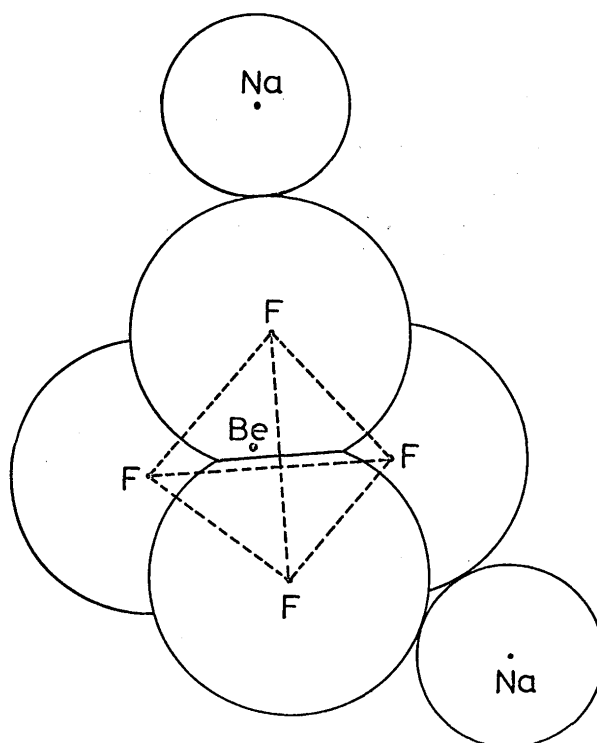


Figure 4. Schematic diagram of model.

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, $\langle \Delta r_{ij}^2 \rangle^{1/2}$.

i	j	N_{ij}	r_{ij} (Å)	$\langle \Delta r_{ij}^2 \rangle^{1/2}$ (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°	

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 $D(r)/r$.

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