X-ray Structural Analysis of Molten LiF – LiCl System

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The short range structures of molten LiF – LiCl (1 : 2) and (1 : 1) mixtures with the common cation were investigated by an X-ray diffraction method and compared with those found in the pure melts and the molten alkali halide mixtures with the common anions. In both the mixtures, the nearest neighbor arrangements of the unlike ion pairs were similar to those in the pure melts. On the other hand, the nearest distances between like ions changed by mixing.

1. Introduction

Lantelme et al. [1] studied the mixing effects in the molten LiCl – KCl over the full composition range and the effect of temperature at the eutectic composition by a molecular dynamics simulation. Changes in the distance between like ions were detected while for unlike ions no changes were found. Okada et al. [2] investigated the dynamics of this system at the eutectic composition by X-ray diffraction analysis and molecular dynamics simulation and obtained similar results. Recently, studies on the structure of molten alkali fluoride mixtures were carried out by Igarashi et al. [3, 4]. In all the mixtures studied, the nearest neighbor structure was found to be almost the same as that in the pure melts. As for mixtures of molten univalent and divalent chlorides, Iwamoto et al. [5] investigated LiCl – $CaCl_2$ by X-ray diffraction analysis. Also in this system the nearest neighbor structure was similar to that of the pure melts.

Similar results may be expected in mixtures with a common cation. In this work, the short range structure of molten LiF – LiCl (1 : 2) and (1 : 1) mixtures, were investigated by X-ray diffraction analysis. LiF – LiCl (1 : 2) is close to eutectic composition.

2. Experimental

LiF and LiCl of analytical reagent grade were dried at 400 °C under reduced pressure for 10 hours. They were mixed to the prescribed composition in an atmosphere of dried N_2 and melted in a platinum crucible. The experimental temperatures were 550 °C for LiF – LiCl (1 : 2) and 620 °C for (1 : 1), respectively.

Prior to the measurements, the moisture was thoroughly removed from the air-tight sample chamber and dried He gas was introduced. The temperature was controlled to a maximum error of 10 °C. The X-ray scattering intensity was measured by a diffractometer having parafocusing reflection geometry of the $\theta - \theta$ type using a Mo Kα beam ($\lambda = 0.7107$ A) monochromatized with a curved graphite crystal. A step-scanning technique for a fixed count was applied. The intensity data were collected for scattering angles of 3° up to 54°.

Corrections for background, polarization, absorption, and Compton radiation were made by the usual methods [6]. The corrected data were scaled to the independent scattering factor [7, 8] of the stoichiometric unit by the combined use of the high angle region method and the Krogh-Moe-Norman method [9, 10]. The reduced intensity function $S \cdot i(S)$ and the correlation function $G(r)$ were calculated by the equations

$$G(r) = 1 + \frac{\sum_m (\bar{K}_m)^2}{2\pi^2 g_0 r} \int_0^{S_{\max}} S \cdot i(S) \sin(rS)\, dS,$$

$$S \cdot i(S) = S\left[I_{\text{eu}}^{\text{coh}}(S) / \sum_m f_m^2(S) - 1\right],$$

$$g_0 = \left(\sum_m \bar{K}_m\right)^2 \varrho_0,$$

and

$$S = 4\pi \sin\theta/\lambda,$$

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Table 1. Parameters used in the calculations of $S \cdot i(S)$ and $G(r)$.

Composition (LiF : LiCl)	1 : 1	1 : 2
Temperature/°C	550	620
Density [11]/g cm^{-3}	1.5897	1.6073
Effective electron number		
$\bar{K}_{\mathrm{Li}}$	2.3096	2.3769
$\bar{K}_{\mathrm{F}}$	7.7135	7.9361
$\bar{K}_{\mathrm{Cl}}$	18.6781	19.9361
$S_{\max}$/Å^{-1}	14.3	14.3
ϱ_0/Å^{-3}	0.00865	0.01418

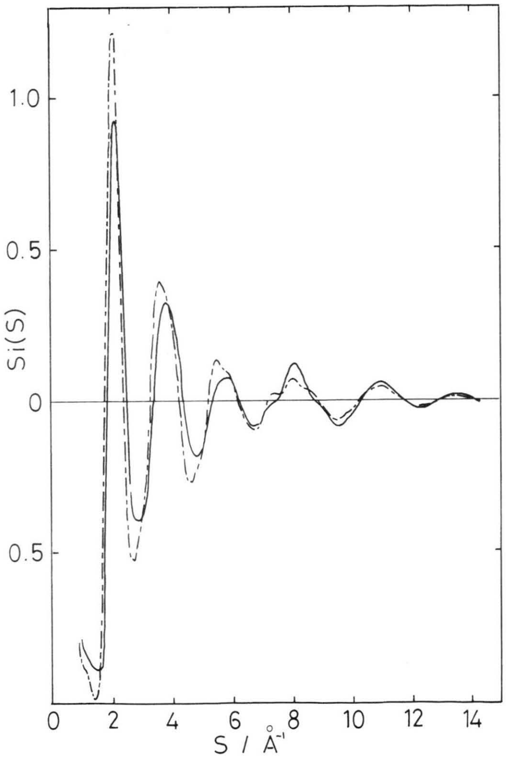

Fig. 1. The reduced intensity functions $S \cdot i(S)$ for LiF–LiCl (1:1): solid line, and (1:2): dash dotted line.

where ϱ_0 is the number of stoichiometric units per A^{-3}, $\bar{K}_m$ the effective electron number in the atom m, f_m the independent scattering intensity, $I_{\mathrm{eu}}^{\mathrm{coh}}(S)$ the total coherent intensity, and $S_{\max}$ the maximum value of S reached in the experiment. The parameters used in the calculations are listed in Table 1 [11].

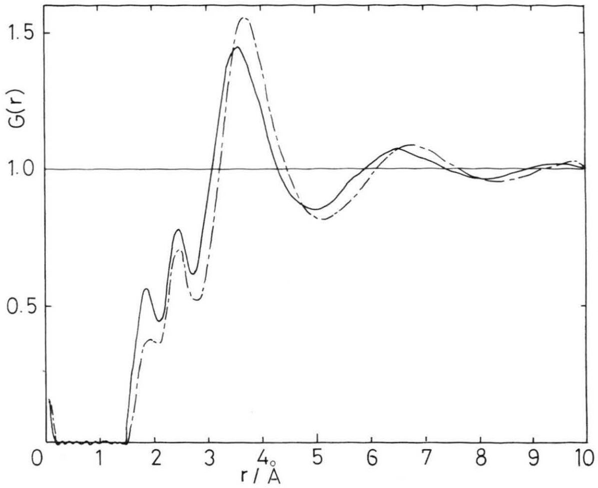

Fig. 2. The correlation functions $G(r)$ for LiF–LiCl (1:1): solid line, and (1:2): dash dotted line.

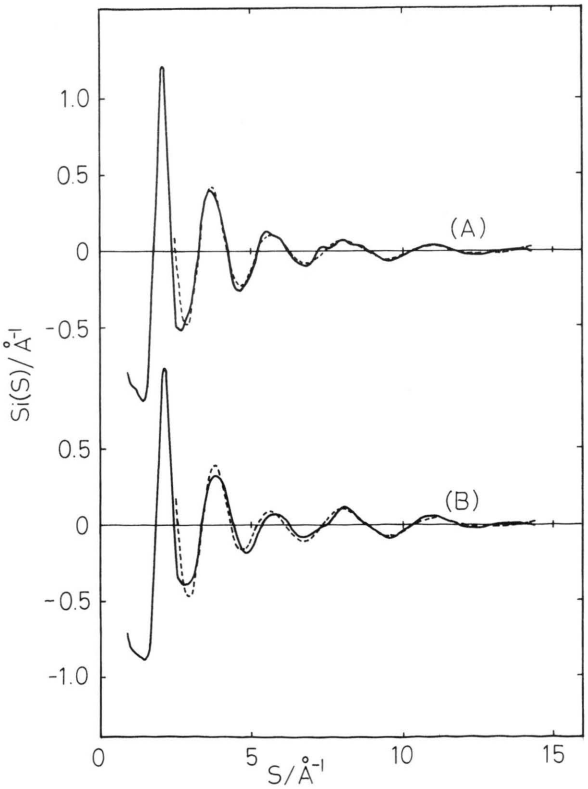

Fig. 3. The observed (solid line) and the calculated (dotted line) reduced intensity functions $S \cdot i(S)$. (A) LiF–LiCl (1:2) system; (B) LiF–LiCl (1:1) system.

Table 2. System LiF – LiCl. Coordination numbers n_{ik}, the number of interactions N_{ik}, the average distances r_{ik} (in Å), and the associated root mean square displacements $\langle \Delta r_{ik}^2 \rangle^{1/2}$ of the $i-k$ ion pair.

	LiF – LiCl (1:1)			LiF – LiCl (1:2)		
$i-k$	N_{ik} (n_{ik})	r_{ik}	$\langle \Delta r_{ik}^2 \rangle^{1/2}$	N_{ik} (n_{ik})	r_{ik}	$\langle \Delta r_{ik}^2 \rangle^{1/2}$
Li^+-F^-	6.3 (3.2)	1.83	0.13	6.6 (3.3)	1.84	0.10
Li^+-Cl^-	8.6 (4.3)	2.41	0.22	16.7 (4.2)	2.44	0.24
Cl^--Cl^-	5.1 (5.1)	3.76	0.53	14.5 (7.3)	3.79	0.51
Cl^--F^-	7.8 (3.9)	3.33	0.43	8.4 (2.1)	3.35	0.40

Table 3. The average distances (in Å) and the coordination numbers for the molten alkali halide pure and mixture melts.

	Li^+-F^-		Li^+-Cl^-		Cl^--Cl^-			
	n_{ik}	r_{ik}	n_{ik}	r_{ik}	r_{ik}	Temp./° C	Ref.	
LiF – LiCl (1:1)	3.2	1.83	4.3	2.41	3.76	550		(X)[b]
LiF – LiCl (1:2)	3.3	1.84	4.2	2.44	3.79	620		(X)
LiF – NaF (3:2)	3.0	1.84				690	[3, 4]	(X)
LiF – KF (1:1)	3.0	1.85				545	[3, 4]	(X)
LiF – NaF – KF[a]	3.3	1.83				520	[16]	(X)
LiF	3.0	1.85				875	[13]	(X)
LiCl – KCl[a]			4.0	2.38	3.56	395	[2]	(X)
LiCl – $CaCl_2$ (2:1)			4.0	2.45	3.75	570	[5]	(X)
LiCl – $CaCl_2$ (1:1)			4.0	2.45	3.70	607	[5]	(X)
LiCl			4.0	2.47	3.85		[14]	(X)
^{7}LiCl			3.5	2.45	3.80		[14]	(N)
LiCl			4.0	2.40	3.86	650	[15]	(X)

[a] The data observed at the eutectic composition.

[b] X in parenthesis represents X-ray diffraction; N, neutron diffraction.

3. Results and Discussion

The reduced intensity functions $S \cdot i(S)$ and the correlation functions $G(r)$ for both mixtures are shown in Figs. 1 and 2, respectively. In both mixtures, $G(r)$ has the first and second peaks at 1.85 and 2.45 Å, respectively. The third peak was observed at 3.55 Å for LiF – LiCl (1:1), and at 3.75 Å for the (1:2) mixture. Further on the phases of $G(r)$ clearly differed.

The peak at 1.85 Å is to be assigned to the nearest neighbor Li^+-F^- interaction. As expected, this peak is higher for the LiF – LiCl (1:1) mixture than for the (1:2) mixture. The peak at 2.45 Å seems to be due to the Li^+-Cl^- interaction. Contrary to the expectation, also this peak is higher for the LiF – LiCl (1:1) mixture than for the (1:2) mixture. The third peaks appear to be due to Cl^--Cl^-, Cl^--F^-, F^--F^- and Li^+-Li^+ pairs.

The average distance and the number of interactions were derived from the following equation reported by Narten et al. [12]:

$$S \cdot i(S) \left[\sum_{i=1}^{m} f_i^2(S) \right] = \sum_{i=1}^{m} \sum_{k} [N_{ik} \exp(-b_{ik} S^2) \cdot f_i(S) f_k(S) \sin(S r_{ik})]/r_{ik},$$

where N_{ik} represents the number of interaction, r_{ik} the average distance between ions i and k, and b_{ik} the temperature factor. The structural parameters are obtained by the least squares method using the observed $S \cdot i(S)$ curves beyond $S = 3.0$ Å^{-1}, and are listed in Table 2. The nearest neighbor distances and coordination numbers of the Li^+-F^- and Li^+-Cl^- pairs were almost the same in both mixtures. Similarly, the nearest neighbor distances and the number of the Cl^--F^- pairs were almost the same in both the mixtures. On the other hand, for the Cl^--Cl^- ion pairs the distances were the same but the numbers of interactions differed largely. Thus the shift to the long distance side of the third peak for the (1:2) mixture compared to (1:1) mixture is attributable to the increased number of Cl^--Cl^- pairs with the average distance 3.79 Å as compared to 3.35 Å for Cl^--F^- pairs. The observed and the calculated $S \cdot i(S)$ are shown in Figure 3.

The results obtained in this work were compared with previous experimental values obtained by diffraction analysis [2–5, 13–15]. They are summarized in Table 3. The nearest distances of the unlike pairs are found to be similar in all the systems, whether pure or mixed. But those found in the present work for the Cl^--Cl^- ion pairs are slightly shorter than those in the pure melts as well as those in the mixtures with common anions.

The molar volume is relatively sensitive to the structure of a melt. Generally, the melt contracts with decrease of temperature. Lantelme et al. [1] reported that the contraction of melt at low temperature induces a decrease of the distances of the like ion pairs. The results obtained in this work support this statement, i.e. the decrease of the second interionic distance seems to be caused by the decrease of the molar volume.

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