XAFS Study of Molten $ZrCl_4$ in LiCl-KCl Eutectic

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The local structure of motlen $ZrCl_4$ in LiCl-KCl eutectic was investigated by using an X-ray absorption fine structure (XAFS) of the Zr K-absorption edge. The nearest $Zr^{4+}–Cl^{-}$ distance and coordination number from the curve fitting analysis were (2.51 ± 0.02) Å and 5.9 ± 0.6, respectively. These suggest that a 6-fold coordination $(ZrCl_6)^{2-}$ is predominant in the molten mixture.

Key words: XAFS; Molten Salt; Zirconium Tetrachloride; Coordination.

1. Introduction

The structure of trivalent halide (MX_3) melts has been widely investigated by various experimental and theoretical techniques [1–4]. They show that the structure of trihalide melts cannot be modeled properly by simple schemes as used in alkali halide melts. For example, a stable octahedral complex $(MX_6)^{3-}$ was proposed for molten rare earth trichlorides by Raman spectroscopic studies [1]. An FSDP (first sharp diffraction peak) corresponding to medium ranged structural order (MRO) was detected in the diffraction studies of some trichloride melts [3]. They are not generally observed in molten alkali halides. We have thought that the transport properties of trihalide melts are much affected by the complex ion and the MRO. Also in the thermodynamic properties it has been considered that some results (for example on the mixing enthalpy of lanthanide and alkali chloride binary systems) are closely related to the structural features of the trihalide melts [5]. In computer simulations, the rigid ion model [6, 7] does not give good results for molten rare earth trihalides, though it has been effective for the molten alkali halides. We have to use another model (the polarizable ion model [4] is successful for many trihalide systems). We can suppose that the structure and physical properties of tetravalent melts are more complicated than those of trihalide melts. Zirconium tetrachloride $ZrCl_4$ is a typical tetravalent chloride. It is an important material also in pyrochemical processes of spent nuclear fuel [8]. Some physical properties, such as vapor pressure, surface tension and viscosity were reported by Nisel’son et al. [9]. Photiadis and Papatheodorou [10] have studies the structure of this melt by of Raman scattering. In the present work we measured the Zr K-edge XAFS of molten $ZrCl_4$ with LiCl-KCl eutectic (LiCl : KCl = 58.8 : 41.2 mol%) to obtain more real space structural information.

2. Experimental

The $ZrCl_4$ sample (Aldrich 99.9% purity) was dried at 400 K under reduced pressure to avoid moisture. Then the prescribed $ZrCl_4$ (20% for LiCl-KCl eutectic) was mixed with the LiCl-KCl eutectic at 700 K. During the mixing process, some of the $ZrCl_4$ was lost by sublimation. We estimated that the final content was 12% $ZrCl_4$ by weighing the sublimed portion.

The XAFS measurement in transmission geometry was carried out at the BL27B beamline of the High Energy Acceralation Research Organization (KEK), Tsukuba, Japan, where a continuous X-ray beam from 5 to 20 keV is available. The K absorption edge of Zr (E_0 = 17.999 keV) was used to obtain the XAFS spectrum. Details of the measurement system, such as electric furnace and quartz cell, are described in [11]. The sample was sealed in the quartz cell under high vacuum. The cell is designed to obtain a thin liquid film (0.2 mm thickness) for the XAFS measurement based on transmission geometry. The XAFS spectrum data were collected in an energetic range from 17.6 to 18.7 keV at 723 K. The XAFS spectra were analyzed by using the WinXAS2.1 code developed by Ressler [12].

The following standard XAFS equation was used in the curve fitting:

$$\chi(k) = \sum_j N_j S_j(k) F_j(k) \exp(-2\sigma_j^2 k^2) \cdot \exp(-2r_j/\lambda) \sin(2kr_j + \phi_j(k))/(kr_j^2), \quad (1)$$

where $F_j(k)$ is the backscattering amplitude function from each of the N_j neighboring ions j in an averaged distance r_j with mean-square displacement σ_j^2, $\phi_j(\boldsymbol{k})$ is the total phase shift from both the central absorber and the neighboring scatterer, and λ is the photoelectron mean free path. The three parameters $F_j(k)$, $\phi_j(k)$ and λ were evaluated by using the FEFF7 code [13]. The photoelectron wave vector k is defined by

$$k = \sqrt{2m_e(E - E_0)/h}, \quad (2)$$

where E_0 is the threshold energy. It was determined by the peak top of the 1st derivative of the spectra at the absorption edge. The coordination number N_j, interionic distance r_j, and Debye-Waller factor σ_j^2 for the central Zr^{4+} ion was obtained by the curve fitting. Details of the data analysis are summarized in [14].

3. Results and Discussions

The raw absorption spectrum of molten 12% ZrCl$_4$-(LiCl-KCl eutectic) is shown in Fig. 1, together with that of solid ZrCl$_4$. The extracted XAFS function $k^3\chi(k)$ and the fourier transform magnitude |FT| are shown in Figs. 2(a) and (b). It can be seen that the oscillation of the $k^3\chi(k)$ function and peak height of |FT| for the solid ZrCl$_4$ is smaller than those for the melt. This is very strange, since the structural ordering in melts is usually lower than that in solids. Generally, the coordination number decreases and the Debye-Waller factor (sometimes called temperature factor in diffraction studies) increases by melting. The strange result is due to the peculiarity of the crystal structure of ZrCl$_4$. According to the report by Krebs [15], the 6-fold coordinate (ZrCl$_6$)$^{2-}$ connects in the form of a zigzag chain with the next coordinate in the solid state. There are three distinct nearest Zr^{4+}–Cl$^-$ correlations. The distances are 2.307 Å, 2.498 Å and 2.655 Å, respectively. The difference between them reaches 0.348 Å.

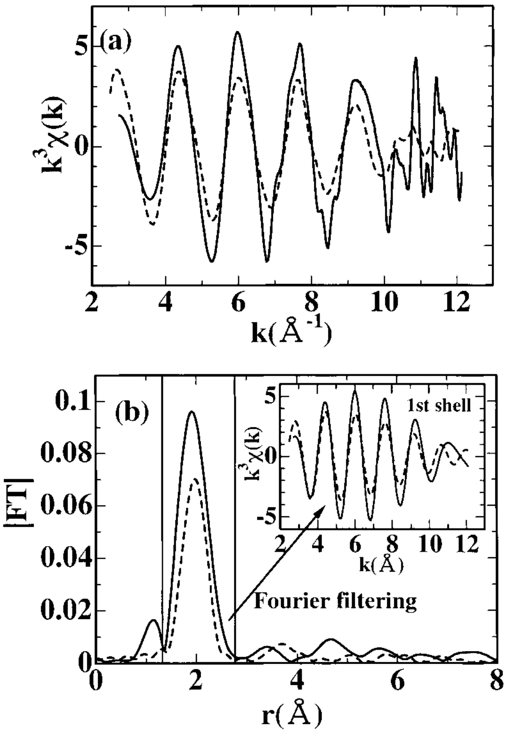

Fig. 2. (a) Zr K-edge XAFS function $k^3\chi(k)$ and (b) Fourier transform |FT| of solid ZrCl$_4$ (solid line) and molten 12% ZrCl$_4$-(LiCl-KCl eutectic) (dashed line). Insert in (b) shows the 1st shell (Zr^{4+}–Cl$^-$) $k^3\chi(k)$ component calculated by fourier filtering.

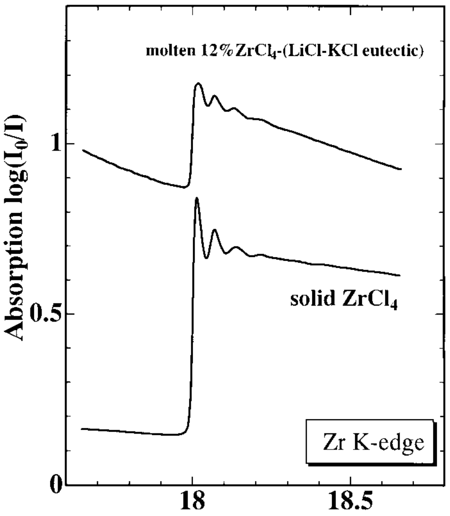

Fig. 1. Raw XAFS spectra of solid ZrCl$_4$ and molten 12% ZrCl$_4$-(LiCl-KCl eutectic).

The structural parameters from the curve fitting are listed in Table 1. The fitting results are shown in Fig. 3 for the solid ZrCl$_4$ and Fig. 4 for the melt. In the solid

Table 1. Structural parameters: coordination number N, interionic distance r, Debye-waller factor σ^2 in solid $ZrCl_4$ and molten 12% $ZrCl_4$-(LiCl-KCl eutectic) based on Zr K absorption edge.

(a) solid $ZrCl_4$

	N	r(Å)	σ^2(Å^2)	Residual
Zr^{4+}–Cl^-	2.0 (fix)	2.307 (fix)	0.0043±0.0004	27.94
Zr^{4+}–Cl^-	2.0 (fix)	2.498 (fix)	0.0046±0.0004	
Zr^{4+}–Cl^-	2.0 (fix)	2.655 (fix)	0.0049±0.0004	
Zr^{4+}–Zr^{4+}	2.0 (fix)	3.962 (fix)	0.0132±0.0017	

(fix): parameter was fixed in the curve fitting procedure. Residual is defined by

$$R = \sum_{i=1}^{N} |k^3\chi_{\rm exp}(k) - k^3\chi_{\rm cal}(k)| / \sum_{i=1}^{N} |k^3\chi_{\rm exp}(k)|,$$

where the letters 'exp' and 'cal' correspond to experimental and calculational

(b) molten 12% $ZrCl_4$-(LiCl-KCl eutectic)

	N_{Cl}	r(Å)	σ^2(Å^2)	Residual
Zr^{4+}–CL^-	5.9±0.6	2.51±0.02	0.0105±0.0013	4.54

data, the coordination number and interionic distance were fixed at the fitting procedure. The 1st peak in the |FT| function was nicely reproduced by using the three kinds of correlations. The weak 2nd peak observed around 3.7 Å is assigned to be the 1st Zr^{4+}–Zr^{4+} correlation. The distance and coordination number for the nearest Zr^{4+}–Cl^- correlation in the melt were (2.51±0.02) Å and 5.9±0.6, respectively. The 1st peak of the |FT| for the mixture melt was fitted nicely with a single correlation as shown in the Fig. 4(b) and the Table 1(b). The nearest distance is almost the same as the sum of the ionic radii: 0.71 Å for 6-fold Zr^{4+} and 1.81 Å for Cl^-. It is concluded that the local coordination around the Zr^{4+} ion in the 12% $ZrCl_4$-(LiCl-KCl eutectic) is 6-fold. This result is compatible with the Raman study [10].

4. Conclusion

The local structure around Zr^{4+} ion in 12% $ZrCl_4$-(LiCl-KCl eutectic) was investigated by the Zr K-edge

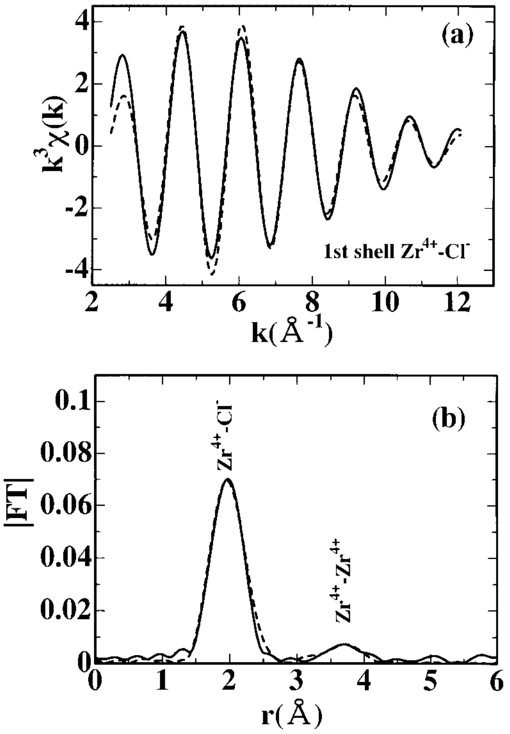

Fig. 3. Curve fitting results in (a) k-space and (b) R-space for solid $ZrCl_4$.

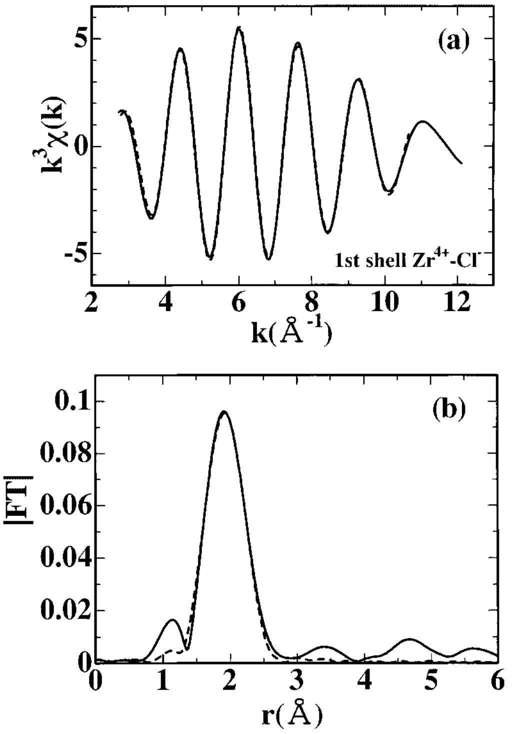

Fig. 4. Curve fitting results in (a) k-space and (b) R-space for molten 12% $ZrCl_4$-(LiCl-KCl eutectic).

XAFS measurement. The |FT| function in the melt shows higher structural ordering than in the solid $ZrCl_4$. The curve fitting result suggests 6-fold coordination in the melt.

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