

X-ray absorption study of molten uranium chloride system

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The local structure of molten UCl_3 in LiCl-KCl eutectic was studied by using a high-temperature X-ray absorption fine structure (XAFS) technique. The coordination behavior of Cl^- ion around U^{3+} ion was investigated by XAFS of the U L_{III} -absorption edge. The distance and the coordination number of the 1st $\text{U}^{3+}\text{-Cl}^-$ correlation were $2.82 \pm 0.1 \text{ \AA}$ and 7.3 ± 0.6 , respectively. It is concluded that the uranium ion has trivalent state in the melt by comparing with the XANES spectra of tetravalent uranium compounds and solid UCl_3 .

KEYWORDS: XAFS, molten salt, molecular dynamics, local structure, uranium chloride

I. Introduction

We reported¹⁾ the result of high-temperature X-ray diffraction (XRD) of molten UCl_3 . It was concluded that U^{3+} ion was surrounded by six Cl^- ions with distance $2.84 \text{ \AA}$. This is very similar to the molten structure of rare earth trichloride. We confirmed that structural parameters derived from the XRD of molten UCl_3 were almost the same as those of molten LaCl_3 . Recently, it has been reported by neutron diffraction (ND)²⁻⁴⁾ and molecular dynamics (MD)⁵⁾ simulation that coordination number of Cl^- ion around a metal ion in some molten rare earth trichlorides is larger than 6. The coordination number in molten LaCl_3 was 8.2 in the ND and 7.9 in the MD simulation. This is not compatible with our XRD result of molten UCl_3 . We have thought that it is difficult to determine the coordination number in the pure trichloride melts, since a boarder between the 1st and the 2nd correlation is not clear. For example, 6-fold octahedral coordinate $(\text{YCl}_6)^{3-}$ in the pure YCl_3 melt is not stable. It is stabilized by adding alkali chloride⁶⁾. We observed change in the nearest $\text{Y}^{3+}\text{-Cl}^-$ correlation using the Y K-edge XAFS measurement of molten YCl_3 -alkali chloride mixture systems⁷⁾. In the present work, high-temperature XAFS measurement of molten UCl_3 in LiCl-KCl eutectic was carried out to study coordination behavior of Cl^- ion around U^{3+} .

II. Experimental and MD simulation

The preparation of UCl_3 sample is described in ref.1). Eutectic $\text{LiCl-41\%KCl}$ (99.99% purity, APL Engineered Materials, Inc.) was dried under high vacuum at 473K for two days. The $15\%\text{UCl}_3$ -(eutectic LiCl-KCl) sample was prepared by melting in a quartz vessel at 873K . The XAFS measurements using a transmission technique were carried out at BL27B (X-ray ranging from 5 to 20keV) of the Photon Factory in the Institute of Materials Structure Science of the High Energy Accelerator Research Organization in Tsukuba, Japan. The ring energy was 2.5GeV and the current during the experiments was ranging

from 250 to 400mA . The radiation was monochromatized by a $\text{Si}(111)$ double-crystal. XAFS measurements based on the U L_{III} -absorption edge ($E_0=17.167\text{keV}$) were performed for molten $15\%\text{UCl}_3\text{-(LiCl-KCl eutectic)}$ at 823K . The XAFS measurement system for high-temperature liquid is reported in ref.8). The WinXAS program ver.2.1⁹⁾ was used in the XAFS data analysis. The curve fitting including 3rd cumulant was performed in the program. The phase shift and the backscattering amplitude in the curve fitting process were obtained by using the FEFF8 code.¹⁰⁾ The liquid structure for the input data in the FEFF computation was based on results of the molecular dynamics simulation.

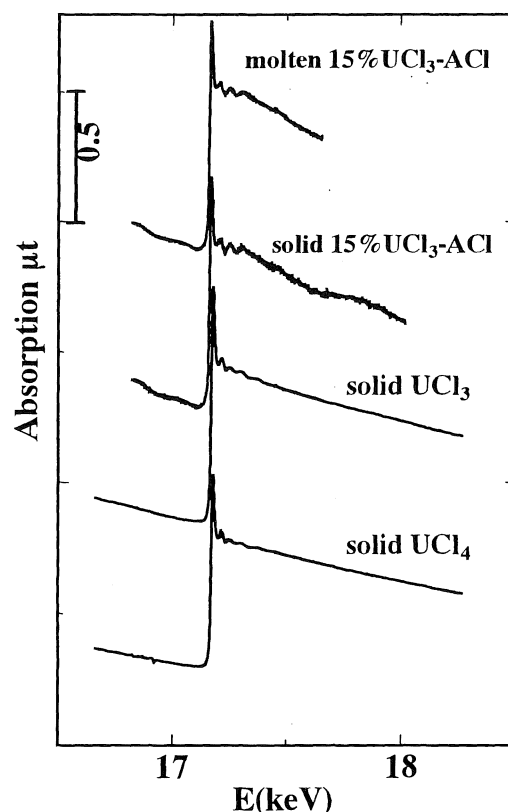


Fig.1 U L_{III} -edge XAFS spectra of molten UCl_3 systems, with solid uranium chlorides

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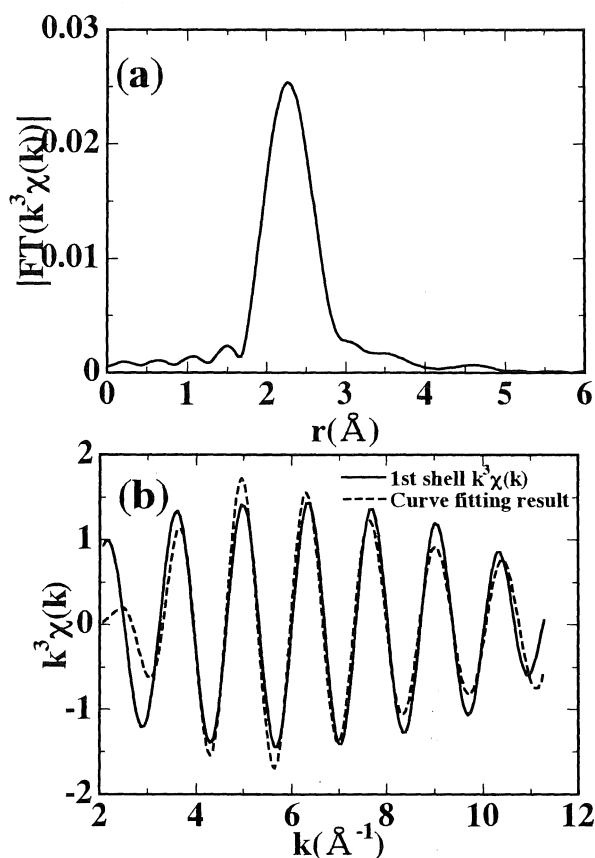


Fig.2 (a) Fourier transform magnitude $|FT(k^3\chi(k))|$ and (b) 1st shell $k^3\chi(k)$ function of molten 15% UCl_3 -(LiCl-KCl eutectic)

Table 1 Structural parameters of molten 15% UCl_3 -(LiCl-KCl eutectic) from the curve fitting analysis

Coordination number	7.3 ± 0.6
distance	$2.82 \text{ \AA} \pm 0.01$
Debye-Waller factor	$0.02699 \text{ \AA}^2 \pm 0.00046$
3rd Cumulant	$(0.922 \pm 0.121) \times 10^{-3} \text{ \AA}^3$

III. Results and discussions

The raw EXAFS spectrum of molten 15% UCl_3 -(LiCl-KCl eutectic) is shown in Fig.1, together with those of the solid compounds. The fourier transform magnitude $|FT(k^3\chi(k))|$ of the molten 15% UCl_3 system is shown in Fig.2(a). Only a peak corresponding to the nearest U^{3+} -Cl interaction was observed in the $|FT|$. The $k^3\chi(k)$ function for the 1st coordination shell was obtained by filtering the FT from $r=1.6 \text{ \AA}$ to $3.0 \text{ \AA}$. It is shown in Fig.2(b), together with a

curve fitting result (dashed curve in the figure). Structural parameters obtained from the fitting are listed in Table 1. The nearest U^{3+} -Cl distance $2.82 \text{ \AA}$ is close to the XRD result¹⁾ and shorter than that of solid UCl_3 . It suggests that the coordination environment around U^{3+} ion does not change drastically by mixing with alkali chlorides. The coordination number of Cl⁻ ion around U^{3+} was 7.3 ± 0.6 . This is slightly larger than 6 expected in the octahedral coordinate similarly in the ND and the MD results of molten LaCl_3 .

The coordination number of the nearest correlation in molten rare earth trichlorides has been in confusion. For example, the coordination number in molten YCl_3 is about 6 from the XRD¹¹⁾, the ND¹²⁾ and the Raman⁶⁾ studies. On the other hand, that in molten LaCl_3 is about 6 from the XRD¹¹⁾ and the Raman¹³⁾ studies, but is larger than 7 from the ND²⁾ and the MD⁵⁾ studies. It is difficult to determine a coordination number in molten salt systems, since a boarder between the 1st and the 2nd coordination shell is not clear in many systems. The partial correlation function $G_{\text{U-Cl}}(r)$ calculated from the MD simulation is shown in Fig.3. The boarder is not clear, because the minimum between the 1st and 2nd peak is not zero. It means that the fourier filtering of the 1st coordination shell in the XAFS data analysis is questionable for molten salt systems. The curve fitting method, which is most popular analytical technique in the XAFS study, should not be used for molten salt system. In the present study, we used a new technique in the XAFS data analysis. We have used the MD technique in

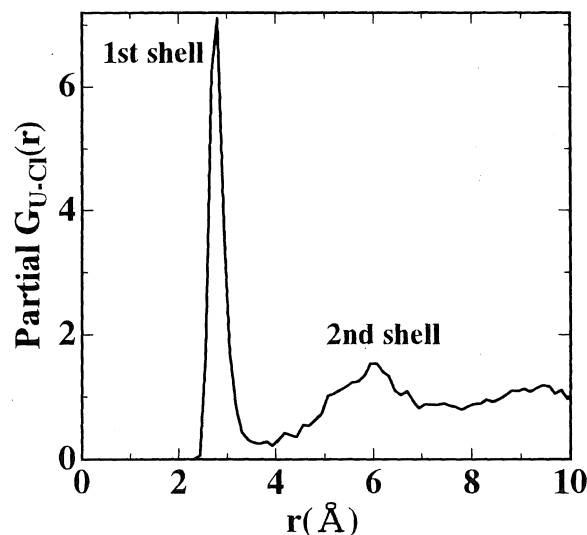


Fig.3 Partial correlation function $G_{\text{U-Cl}}(r)$ of molten UCl_3 by molecular dynamics simulation (It is difficult to separate precisely the 1st shell from the 2nd shell.)

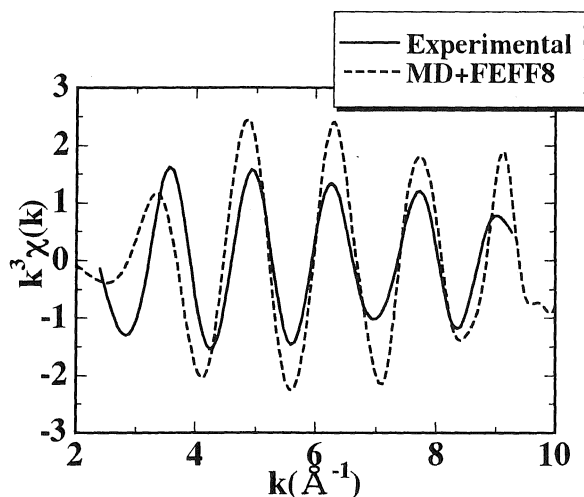


Fig.4 The MD+FEFF8 computation results for XAFS function $k^3\chi(k)$ of the molten UCl_3 system

the molten salt study^{14,15}. Output information in the MD simulation is atomic configuration. Input information in the FEFF computation is basically atomic configuration. We used the output in the MD simulation as the input data in the FEFF computation. It was assumed that fluctuation is supplied by accumulating the FEFF computations (it corresponds to MD step number). We confirmed that FEFF computations averaging more than 1000 gave a convergent XAFS function. Parameters used in the MD simulation are described in ref.1). We confirmed that the simulation gave good agreement with the XRD result. The XAFS function calculated from 2500 FEFF computations is shown in Fig.4. The phase amplitude was overestimated in the simulation, though the phase is in good agreement. The disagreement is due to the potential parameters. It is thought that this procedure is effective in the XAFS data analysis of the high-temperature liquids like molten salts.

The XANES spectra for molten 15% UCl_3 system and other uranium compounds are shown in Fig.5. As observed in the solid compounds, a white line of trivalent UCl_3 shows a peak at lower energy by 3-4eV than those of tetravalent compounds. In the mixture melt, the peak position is almost same as that of UCl_3 . It is concluded that valence of uranium is trivalent in the melt.

IV. Conclusion

The high-temperature XAFS measurement of molten 15% UCl_3 -(LiCl-KCl eutectic) system was carried out to investigate local structure and valence state of U^{3+} ion. The nearest U^{3+} -Cl⁻ distance 2.82 Å is close to the XRD result. The coordination number of Cl⁻ ions around U^{3+} was 7.3. It is larger than the XRD result. The XAFS function was

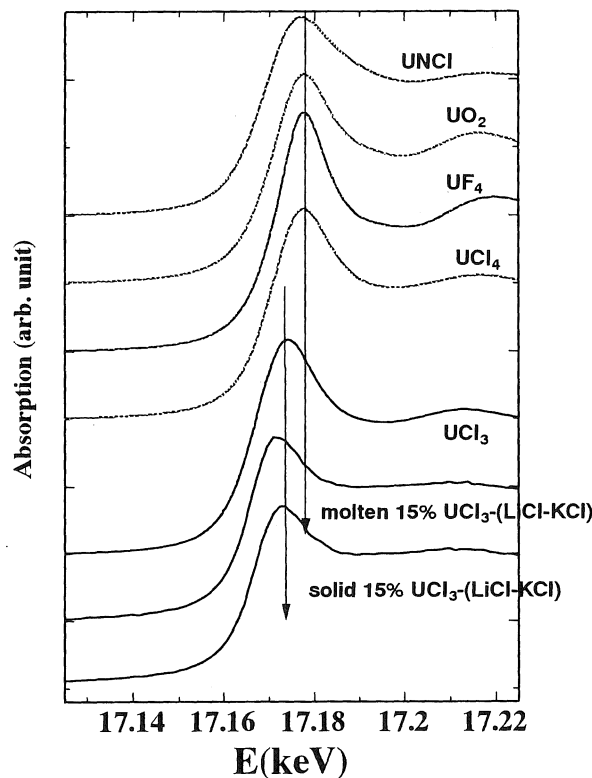


Fig.5 XANES spectra of the molten UCl_3 system, together with some solid uranium chlorides

reproduced by the combined use of the MD and the FEFF computations. We showed that the MD-FEFF analysis is useful in the high-temperature XAFS analysis. It was confirmed by the XANES analysis that uranium ion has trivalent state in the mixture melt.

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