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Structure and dynamic properties of molten uranium trichloride

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Abstract

High temperature X-ray diffraction analysis was performed to study structure of molten UCl_3. The nearest neighbor distance and coordination number of U–Cl pair were 0.284 nm and 6, respectively. Short range structure of molten UCl_3 is described as octahedral coordination where six Cl^- ions surrounds U^{3+} ion. The obtained structural data were analyzed by using a Debye scattering equation and a molecular dynamics (MD) simulation. Dynamic properties such as shear viscosity and electrical conductivity calculated from structurally optimized MD simulation were compared with the experimental data in the literature. © 1998 Elsevier Science S.A.

Keywords: Molten uranium trichloride; High temperature X-ray diffraction; Molecular dynamics simulation

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1. Introduction

Recently, molten salt technology has been widely tested in the field of nuclear fuel cycle using pyrochemistry [1] and the transmutation process of minor actinides with a proton accelerator [2]. Physical and chemical properties of molten salts, especially of molten actinide chlorides, are important in developing the above processes.

Uranium trichloride is one of the typical compounds in the pyrochemical process. Molar volume and some dynamic properties of molten UCl_3 have been studied by Desyatnik et al. [3,4]. Recently, heat of fusion and infrared spectra were measured by Kovacs et al. [5]. Little information on liquid structure, however, is known for molten UCl_3. In the present work, structure of molten UCl_3 was investigated by high-temperature X-ray diffraction measurements and a molecular dynamics (MD) simulation. In addition, thermodynamic and dynamic properties were calculated based on the MD simulation thus structurally optimized.

2. Experimental

The preparation of UCl_3 sample is described elsewhere [6]. High-temperature X-ray diffraction (XRD) measurement of molten UCl_3 was performed by using a diffractometer (Rigaku RINT2500TR) with a curved graphite monochromator and scintillation counter. The sample was sealed in a quartz cell (0.5 mm thickness) with evacuation. The Mo K_α radiation (0.071069 nm wavelength) at 12.5 kW (50 kV–250 mA) was used to obtain the XRD pattern. Data were accumulated at 1200 K by step scanning. Measurement was terminated after 10 h where the reaction of the quartz cell with the melt became visually noticeable. Then only the data obtained at the first step scanning was used in the structural analysis in order to avoid effects of the reaction.

The obtained diffraction data were corrected and normalized to calculate the reduced intensity function $Qi(Q)$ and the radial distribution function $G(r)$ [7]. Comparative measurement of molten $LaCl_3$ was carried out under the same temperature. Molten structures of molten $LaCl_3$ and some other rare earth trichlorides were reported by Mochinaga et al. [7].

3. Molecular dynamics simulation [8]

Molecular dynamics (MD) simulation was performed by using 1000 particle system (U:250 and Cl:750). Pair potential used in the simulation is a combination of the ionic Busing-type potential and the covalent Morse potential as follows,

$$\phi_{ij}(r) = \frac{n_1^2 z_i z_j e^2}{r} + n_2 b(f_i + f_j)\exp\left[\frac{\sigma_i + \sigma_j - r}{f_i + f_j}\right] + D_{\mathrm{M}}\{\exp[-2\alpha(r - r_0)] - 2\exp[-\alpha(r - r_0)]\} \quad (1)$$

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Table 1
Pair potential parameters used in the simulation

(a) Busing-type potential

Parameter	U	Cl
z_i	+3	−1
f_i (nm)	0.0110	0.0238
σ_i (nm)	0.1435	0.1710
b (J m^{-1})	1.153×10^{-9}	

(b) Morse potential (including calculated values of ν_1 Raman mode and 1st peak of $g_{\mathrm{U-Cl}}(r)$)

Ionicity	D_M (eV)	α (nm^{-1})	r_0 (nm)	ν_1 (cm^{-1})	$r_{\mathrm{U-Cl}}$ (nm)
100%	0.0	12.1	0.241	242.40	0.265
90%	0.289	↓	↓	243.73	0.270
80%	0.589	↓	↓	243.39	0.274
70%	0.675	↓	↓	244.75	0.280
60%	0.813	↓	↓	244.53	0.282
50%	1.003	↓	↓	243.39	0.282

where z_i, σ_i and f_i are electric charge, size parameter and repulsion constant of ion i, respectively. Parameter b is a constant. The n_1 means ionicity in the melts. On the other hand, n_2 represents adjustable parameter of the repulsion term. In the present study, $n_1=n_2$ was assumed for simplicity. In the third term of Eq. (1) corresponding to the Morse potential, D_M, α and r_0 are dissociation energy, sharpness and equilibrium distance of covalent bonding. The Morse potential was applied only to the nearest neighbor U–Cl pair. In the fully ionic model, $n_1=n_2=1.0$ and D_M was zero. Parameters for the fully ionic model and the partially ionic models (90%–50%) are listed in Table 1. Raman frequency of $\nu_1(A_{1g})$ mode calculated from the General Valence Force Fields (GVFF) model [9] and the nearest U–Cl distance obtained from the MD simulation were also listed in Table 1.

Thermodynamic and structural properties were obtained by calculating for 50 000 steps. The dynamic properties were calculated by Kubo-type formula [10] from 200 000 steps data. Step width in the simulation was 2.0 fs.

4. Results and discussion

4.1. X-ray diffraction analysis of molten UCl_3

X-ray diffraction pattern of molten UCl_3 is shown in Fig. 1 as a solid line. A first sharp diffraction peak (FSDP) was found at $Q=15$ nm^{-1} with a strong intensity. The FSDP suggests that there is a medium range order in the melts [11]. The $G(r)$ is shown in Fig. 2 as a solid line. The first peak at 0.284 nm corresponds to the nearest U–Cl interaction. Coordination number of Cl^- ions around U^{3+} ion was calculated to be ca. 6 based on the assumption the coordination shells are symmetric about the maximum in the function $r\cdot G(r)$ [7]. It suggests that there is an octahedral coordination in molten UCl_3 similar to many rare earth trichlorides [7]. In comparison with crystalline UCl_3 [12], the distance is slightly shorter and the coordination number decreases from 9 to 6 by melting. The Cl–Cl interaction does not have a peak, since its contribution is extremely small due to low atomic number. A broadened peak at 0.525 nm is assigned to the second neighbor U–U and U–Cl interactions.

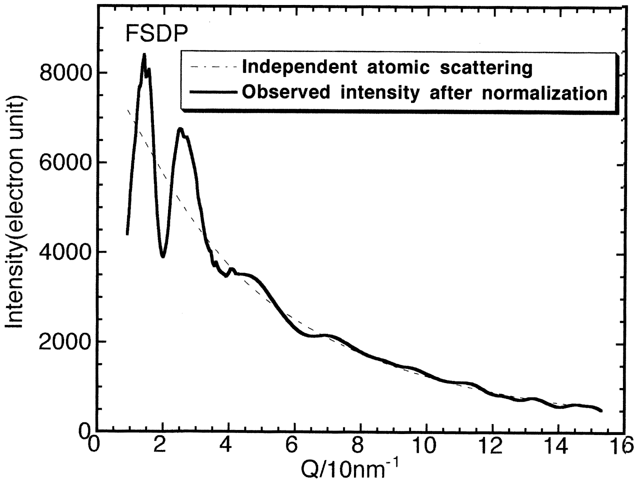

Fig. 1. X-ray diffraction pattern of molten UCl_3 at 1200 K.

4.2. Analysis by Debye scattering equation

The function $Qi(Q)$ can be synthesized by the following Debye scattering equation [7] with three parameters; interionic distance r_{ij}, correlation number n_{ij} and temperature factor b_{ij}.

$$Qi(Q)=\sum_{i=1}^{n}\sum_{j} n_{ij}\, f_i(Q)f_j(Q)\exp(-b_{ij}Q^2)\sin(Qr_{ij})/r_{ij} \qquad (2)$$

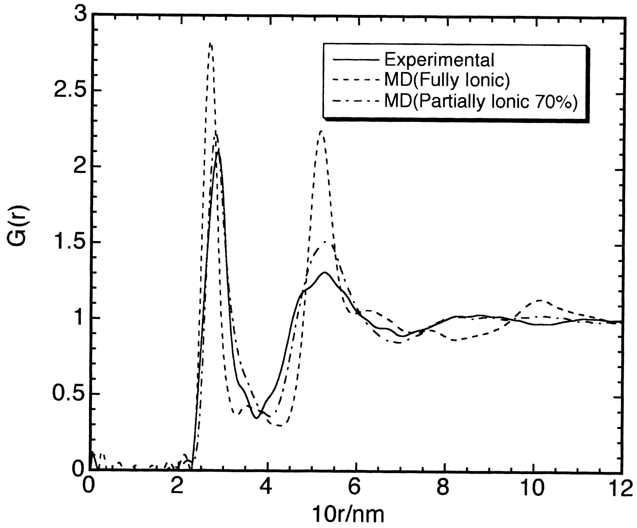

Fig. 2. Radial distribution functions $G(r)$ of molten UCl_3 at 1200 K.

Table 2
Parameters of Debye scattering equation of molten UCl_3 at 1200 K

Interaction	n_{ij} (N_{ij} ^{a}))	r_{ij} (nm)	b_{ij} (10^{-2} nm^2)
U–Cl	12 (6)	0.284	0.025
Cl–Cl	24 (8)	0.402	0.095
U–U	5 (5)	0.520	0.200
U–Cl	24 (8)	0.580	0.350

[a] N_{ij} is coordination number of ion j around ion i.

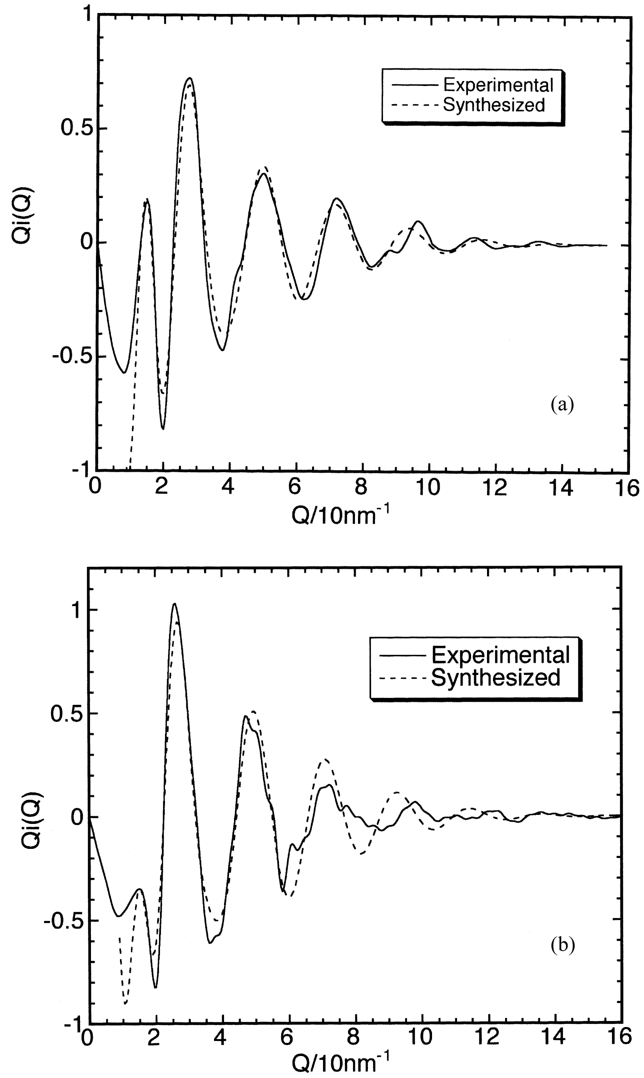

Fig. 3. Experimental (solid lines) and synthesized (broken lines) reduced intensity function $Qi(Q)$ of molten (a) UCl_3 and (b) $LaCl_3$ at 1200 K.

where $f_i(Q)$ is an atomic scattering factor of atom i. The parameters for molten UCl_3 determined by least square fitting to the experimental $Qi(Q)$ are listed in Table 2. In Fig. 3(a), synthesized $Qi(Q)$ of molten UCl_3 is shown as dotted line. The experimental $Qi(Q)$ of molten UCl_3 is reproduced by taking four kinds of interactions into account.

The function $Qi(Q)$ of molten $LaCl_3$ is shown in Fig. 3(b) as solid line. The experimental $Qi(Q)$ of molten $LaCl_3$ is quite different from that of molten UCl_3 in spite of similar cation size, melting point and molar volume. The synthesized $Qi(Q)$ of molten $LaCl_3$ by using the same parameters as molten UCl_3 in Table 2 is shown by dotted line in Fig. 3(b). The synthesized $Qi(Q)$ is in good agreement with the experimental $Qi(Q)$ of molten $LaCl_3$., though discrepancy over $Q=60$ nm^{-1} is detected. It means structures of molten UCl_3 and molten $LaCl_3$ are very close to each another.

4.3. MD calculations

Simulated $G(r)$ from the fully ionic MD simulation is shown by broken line in Fig. 2. The fully ionic model gave a poor agreement with the experimental $G(r)$. Inadequacy of the fully ionic model has been pointed out on molten rare earth trichlorides [8]. The partially ionic model including a covalent contribution in the nearest neighbor unlike ion pair showed better agreement. The function $G(r)$ with the 70% ionicity are shown as broken line in Fig. 2. Agreement with the experimental curve was drastically improved by introducing convalency into the interaction of the nearest U–Cl pair. Calculated enthalpy increment $H(T)$–$H(1110)$ from the 70% ionicity model shows good agreement with the experimental data [13], similarly in case of molten structure.

Calculated dynamic properties such as shear viscosity, electrical conductance and self-diffusion coefficients by the MD simulations with the structure optimization described above are listed in Table 3 together with the experimental values. The 70% ionicity model gave an improved agreement with the experimental data in the literature.

5. Conclusion

Structure of molten UCl_3 was investigated by the high-temperature X-ray diffraction analysis. The nearest U–Cl

Table 3
Dynamic properties of molten UCl_3 at 1200 K calculated from MD simulation

Properties	Fully ionic	70% ionicity	Experimental
Shear Viscosity (cP)	16.222	2.924	2.276 [3]
Electrical Conductance (S m^{-1})	29.516	109.817	128.3 [4]

distance was 0.284 nm in molten state. U^{3+} ion is surrounded by six Cl^{-} ions and there is the FSDP indicating the existence of a medium range order. It was shown that molten UCl_3 have a fundamentally similar structure to molten $LaCl_3$.

Structure of molten UCl_3 could not be reproduced by the fully ionic model. This discrepancy was improved by considering the 70% ionicity model in which partial covalency is supposed to exist in the nearest U–Cl interaction. The 70% ionicity model also gave a good agreement with experimental data of dynamic properties in the literature.

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