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Electronic Supporting Information for: Examination of the short-range structure of molten salts: ThF_4, UF_4, and related alkali actinide fluoride systems

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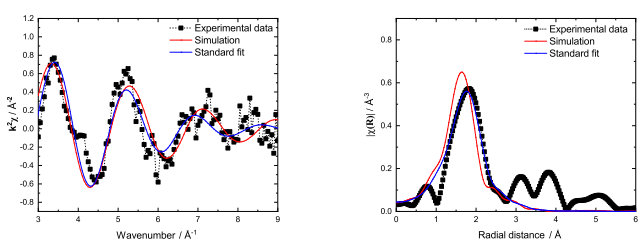
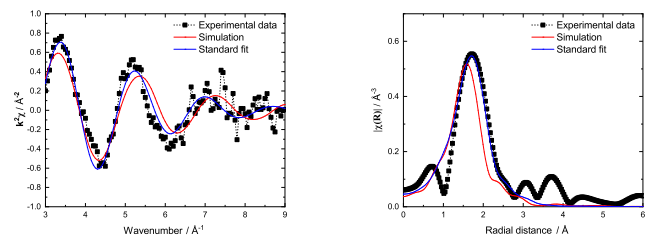
1 Coordination environment of the actinide cations

Herein are the EXAFS measurements carried out in the molten state for seven different alkali actinide fluoride systems at a few representative compositions. Accompanying the experimental data are the simulated EXAFS oscillations, generated using molecular dynamics (MD) positions as input and those via fitting of the standard EXAFS equations. The Fourier Transform moduli of the signals are shown alongside the EXAFS oscillations (Figs. 1 to 12).



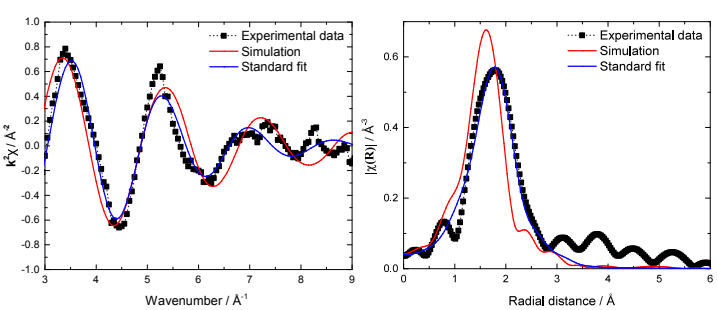
(a) (b)

Fig. 1 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (LiF:ThF_4) = (0.90:0.10) (fluorescence, T = 1133 K, data from[1]). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



(a) (b)

Fig. 2 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (LiF:ThF_4) = (0.50:0.50) (fluorescence, T = 1193 K, data from[1]). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



(a) (b)

Fig. 3 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (NaF:ThF_4) = (0.67:0.33) (data taken from[1], T = 1073 K measured in absorption). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.

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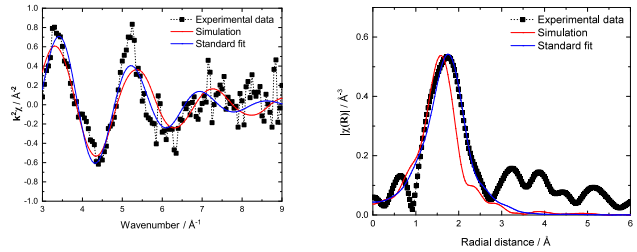
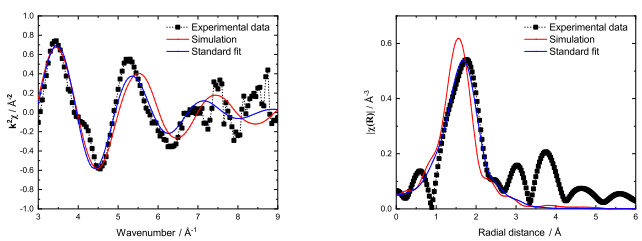


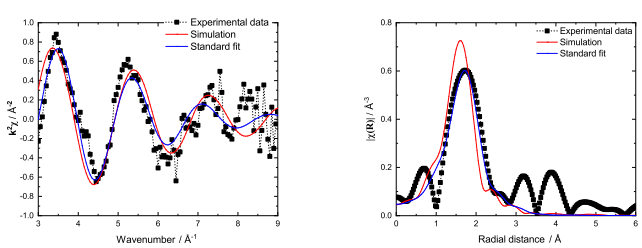
(a) (b)

Fig. 4 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (NaF:ThF_4) = (0.50:0.50) (fluorescence, data taken from[1], T= 1108 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



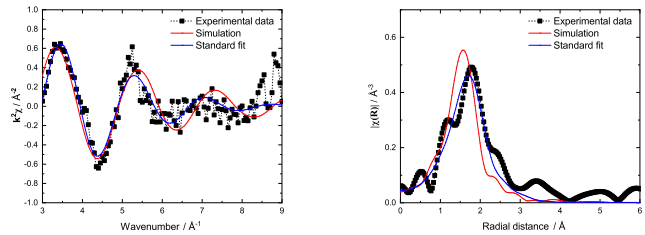
(a) (b)

Fig. 5 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (NaF:UF_4) = (0.50:0.50) (absorption, T= 1033 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



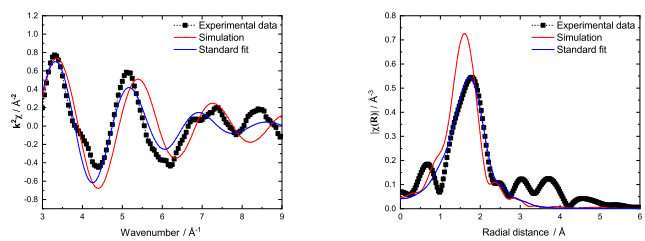
(a) (b)

Fig. 6 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (KF:ThF_4) = (0.833:0.167) (fluorescence, T= 1060 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



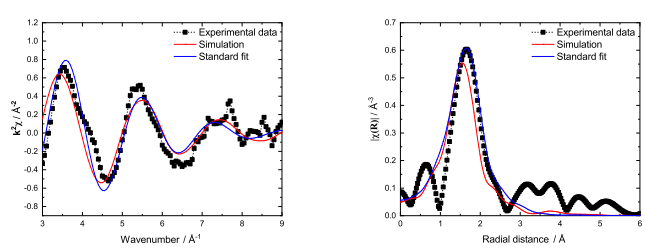
(a) (b)

Fig. 7 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (KF:ThF_4) = (0.50:0.50) (fluorescence, T= 1209 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



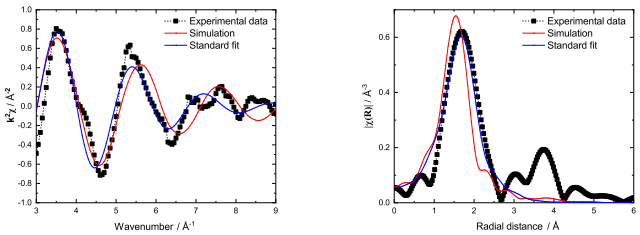
(a) (b)

Fig. 8 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (KF:ThF_4) = (0.33:0.67) (absorption, T= 1266 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



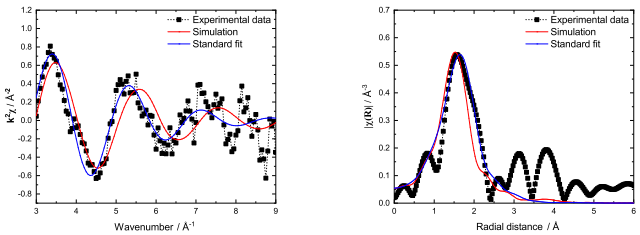
(a) (b)

Fig. 9 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (KF:UF_4) = (0.33:0.67) (absorption, T= 1090 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



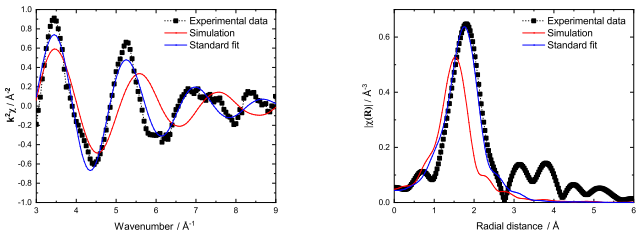
(a) (b)

Fig. 10 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (CsF:UF_4) = (0.50:0.50) (absorption, T= 1058 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



(a) (b)

Fig. 11 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (CsF:UF_4) = (0.33:0.67) (fluorescence, T= 1191 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.



(a) (b)

Fig. 12 (a)Experimental (■), simulated (red), and fitted (blue) $k^2\chi(k)$ oscillations of (CsF:ThF_4) = (0.50:0.50) (absorption, T= 1201 K). (b) Fourier transform modulus $|\chi(R)|$ of the EXAFS spectra.

2 Radial distribution functions of the liquid mixtures

The An-F, An-An, and A-F RDFs have been plotted for the three most representative compositions: X(AnF_4) = 0.25 along with 0.33, 0.50, and 0.67 in Figs. 13-15.

3 XANES data

Both Th and U remained in the tetravalent oxidation state as revealed by the XANES data. Uranium in particular is problematic, as it has several valence states and may oxidize when exposed to the synchrotron beam, whereas Th may be expected to oxidize only as Th(IV). XANES data of uranium-bearing samples in this work are compared to data of uranium samples in three oxidation states: UO_2 (U(IV)), schoepite (hydrated UO_3, U(VI)), U_3O_8 (U(V)/U(VI)), measured at the same beamline with a metallic yttrium reference, taken from Kegler et al.[2] and Böhler et al.[3]. UO_2, used as a reference for UF_4 at room temperature in this work, is also included. The energy positions of the inflection points and of the white lines are tabulated in Table 1.

Table 1 Energies of the Inflection Points and White Lines of Th-L_3 and U-L_3 XANES Spectra

sample	inflection point (eV)	white line (eV)
ThF_4	16299.9(5)	16305.3(5)
ThO_2 RT	16300.0(5)	16305.2(5)
(LiF:ThF_4) = (0.90:0.10)	16300.0(5)	16304.9(5)
(LiF:ThF_4) = (0.75:0.25)	16298.9(5)	16304.9(5)
(LiF:ThF_4) = (0.50:0.50)	16300.8(5)	16305.1(5)
(NaF:ThF_4) = (0.67:0.33)	16300.1(5)	16304.9(5)
(NaF:ThF_4) = (0.50:0.50)	16299.1(5)	16304.9(5)
(NaF:ThF_4) = (0.33:0.67)	16300.7(5)	16305.1(5)
(KF:ThF_4) = (0.833:0.167)	16298.5(5)	16304.7(5)
(KF:ThF_4) = (0.50:0.50)	16301.0(5)	16305.6(5)
(KF:ThF_4) = (0.33:0.67)	16300.9(5)	16305.0(5)
(CsF:ThF_4) = (0.75:0.25)	16301.2(5)	16305.1(5)
(CsF:ThF_4) = (0.50:0.50)	16302.1(5)	16306.1(5)
UF_4 RT	17169.6(5)	17174.6(5)
UO_2 RT	17170(5)	17175.8(5)
UF_4	17170.4(5)	17176.3(5)
(NaF:UF_4) = (0.50:0.50)	17171.5(5)	17177.0(5)
(NaF:UF_4) = (0.33:0.67)	17170.5(5)	17176.1(5)
(KF:UF_4) = (0.50:0.50)	17170.7(5)	17176.5(5)
(KF:UF_4) = (0.33:0.67)	17171.2(5)	17176.2(5)
(CsF:UF_4) = (0.75:0.25)	17171.2(5)	17176.1(5)
(CsF:UF_4) = (0.50:0.50)	17171.2(5)	17176.1(5)
(CsF:UF_4) = (0.33:0.67)	17170.9(5)	17175.7(5)
Comparison with samples of Kegler et al.[2] (UO_2, schoepite) and Böhler et al.[3] (U_3O_8), RT.		
UO_2	17169.3(5)	17177.72(5)
schoepite	17175.5(5)	17179.73(5)
U_3O_8	17171.7(5)	17180.9(5)

Samples are at high temperature, unless otherwise labeled with room temperature (RT).

Notes and references

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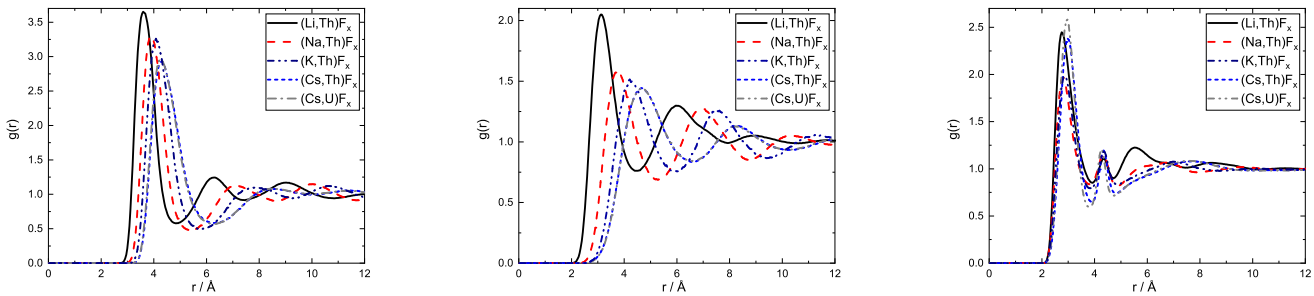
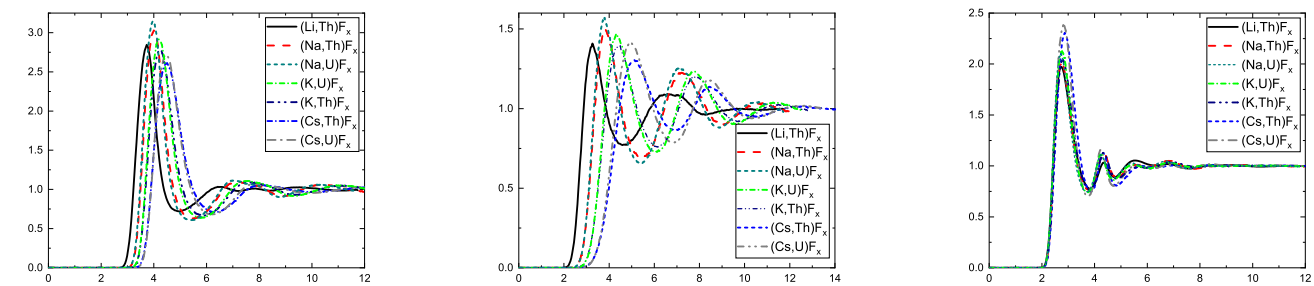


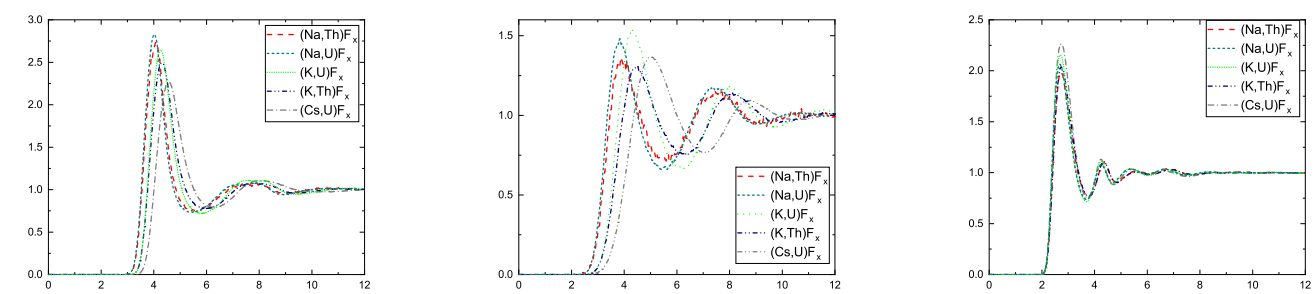
(a) **(b)** **(c)**

Fig. 13 Radial distribution functions: (a) An-A, (b) A-A, and (c) F-F in the AF-AnF$_4$ melts at composition X(AnF$_4$) = 0.25 (Li and Cs-based melts) and X(AnF$_4$) = 0.33 (Na and K-based melts).



(a) **(b)** **(c)**

Fig. 14 Radial distribution functions: (a) An-A, (b) A-A, and (c) F-F in the AF-AnF$_4$ melts at composition X(AnF$_4$) = 0.50.



(a) **(b)** **(c)**

Fig. 15 Radial distribution functions: (a) An-A, (b) A-A, and (c) F-F in the AF-AnF$_4$ melts at composition X(AnF$_4$) = 0.67.