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Local Structure Analogy of Lanthanide Fluoride Molten Salts[1]

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The objective of this paper is to describe the local structure of lanthanide fluoride melts of nuclear interest. An experimental approach combining NMR and EXAFS spectroscopy, both sensitive to the microstructure of solid or liquid materials, is presented. These techniques can be used to determine the coordination number, the nature of neighbors, and then to identify the complex formation. NMR and EXAFS spectroscopy have been applied to the molten LaF_3–LiF and LuF_3–LiF systems. The influence of melt compositions and temperature was studied.

KEY WORDS: EXAFS; high temperature; lanthanide fluorides; molten salts; NMR; speciation.

1. INTRODUCTION

Interest in molten rare-earth fluorides is raised again due to the nuclear realm. Indeed, the first generation of nuclear reactors has come to an end, and we now face the problems of their demolition and of nuclear waste treatment. Different pyrochemical processes are proposed using molten mixtures of alkali fluorides and chlorides salts, where the radioactive elements are dissolved before electrolytic separation [1,2]. Separation of elements in such processes is based on the possibility of modifying the oxidation state by electrolysis or by addition of a chemical agent. The second nuclear realm is the molten salt reactor (MSR) technology [3,4] with a growing interest in nuclear reactors using thorium [5,6] because

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of its lower radio-toxicity compared with the fast spectrum uranium reactor. This MSR reactor is one of the seven options retained at the Generation IV International Forum [7]. Its principle is based on molten mixtures of fissile materials with fluoride salts: ThF_4 and LiF plus possible BeF_2, NaF. The nuclear reaction produces a long series of elements that poison the reaction itself. It is thus necessary to remove them. Among these poisons are the rare earths. One great advantage of molten fissile materials is that their partial extraction from the core is easy. Once out, each element can be extracted selectively. In a molten salt this process is complicated by different complexation phenomena and by the influence of temperature. A knowledge of the chemical species that could be involved in the reactive medium, depending on the composition, is imperative in order to better predict the efficiency of the process. Notwithstanding this need, manipulation hindrances of molten fluorides have resulted in scarcity of experimental data. They are indeed highly corrosive and volatile, and the melting temperatures are high (700–1800 K). Most of the previous work deals with the electrochemical [8,9] and thermodynamic properties [10,11] and very few spectroscopic studies [12–15] have been done. The latter are important to provide coordination numbers and interatomic distances and are helpful for electrochemical experiment analysis and for building potentials in numerical simulations. These simulations provide transport and thermodynamic coefficients and may provide data when no experiment can be performed.

In this paper we have studied the LaF_3–LiF and LuF_3–LiF binary mixture using nuclear magnetic resonance (NMR) and extended X-ray absorption fine structures (EXAFS) spectroscopy. NMR and EXAFS techniques are complementary. NMR gives the nature and population of the different sites for a given nucleus. It is better adapted for the structural description of the lighter elements, for ^{7}Li or ^{19}F, while for the heavier elements we choose the EXAFS approach that should give the coordination and distance from close neighbors.

In this paper, the LaF_3–LiF and LuF_3–LiF systems have been selected because of several considerations. First, rare earth elements may be divided into two main groups according to their phase diagrams and structural properties. We may consider that lanthanum acts as a model for the large cations (La–Nd) and lutetium for the smaller (Sm–Lu) ones. Moreover, since lanthanum and lutetium are the lightest and heaviest, respectively, the differences in their properties are expected to be the most important. The second reason that has led us to choose these two systems is related to NMR limitations. Most of the lanthanides ions (Ln^{3+}) are paramagnetic. The single electrons produce magnetic fields that are 1000 times higher than those produced by NMR coils. This parasitic field induces strong enhancement of the magnetization relaxation of the surrounding nuclei; in worst cases, no NMR signal can be obtained, and in best cases, the NMR peaks are broadened and shifted. Fortunately, La^{3+} and Lu^{3+} are diamagnetic and NMR experiments can thus be performed.

This study belongs to a more extensive study of speciation in rare earth fluorides—alkali molten mixtures. Preliminary results have been published on the lanthanum system to present the suitability of the cell we have designed specifically for EXAFS studies of molten fluorides [15,16].

2. EXPERIMENTAL METHODS

2.1. High Temperature NMR

The fluoride salts (purity 99.99%) were purchased from Aldrich with no further purification.

High temperature NMR spectra were obtained with the CO_2 laser heating system developed in our laboratory in Orleans [17,18]. The sample (50–65 mg) is contained in a sealed boron nitride crucible, filled in a glove box under dry argon, to avoid any contamination by the atmosphere. The crucible is heated inside the NMR probe with a CO_2 laser beam. In order to avoid any oxidation of the boron nitride, an argon stream is flowed around the crucible. This system can be used for heating the sample rapidly up to 1600 K, and keeping the temperature stable during the NMR data acquisition. The spectra presented here were collected at approximately 20 K above the corresponding melting points. The NMR spectra were recorded using Bruker DSX 400 and DSX 300 NMR spectrometers, operating at 9.40 and 7.04 T, respectively.

The various spectra were acquired using a single pulse sequence, with $\pi/12$ pulses, a recycle delay of 0.5 s, and 8–128 accumulations. ^{19}F NMR spectra were referenced to $CFCl_3$ 1 M and ^{139}La–$LaCl_3$ 1 M solutions.

2.2. EXAFS Measurements in Molten Fluorides

As for NMR measurements, salts were conditioned in a glove box under argon. The cells used here have been designed in our laboratory especially for high-temperature X-ray absorption measurements in both solid and molten lanthanide fluorides [16]. They are made of two plates of pyrolitic boron nitride fitted hermetically together around the sample in order to avoid any evaporation and atmosphere interaction. The thickness of each plate is 1 mm. One cavity of 10 mm diameter and 200 μm depth has been hollowed into one of the plates, to host the sample. Mixtures of fluoride salts and BN powder were pressed in a small pellet. The cell was placed in a tubular furnace under vacuum. Due to the geometry of the furnace, *in situ* EXAFS spectra were recorded in a transmission mode using a Si photodiode as a detector placed behind the furnace. The heating rate was $10\,\mathrm{K \cdot min^{-1}}$ up to 1200 K. A more precise description has been given in a previous publication [16].

The EXAFS experiments have been performed on the H10 beam line at LURE/DCI [19] (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, France). Spectra were obtained on the La L_{III} ($E_0 = 5.483\,\mathrm{keV}$) and Lu L_{III} ($E_0 = 9.244\,\mathrm{keV}$) absorption edges for 10–90 and 20–80 mol% LaF_3–LiF, and 20–80 and 58–42 mol% LuF_3–LiF mixtures, respectively. The data analysis has been performed using the WINXAS software [20].

3. RESULTS

^{19}F NMR spectra were recorded for LaF_3–LiF and LuF_3–LiF binary mixtures at approximately 20 K above their melting point. The compositions and temperatures of experiments are reported on phase diagrams in Fig. 1a, b. The spectra did not vary more than 1 ppm in the range of investigated temperatures. The compositions were varied from 0–100 to 60–40 mol% in the case of LaF_3–LiF (temperature limitation of our heating device) and from 0–100 to 100–0 mol% in the case of LuF_3–LiF. In the melt, the NMR spectrum is a single Lorentzian peak. Indeed, the characteristic time of NMR measurement is much higher than the lifetime of the complexes present in the liquid. The detected signal is thus the signature of the average environment around the nucleus. The measured chemical shift δ, given by the position of the peak, is the weighted average of the different contributions in the melt. The evolution of ^{19}F chemical shifts is presented in Fig. 2 as a function of the melt composition. It varies in a monotonic way from the value in pure LiF (−201 ppm) to the value in pure LnF_3 (Ln = lanthanide). Three interesting points appear. The first one is that no particular feature occurs around the eutectic points. The second one is that the variation of δ is nonlinear. If fluorine ions are in rapid exchange between several complexes, the measured chemical shift is $\delta = \Sigma n_i x_i \delta_i$, where n_i is the number of fluorine involved in the ith complex, x_i is the molar fraction, and δ_i is its chemical shift. The deviation from linearity observed in the LnF_3–LiF systems indicates the existence of more than two kinds of fluorine environments. This observation is in agreement with the work of Papatheodorou and his co-workers [13, 14] using Raman spectroscopy. They have shown that the LnF_3–AlkF melts (Alk = alkalin) should consist of LnX_6^{3-} octahedral species, more or less connected, depending on the LnF_3 content in the melt. They proposed a

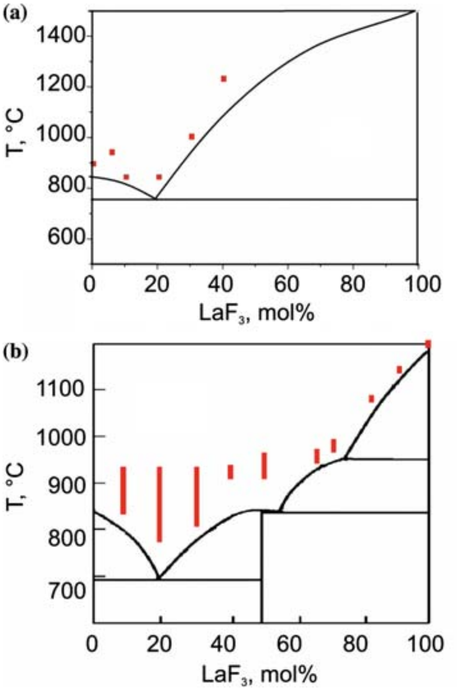

Fig. 1. (a) LaF_3–LiF phase diagram [26]. Points represent experimental conditions for the NMR experiments (temperature and compositions). (b) LuF_3–LiF phase diagram [26]. The bars represent experimental conditions for the NMR experiments (temperature range and compositions).

description of melts rich in LnF_3 as a loose network liquid with shared fluorines between distorted lanthanide octahedra. The ^{19}F NMR provides direct information about the anion environment: from free fluorines in pure LiF to fluorines involved in the first neighbor shell of lanthanum with LaF_3 addition. There are all the more connecting fluorines since the amount of LaF_3 is large.

The third interesting point in Fig. 2 is the similarity of the ^{19}F chemical shift evolution in LaF_3–LiF and LuF_3–LiF systems. It seems that the microscopic behavior of fluorine anions is the same in both systems despite their rather different phase diagrams.

The high temperature ^{139}La NMR spectra have also been recorded for LaF_3–LiF melts [15]. It was not possible to record an NMR Lu spectrum because of its very high quadrupolar coupling constant ($c_q = 350 \times 10^{-30} m^2$,

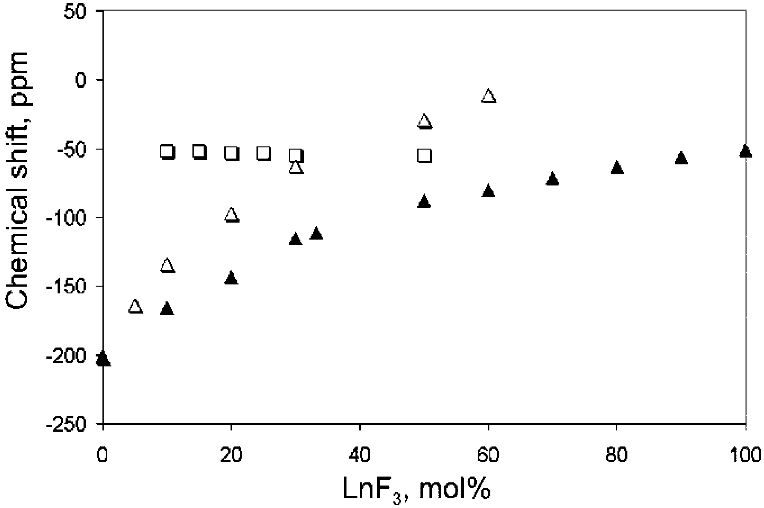

Fig. 2. Variation of the ^{19}F chemical shift in LaF_3–LiF (open triangle) and LuF_3–LiF (solid triangle) molten salts as a function of the molar fraction of LnF_3. Variation of ^{139}La chemical shift in LaF_3–LiF (open square) molten salt.

whereas for ^{139}La, $c_q = 20 \times 10^{-30}\,m^2$). As can be observed in Fig. 2, there is no variation of ^{139}La chemical shifts over the whole range of composition studied. It means that the microscopic environment around cations is not affected when the composition of the melt is changed, in contrast to fluorine anions.

For the eutectic composition, we have also recorded the ^{139}La NMR spectra at several temperatures. They are presented in Fig. 3. The chemical shift slightly increases with temperature: 4 ppm over 200 K above the melting point. The local environment around the lanthanum in the melt is weakly affected by temperature. The temperature may slightly increase interatomic distances and decrease the bond strength between lanthanum and fluorine.

These NMR experiments have been combined with EXAFS experiments. We have measured the X-ray absorption spectra of lanthanum and lutetium in both LnF_3–LiF systems. The EXAFS spectra are presented in Fig. 4a and b for solid and molten mixtures of different compositions of LaF_3–LiF and LuF_3–LiF, respectively. The spectrum of the solid corresponds to the spectrum of pure LnF_3 because the initial sample was prepared by mixing LnF_3, LiF, and BN without heat treatment. An increase of the oscillation length is observed in the spectrum of the melt compared

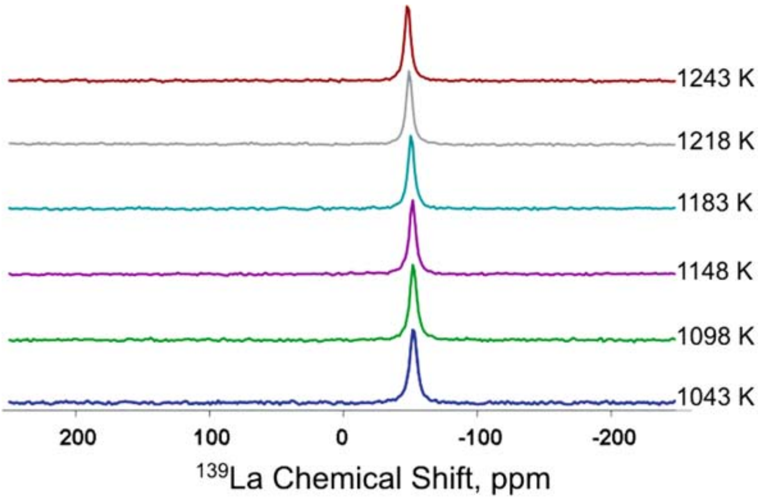

Fig. 3. Temperature evolution of 139La NMR spectra in molten 20/80 mol% LaF_3–LiF.

with the solid. Moreover, they are damped more rapidly because the great motions of atoms in the melt induce a rapid loss of order.

In Fig. 4a, La LIII EXAFS spectra of the molten 10–90 and 20–80 mol% LaF_3–LiF compositions are superimposed. This indicates clearly that the average structure around the lanthanum does not change with the composition of the melt, which is in good agreement with the ^{139}La NMR results.

In Fig. 4b, Lu LIII EXAFS spectra of the molten 20–80 and 58–42 mol% LuF_3–LiF are almost superimposed. At small *k*, the amplitude of the 58–42 mol% LuF_3–LiF spectrum is slightly lower, and at large *k*, the oscillations appear a bit larger. These slight differences have to be confirmed by supplementary experiments. We have also recorded the absorption spectrum of lutetium in a molten equimolar mixture of LuF_3–LiF (30–70 mol%) + LaF_3–LiF (30–70 mol%). It is presented in Fig. 4b. One can notice that it is superimposed on the spectra of pure LuF_3–LiF systems. The presence of another lanthanide does not disturb the local environment, even in large concentrations.

For the 20–80 mol% LaF_3–LiF molten salt, the EXAFS spectra were recorded at three temperatures: 1053, 1123, and 1173. The corresponding spectra, presented in Fig. 5, are nearly identical. Similarly to composition, when the temperature is increased in a moderate range (up to 200 K above

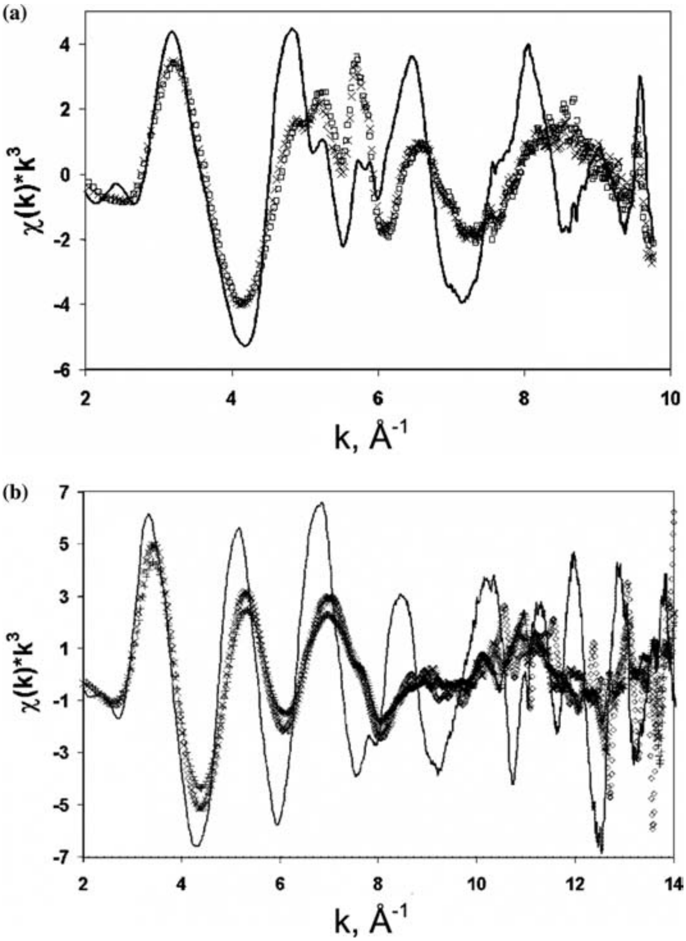

Fig. 4. (a) La LIII EXAFS spectra of LaF_3–LiF mixtures solid (black line) and molten for 10/90 mol% at 1073 K (open square) and 20/80 mol% (cross) at 1053 K. (b) Lu LIII EXAFS spectra of LuF_3–LiF mixtures solid and molten for 20–80 mol% (cross) and 58–42 mol% (plus sign). Lu LIII EXAFS spectrum (open diamond) in a molten equimolar mixture of LuF_3-LiF (30–70 mol%) + LaF_3–LiF (30–70 mol%).

the melting point), the first shell of neighbors is weakly modified, as was observed by NMR.

In Fig. 4a, a strong oscillation occurs around 5.5 $Å^{-1}$. It is due to an electronic double excitation [21–23]. In the lutetium spectra, it is less pronounced but it is present. This double excitation makes the quantitative analysis of the EXAFS spectra difficult. Nevertheless, qualitative

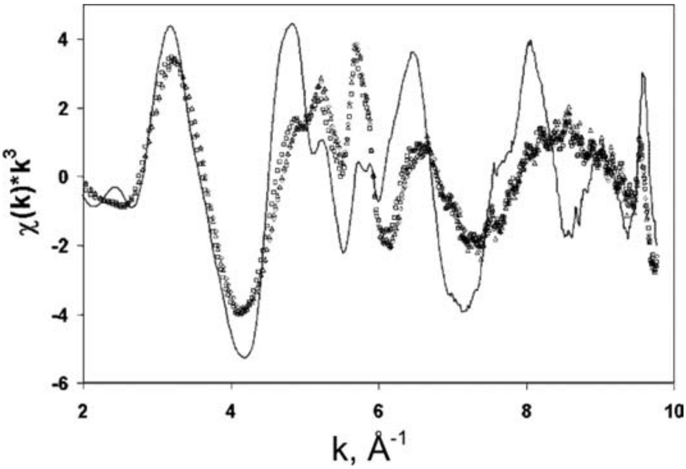

Fig. 5. La LIII EXAFS spectra of LaF_3–LiF 20–80 mol% solid (black line) and molten at 1053 K (open square), 1123 K (open triangle), and 1173 K (open diamond).

information on distances can be obtained by making the Fourier transform of the EXAFS spectra. The relative distance of the neighbors are thus obtained, as presented in Fig. 6. The small peak around 0.7 Å is an artifact of the experiment (absorption noise, limited Fourier transform window ...). The intense peak around 2 Å corresponds to the first shell of fluorine neighbors. A decrease of the average lutetium–fluorine distance (around 0.2 Å) is observed in the liquid compared with the solid. This is in agreement with what we have already obtained in lanthanum fluoride molten salts [15] and what has been reported for rare earth chloride molten salts [24,25].

The EXAFS experiments show that the structural behavior at the local scale in the melt is similar for lanthanum and for lutetium. Their local environment is very stable toward external parameters such as temperature and concentration.

4. CONCLUSION

We have studied the local structure of molten LaF_3–LiF and LuF_3–LiF binary mixtures using NMR and EXAFS spectroscopy. The ^{19}F NMR spectra indicate that the nature of the interaction between fluorine and cations is influenced by the amount of lanthanides in the melt. The higher the quantity of lanthanide, the more bridging are the fluorine ions. The ^{139}La NMR spectra show that the local environment changes weakly with composition and

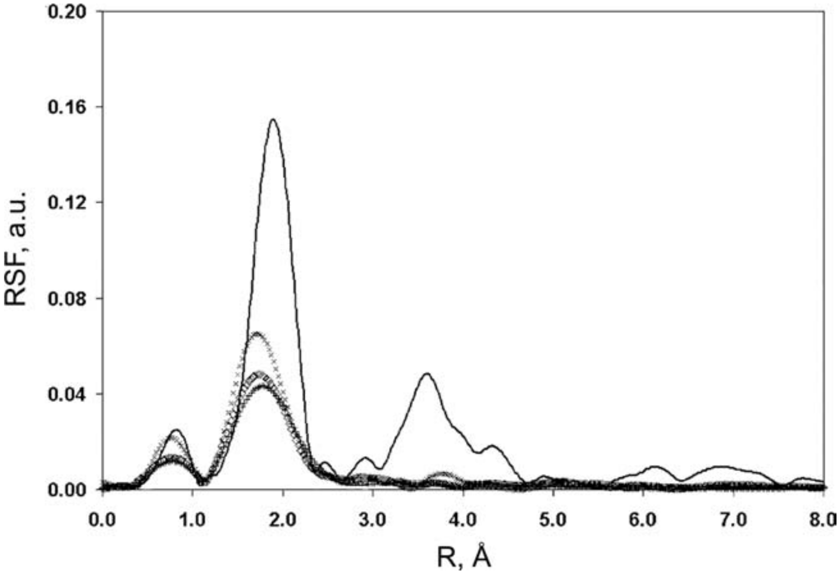

Fig. 6. Fourier transform of Lu LIII EXAFS spectra of LuF_3–LiF mixtures solid and molten for 20/80 mol% (cross) and 58–42 mol% (plus sign). Lu LIII EXAFS spectrum (open diamond) in a molten equimolar mixture of LuF_3–LiF (30–70 mol%) + LuF_3–LiF (30–70 mol%).

temperature, in contrast to fluorine. The EXAFS measurements at the L_{III} edge of lanthanum and lutetium confirm the NMR results. The first shell of neighbors around the lanthanide remains unchanged when the composition is varied. This confirms the existence of relatively strong LnF_x^{3-x} complexes in LnF_3–LiF molten salts.

For both systems, similar behaviors are observed for anions and for cations. It thus appears that extrapolation is possible for the whole lanthanide series. The local structural behavior of the atoms in the molten salt seems to be the same for all the binary mixtures of LnF_3–LiF. Further experiments are planned for high LnF_3 concentration (50–100 mol%) in order to understand the slight differences observed in EXAFS spectra.

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