NMR at high temperature in molten fluorides for nuclear applications: In situ experimental approach of the speciation


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EURACT-NMR Workshop Karlsruhe 27–29 January 2010
In situ structural approach of molten salts at high temperature

Why?
Speciation, nature of the complexes formed in the melt, influence of composition, solvent, oxides content…

How?
Spectroscopy : NMR and EXAFS

Problems?
High temperature, corrosive liquids, interaction with atmosphere…

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Molten salts in nuclear energy

- Pyrochemical treatment of nuclear wastes
- Molten Salt Reactor (Gen IV)
- Coolants for high-temperature reactors
- Metals corrosion…

Experimental characterization of ionic species in molten fluorides mixtures (coordination number, influence of composition, temperature, oxidation number…)

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**In situ** experimental approaches of molten fluorides at high temperature

- high temperatures ~ 1000°C

- volatile, corrosive, hygroscopic…melts

  - specific developments

  ✓ to prevent evaporation or reactions with surrounding atmosphere

  ✓ air tightness

  ✓ heating compatible with the experimental setup

  ✓ gloves box
In situ experimental approaches of molten fluorides at high temperature

- Selective techniques
- Effect of the local environment around a given element
- Solid (crystalline and amorphous) and liquid (solutions and melts) samples

**NMR**

« light » elements

$^{19}$F, $^{17}$O, $^{7}$Li, $^{23}$Na, $^{39}$K, $^{27}$Al, ...

$^{89}$Y, $^{139}$La, $^{91}$Zr

**XAFS**

« heavy » elements

Th, U, Ln (La, Nd, Sm, Gd, Lu, Y..) Zr
High temperature Nuclear Magnetic Resonance

Problems…

Superconducting magnet (cryogenic liquids)

Geometry:
- « free» space inside the coil very limited < 10mm
- RF coil protection: limited to temperatures ~ 150°C

Detection: perturbation of the signal

Heating system: adapted

Sample: container compatible with NMR (no metal)

Solution…

Laser heating
**in situ** high temperature NMR

- Radio-frequency coil
- Thermal shield
- Argon
- ZnSe window
- Boron Nitride crucible
- Sample
- Cryomagnet
- NMR probe
- Laser beam
- He / Ne
- CO₂ laser (250W)
- 1300°C


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**in situ** High temperature NMR

\[ \delta_m(N) = \sum_i X_{A_i}^N \cdot \delta^N(A_i) \]

Molten (HT)

1 sharp and unique signal system in rapide exchange

Chemical shifts \( \delta(X) \) (ppm)

2 species A and B with chemical shifts \( \delta_a \) and \( \delta_b \)

100% of A \( \delta_a \)

100% of B \( \delta_b \)

1 unique species A with chemical shift \( \delta_a \)

NMR in solid Lanthanide fluorides (RT)

La, Ce, Pr, Nd, Sm, Eu - Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu + Y

Non observable by NMR

Strong effects on the NMR spectrum of the observed nuclei:
⇒ important shift and broadening

Paramagnetic properties of the trivalent lanthanide cations Ln(III)
⇒ electronic configuration 4f^n (n= 0 – 14)

La_{III}, Y_{III} and Lu_{III} have no unpaired ē:
\textbf{diamagnetic}

The others have 1-7 unpaired ē:
\textbf{paramagnetic}

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NMR in molten rare earth fluorides

Description of the systems **AF- LaF₃** and **AF- YF₃**, A=Li, Na, K

*In situ* NMR measurements of the different nuclei of the melt

- **¹⁹F**
  - Anion point of view
  - Free F, connectivity

- **¹³⁹La, ⁸⁹Y**
  - Cation point of view Ln³⁺
  - Coordination, complexes

- **⁷Li, ⁲³Na, ³⁹K**
  - Alkali point of view
  - Complexes, conductivity

Chemical shifts scales established from known cristallographic structures of solids compounds (coordination, bridged and non bridged fluorines, symmetry…)

*correlation chemical shifts / structure*
Molten lanthanide fluorides (HT)

- structure of molten rare earth halides
  (Chlorides, Bromides, Iodides)
  
  **XRD, Neutrons, Raman, MD...**

- In pure trihalide melts:
  Octahedral coordination \((\text{LnX}_6)^{3-}\)

- In binaries melts:
  Medium range order generated by bridging fluorine between octahedra (compositions rich in \(\text{LnX}_3\))

\[
\begin{align*}
\text{X (LnF}_3\text{)} &\le 0.25 \quad \text{LnF}_6^{3-} \quad \text{Octahedra} \\
\text{X (LnF}_3\text{)} &> 0.25 \quad \text{LnF}_6^{3-} \quad \text{Octahedra distorted and connected (edges sharing)}
\end{align*}
\]
**Pure LaF$_3$**

LaF$_3$ crystallographic structure
- Trigonal structure [LaF$_9$]$^{6-}$
- 3 different F sites

$T_m$ LaF$_3$ = 1493°C

$\delta_F = 52$ ppm

$\delta_{La} = -129$ ppm

$\delta_{La} = -60$ ppm
Pure LaF$_3$

<table>
<thead>
<tr>
<th>LaF$_3$ $\delta$ in ppm</th>
<th>Solid RT</th>
<th>Molten 1500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{19}$F</td>
<td>20,12, -25</td>
<td>52</td>
</tr>
<tr>
<td>$\delta^{139}$La</td>
<td>-129</td>
<td>-60</td>
</tr>
</tbody>
</table>

Evolution of the anion and cation local structure on melting:
Shift towards more positive values $\Rightarrow$ deshielding
Slight increase of the covalent part of the iono-covalent La-F bond
$\Rightarrow$ **Confirmed by EXAFS measurements : decrease of the La-F bond**

AF-LaF$_3$ A=Li, Na, K, Rb…
MF-LaF$_3$ M=Li, Na, K, Rb

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**NMR**

**LiF-LaF$_3$**

![Graph showing 19F chemical shifts as a function of LaF$_3$ mol%](image1)

- Experimental: 3 species
- Calculated for 2 species

**19F**

- LaF$_3$
  - Experimental: 3 species
  - Calculated for 2 species

**LaF$_3$ mol%**

- 139La
  - LaF$_x^{3-x}$

**139La**

- 139La δ (ppm)
  - LaF$_3$ mol%

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MF-LaF$_3$ M=Li, Na, K, Rb

**19F**

- RbF
- KF
- NaF
- LiF

**139La**

- Rb
- K
- Na
- Li

- Monotonous and no linear evolution
- 3 different environments

**MF**

- F free
- F in [LaF$_x$]$^{3-x}$
- F bridging [LaF$_x$]$^{3-x}$

- 2 domains
- 3 to 2 species depending on LaF$_3$ composition
- Strong influence of the alkali

**LaF$_6$**

- $^3$LaF$_7$
- $^4$LaF$_8$

LaF$_3$ mol%
The environment of the Lanthanum changes with the salt composition:

% LaF$_3$ \(\rightarrow\) \(\delta \rightarrow \delta_\text{La (LaF}_3\) \(\rightarrow\)

\(\Rightarrow\) data in agreement with Molecular Dynamics calculations (PESCA, UPMC, Paris)

- In pure molten LaF$_3$: LaF$_7^{-4}$ & LaF$_8^{-5}$ complexes connected by bridging F
- % AF \(\rightarrow\) F-bridging \(\Rightarrow\) La coordination \(\Rightarrow\)
- Effect of the electronegativity of the alkali

\[\boxed{\text{Not possible to set predictive physical properties of AF- LaF}_3\text{ molten salts on the hypothesis of a single environment whatever the composition and the solvent!}}\]
What about actinide fluorides?

- U, Pu, Th ....non observable by NMR :
  
  $^{234}$U (0.005%) & $^{238}$U (99.3%) I=0
  
  $^{235}$U (0.72%) I = 7/2, $\nu$ = 7.1 MHz
  
  $^{232}$Th (I=0)
  
- Indirect description by the anion and alkali point of view
  
  $^{19}$F, $^{17}$O $^{7}$Li, $^{23}$Na, ...

- Paramagnetism : strong influence on the signals of other atoms in the melt

- EXAFS

- Radioactive : safety constraints (new development of specific containers)

- ZrF$_4$-MF
LiF-ThF$_4$

7 different fluorines in the structure at room temperature

$\delta^{19}$F : 53 to 101 ppm

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Comparison of $^{19}$F chemical shifts evolutions in LiF-ThF$_4$ and LiF-LnF$_3$ (Ln = La, Ce, Sm, Lu, Y)

NMR$^{19}$F

Similar evolution for all lanthanides fluorides

3 Types of fluorines depending on the composition

1. « Free » F
2. F indembed in [ThFx] complexes or [LnFx] in the melt
3. F ‘bridging’ the [ThFx] ([LnFx]) polyhedra

A. L. Rollet et al. PCCP, 2008
Application to ZrF$_4$-MF systems (M=Li, Na, K)

**Advantages**
- Non radioactive
- Good model for actinides
- Observable by NMR and EXAFS

**Problems**
- Only few data available on $^{91}$Zr NMR
- ZrF$_4$ very sensitive to oxygen
- Model?

Olivier Pauvert (PhD Thesis 2009)
$^{91}$Zr solid state NMR

NMR properties of zirconium...

$^{91}$Zr
(I=5/2)

Natural abundance: 11.23 %
Larmor Frequency:
9.4T: 37.20 MHz
17.6T: 69.74 MHz
Quadrupolar coupling: > 10 MHz

Strong chemical shift anisotropy (CSA)

Central transitions are very broad (difficult to observe with standard fields)

- Very High magnetic field (17.6 and 30.0 Tesla)
- Special pulses sequences (VOCS, QCPMG)

750 MHz spectrometer (Bruker)
\(^{91}\text{Zr}\) solid-state NMR at 17.6 and 30.0 Tesla

Zirconium halides (ZrF\(_4\), ZrCl\(_4\), ZrBr\(_4\), ZrI\(_4\)), Alkali and alkaline earth fluorozirconates (Li\(_4\)ZrF\(_7\), Li\(_3\)Zr\(_4\)F\(_{19}\), Na\(_7\)Zr\(_6\)F\(_{31}\), Na\(_5\)Zr\(_2\)F\(_{19}\), Li\(_2\)CaZrF\(_8\), K\(_2\)ZrF\(_6\), Cs\(_2\)ZrF\(_6\), Ba\(_2\)ZrF\(_8\)…)

- Ba\(_2\)ZrF\(_8\) – CN = 8
- Na\(_5\)Zr\(_2\)F\(_{13}\) – CN = 7
- Cs\(_2\)ZrF\(_6\) – CN = 6

Pauvert et al., Inorg. Chem, 2009
**Evolution of $\delta^{91}\text{Zr}$ with ZrF$_4$ content:**

Different kinds of Zr complexes with concentrations depending on %mol ZrF$_4$

- MF
- F free
- $F$ in $[\text{ZrF}_x]^{4-x}$
- $F$ bridging $[\text{ZrF}_x]^{4-x}$
$^{19}\text{F}$ & $^{91}\text{Zr}$ NMR in MF-ZrF$_4$ (M = Li, Na, K)

$^{19}\text{F}$ Chemical shifts measured in molten MF-ZrF$_4$ mixtures between -70 and -145ppm

$^{91}\text{Zr}$ Chemical shifts measured in molten MF-ZrF$_4$ mixtures between -70 and -145ppm

CN(Zr) = 7

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CEMHTI - Orléans EURACT-NMR Karlsruhe 27-29 Jan 2010
High temperature NMR: advantages and limits?

- In situ NMR observation of the different observable nuclei: selectivity
- NMR signature of complexes formed in the melt depending on the composition
  \[ {^{19}F, ^{35}Cl, ^{17}O} \]
  \[ {^{7}Li, ^{23}Na, ^{39}K, ^{89}Rb, ^{133}Cs} \]
  \[ {^{27}Al, ^{89}Y, ^{139}La, ^{91}Zr} \]
- Direct detection of oxides dissolution, precipitation and formation of oxifluorides

Paramagnetism

Observability I \( \neq 0 \)

Paramagnetic lanthanides: Ce, Nd, Gd...

Actinides: Th, U, ...

XAFS
XAFS experiments in molten fluorides

EXAFS
- Transmission mode
- Geometry of the sample and of the heating system
- Thickness / absorption
- Energy

Boron Nitride: > 16KeV Δ ~ 8mm
‘Double barrier cell’

(1) Pellet: sample + BN powder
- Pressed in a gloves box under dried argon (6Tons: 200μm)
- Proportion BN/salt set by the total X-Rays absorption coept
- The salt is « fixed » in a matrix of boron nitride

(2) PBN plates

Holes for screws

Pyrolitic BN plate

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XAFS experiments in molten fluorides

BL27B, PF - KeK (Tsukuba, Japon)

H. Matsuura
H. Akatsuka
A. Nezu
Y. Okamoto
M. Numakura

Vacuum chamber
Heating elements (1500°C)

~50 mm
~60 mm

Heating elements
(1500°C)

ZrF₄ – LiF (15 – 85 mol %)

Experimental
Simulation

Zr K edge (17.9 KeV)

Diffabs (Gif Sur Yvette, France)

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Molecular dynamics and XAFS calculations

Disordered systems:

Molecular Dynamic (calculation of atomic positions)
+ Feff Code (calculation of XAFS oscillations)


Polarizable Ion Model – Ionic liquids
Classical potential is the sum of 4 terms:
charge-charge/dispersion/ overlap repulsion/ polarization

EXAFS oscillations calculated from calculated positions
Comparison with experimental data

LiF-ZrF₄ (25 mol% ZrF₄), 700 °C
X-ray absorption in MF-ZrF₄

LiF-ZrF₄ (21 mol% ZrF₄), 700 °C

Zr K-edge (17998 eV)

blue: experiment
red: Feff calculations

FT

<table>
<thead>
<tr>
<th>System</th>
<th>(\overline{\text{CN}})</th>
<th>(d_{\text{Zr-F}}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-ZrF₄</td>
<td>6.8 ± 0.2</td>
<td>2.050</td>
</tr>
<tr>
<td>NaF-ZrF₄</td>
<td>6.5 ± 0.2</td>
<td>2.038</td>
</tr>
<tr>
<td>KF-ZrF₄</td>
<td>6.3 ± 0.2</td>
<td>2.026</td>
</tr>
</tbody>
</table>
First tests on MARS beam line
(SOLEIL Synchrotron)

Th, U
Conclusion

Structure / Dynamics

Diffusion coefficients measurements up to 1500K in molten fluorides

PFG NMR + Laser heating

Liquid probe 10mm 1H-19F / X (Bruker) / g = 55 G/cm

E. Naumann, F. Engelke – Bruker Karlsruhe
High Temperature Pulse Field Gradient NMR

Constraints:

- geometry: \( d(\text{crucible– rf coil}) \approx 2\text{mm} \)
- Temperature / gradients/ convection

![Diagram showing probe head, crucible, thermal shields, and coils with temperature ranges](image)

- Crucible: <150°C
- Thermal shield #1: <150°C
- Thermal shield #2: <40°C
- Thermal shield #3 (silica tube): <150°C
- Rf coil: <150°C
- Gradients coil: <40°C

References:
- V. Sarou-Kanian et al. PCCP (2009)
High Temperature Pulse Field Gradient NMR

\[ 19F D \times 10^9 \text{ (m}^2/\text{s)} \]

\[ T (\text{K}) \]

- Free F
- KF
- NaF
- Cryolite
- (LiF-NaF)_E
- LiF
- FLiNaK
- (ThF_4-LiF)_E
- (LnF_3-LiF)_E
- Bridging F

F⁻ in AlF_5^2⁻
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