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…

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…)

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

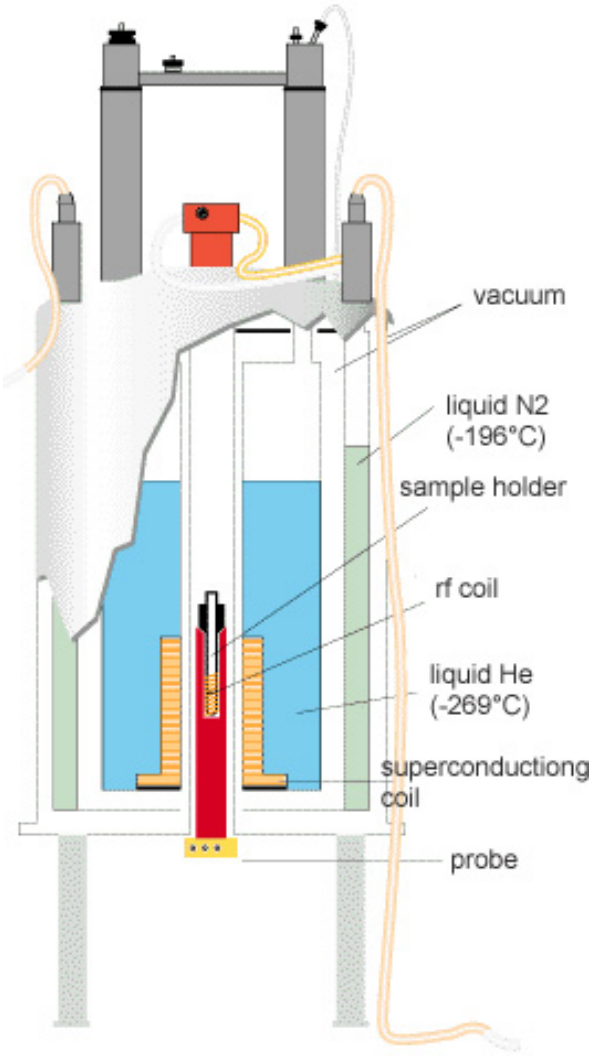
✓ gloves box

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	*XAFS*
« light » elements	**« heavy » elements**
^{19}F, ^{17}O, ^{7}Li, ^{23}Na, ^{39}K, ^{27}Al, …	**Th, U, Ln (La, Nd, Sm, Gd, Lu, Y..) Zr**
^{89}Y, ^{139}La, ^{91}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

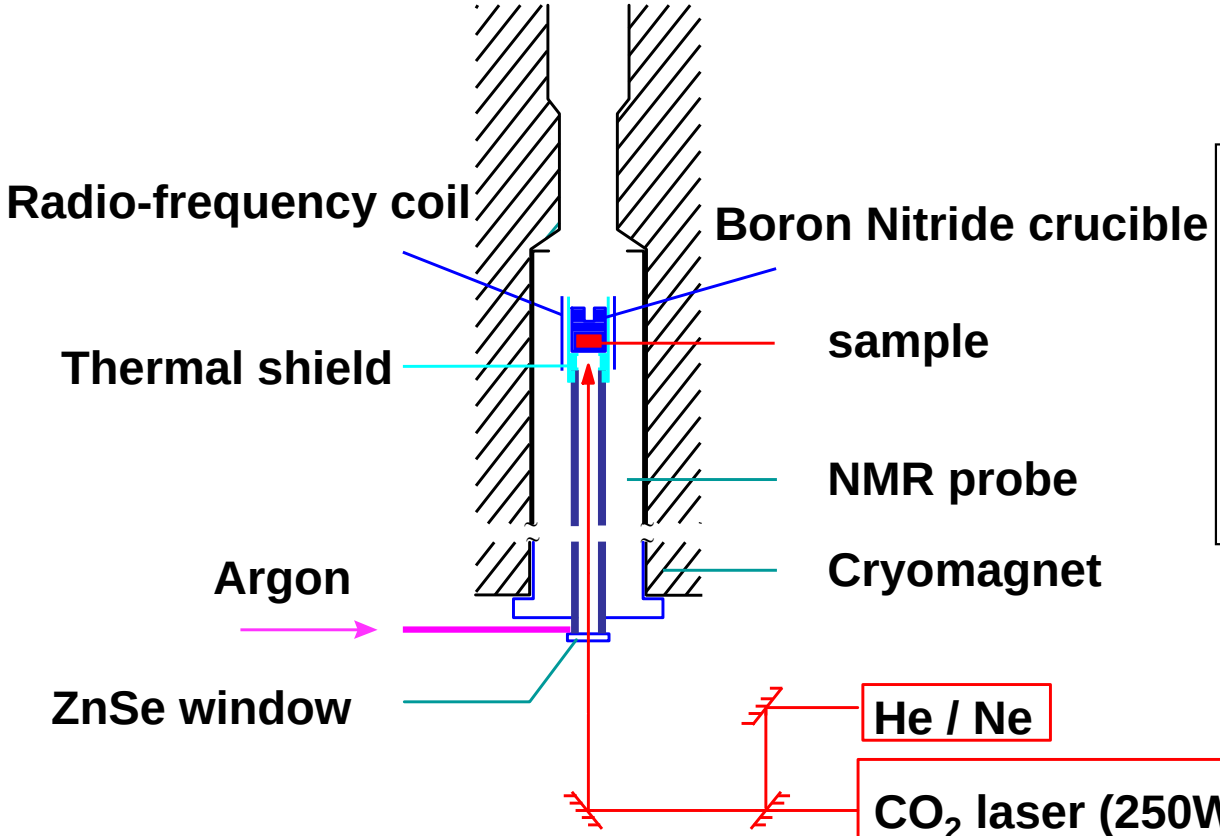
Heating system : adapted

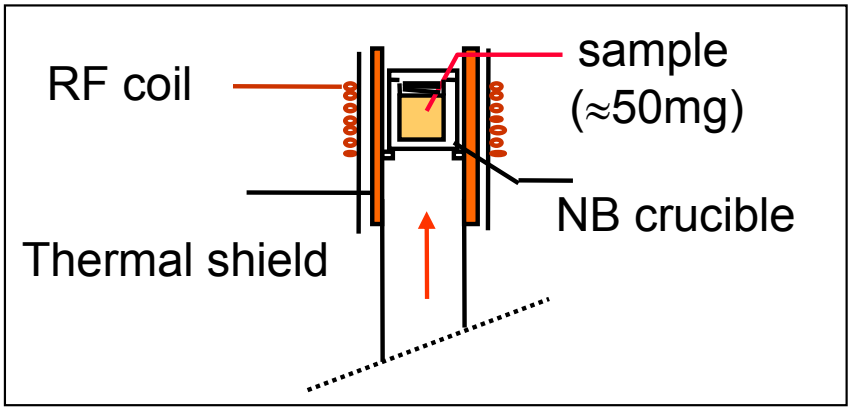
Sample : container compatible with NMR (no metal)

Solution…

Laser heating

in situ high temperature NMR



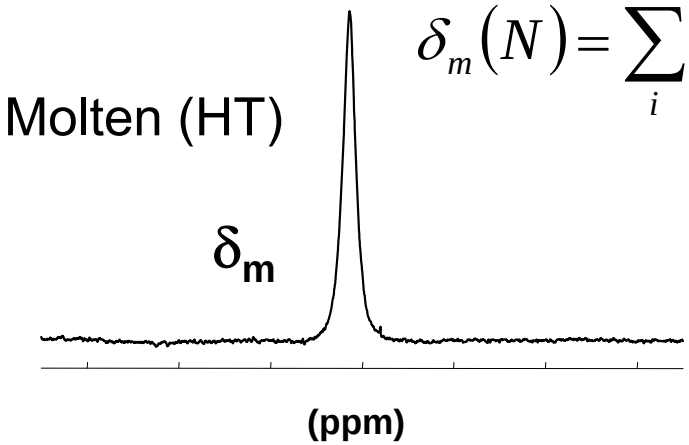


1300°C

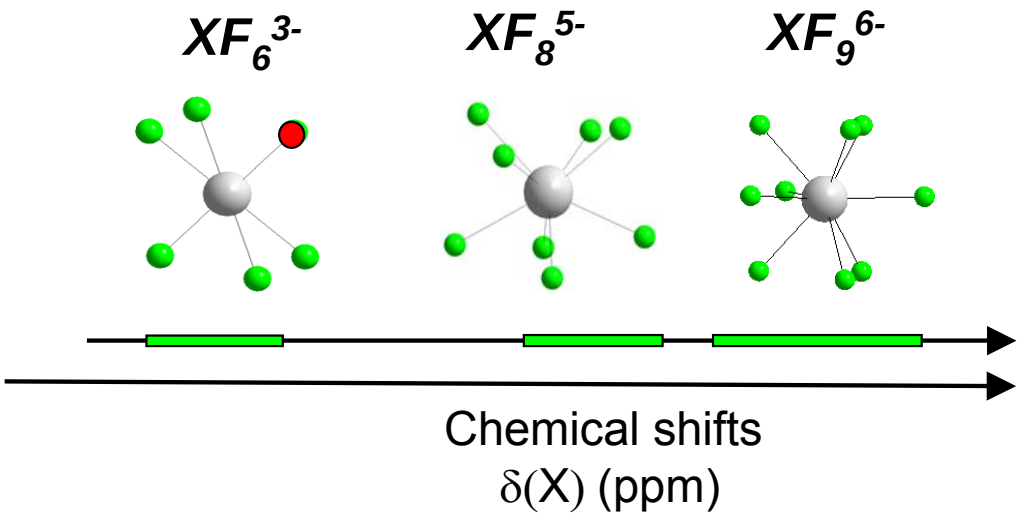
V.Lacassagne et al. J.Phys.Chem. B, 2002

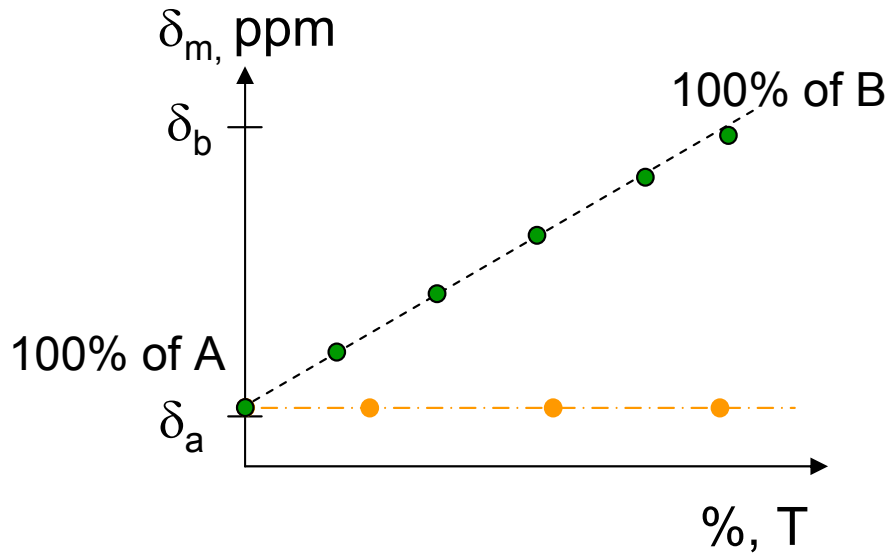
in situ High temperature NMR

$$\delta_m(N) = \sum_i X_{A_i}^N . \delta^N(A_i)$$



1 sharp and unique signal system in rapide exchange





2 species A and B with chemical shifts δa and δb

1 unique species A with chemical shift δa

C.Bessada et al. J.Fluor.Chem.(2008)

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 :
diamagnetic
The others have 1-7 unpaired ē :
paramagnetic

NMR in molten rare earth fluorides

Description of the systems **AF- LaF_3** and **AF- YF_3** , A=Li, Na, K

In situ NMR measurements of the different nuclei of the melt

^{19}F	Anion point of view	Free F, connectivity
^{139}La, ^{89}Y	Cation point of view Ln^{3+}	Coordination, complexes
^{7}Li, ^{23}Na, ^{39}K	Alkali point of view	Complexes, conductivity

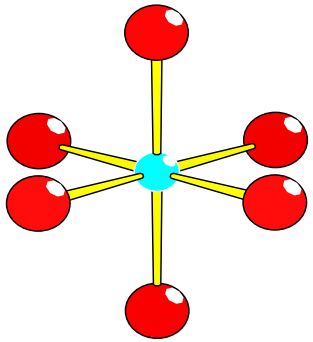
Chemical shifts scales established from known cristallographic structures of solids compounds (coordination, bridged and non bridged fluorines, symetry…)

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 $(LnX_6)^{3-}$

- In **binaries** melts :

  Medium range order generated by bridging fluorine between octahedra (compositions rich in LnX3)

G.Papatheodorou & al.

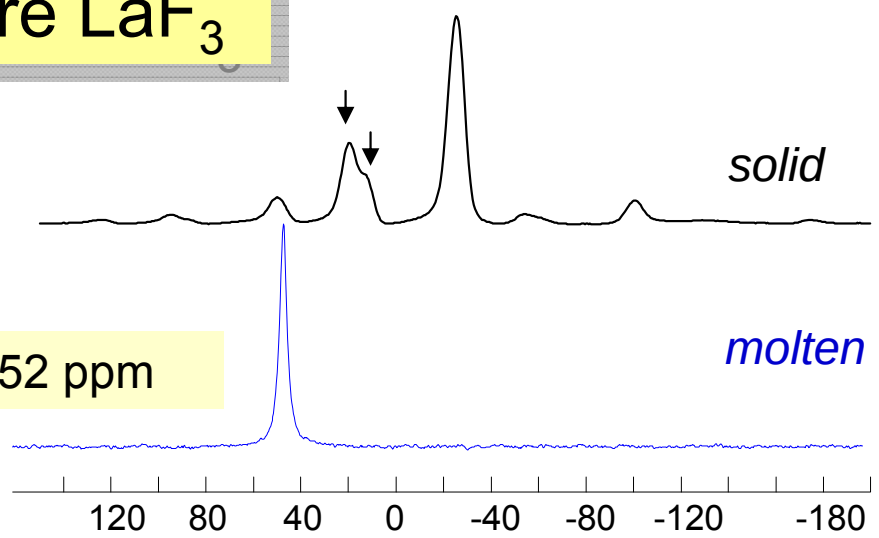
Raman HT

- X (LnF_3) ≤ 0.25 LnF_6^{3-} Octahedra
- X (LnF_3) > 0.25 LnF_6^{3-} Octahedra distorded and connected (edges sharing)

Pure LaF_3

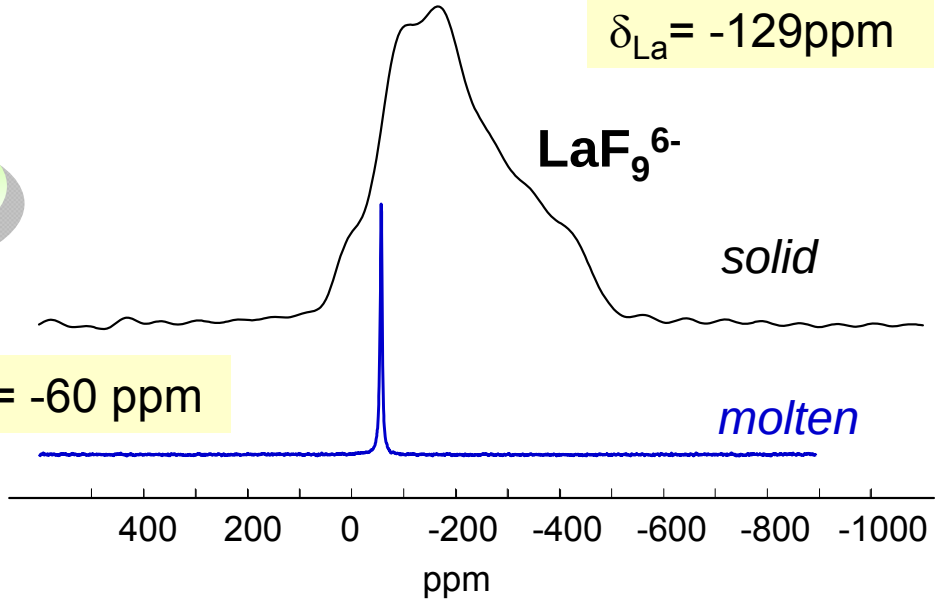
Pure LaF_3

^{19}F



δ_F = 52 ppm

^{139}La



δ_{La}= -129ppm

δ_{La}= -60 ppm

LaF_3 cristallographic structure

- Trigonal structure $[LaF_9]^{6-}$
- 3 different F sites

T_m LaF_3 = 1493°C

LaF_x^{3-x} ?

Pure LaF_3

LaF_3 δ in ppm	Solid RT	Molten 1500°C
$\delta^{19}F$	20,12, -25	52
$\delta^{139}La$	-129	-60

$[LaF_9]^{6-}$

Evolution of the anion and cation local structure on melting :

Shift towards more positive values ⇨ deshielding

Slight increase of the covalent part of the iono-covalent La-F bond

⇨ *Confirmed by EXAFS measurements : decrease of the La-F bond*

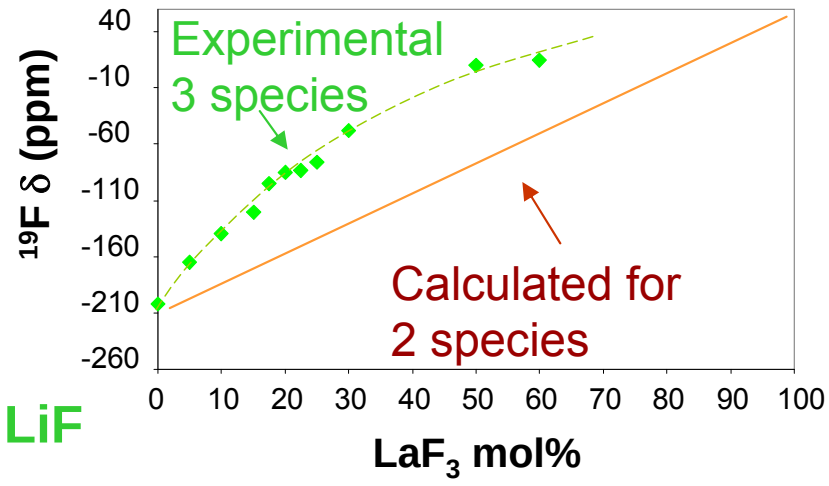
$AF-LaF_3$ A=Li, Na, K, Rb…

NMR

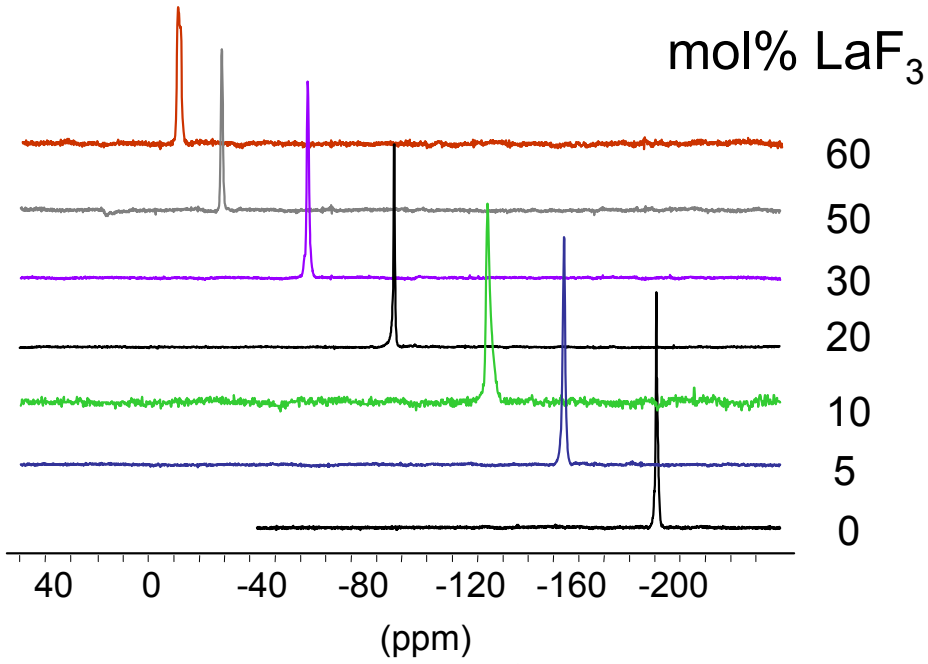
MF-LaF_3 M=Li, Na, K, Rb

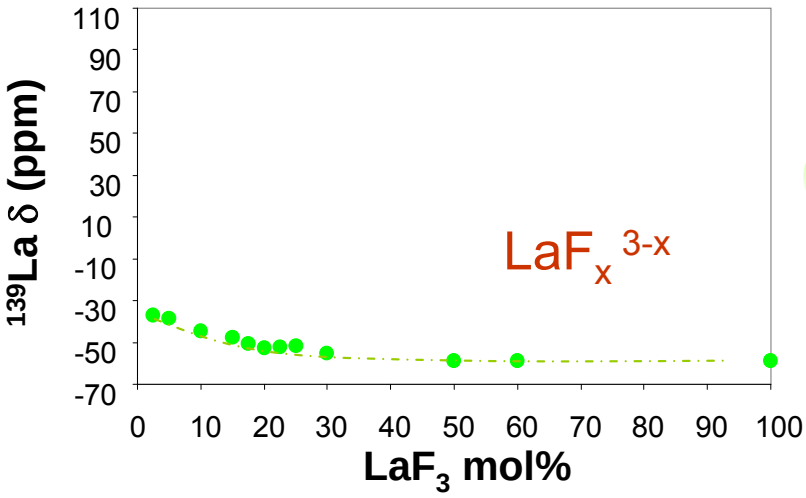
$LiF-LaF_3$

LaF_3

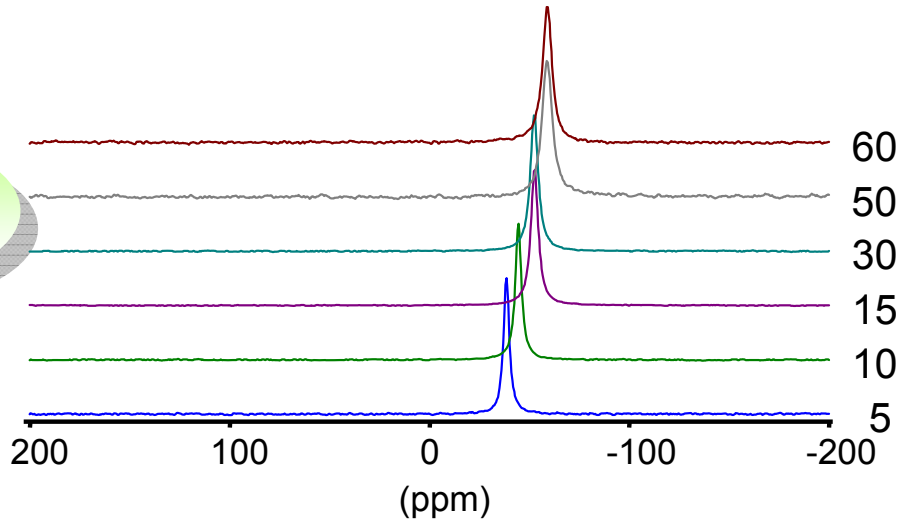


^{19}F





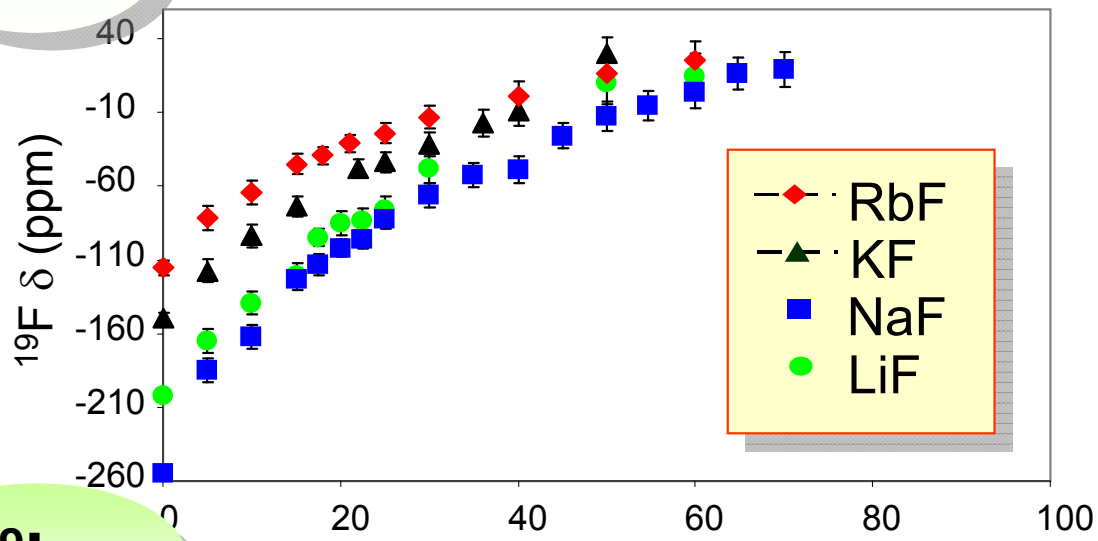
^{139}La



A.-L. Rollet et al.PCCP (2008)

MF-LaF_3 M=Li, Na, K, Rb

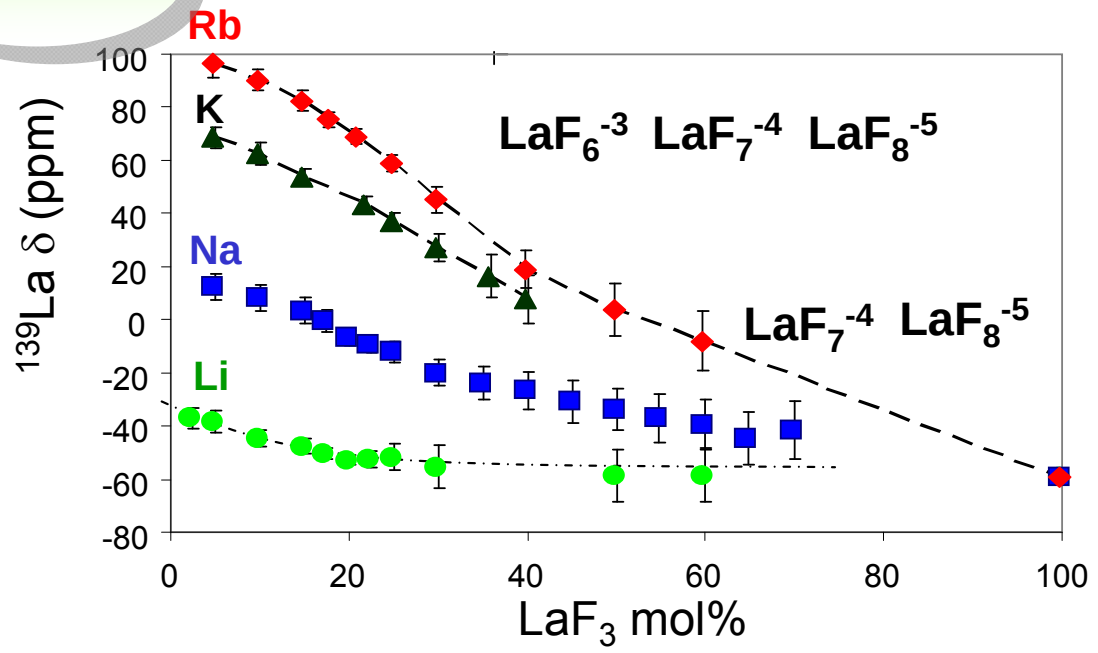
^{19}F



monotonous and no linear evolution
3 different environments

MF → LaF_3
F free
F in $[LaF_x]^{3-x}$
F bridging $[LaF_x]^{3-x}$

^{139}La



2 domains

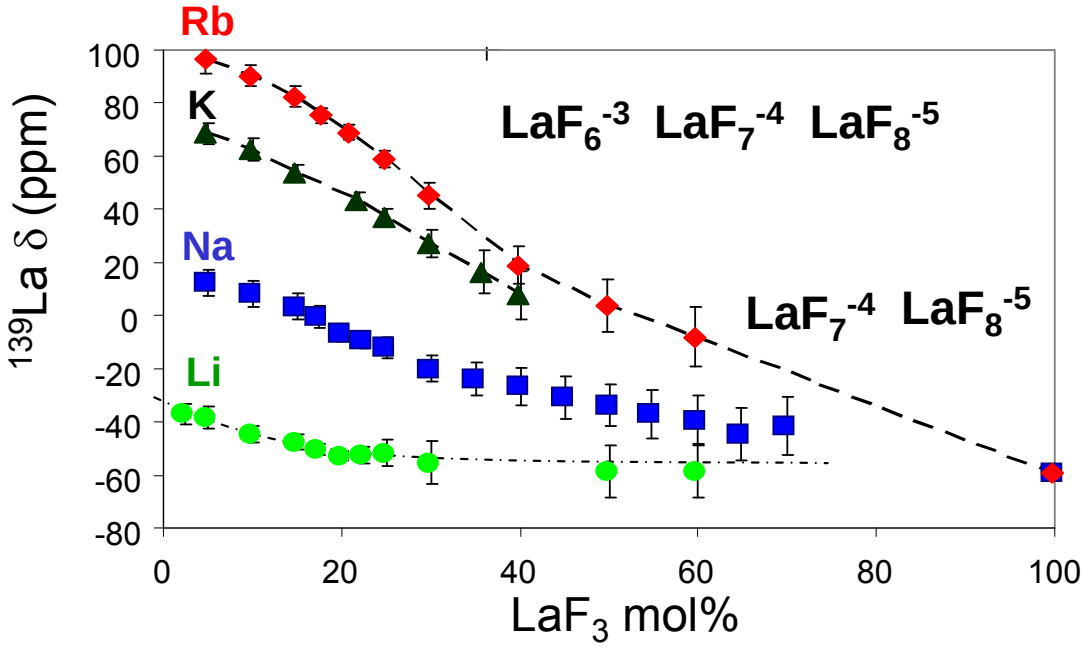
3 to 2 species depending on LaF_3 composition
strong influence of the alkali

⇩

LaF_6^{3-} LaF_7^{4-} LaF_8^{5-}

^{139}La

MF-LaF_3 M=Li, Na, K, Rb



The environment of the Lanthanum changes with the salt composition

% LaF_3 ↗ δ ↘ δ_{La} (LaF_3) CN_{La} ↗

⇨ 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 ↗ F-bridging ↘ La coordination ↘
- Effect of the electronegativity of the alkali

Not possible to set predictive physical properties of AF- LaF_3 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, ν = 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**

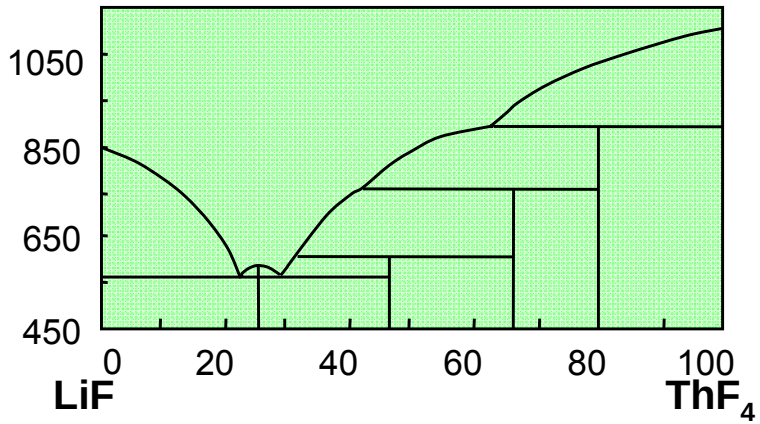
- *Radioactive : safety constraints (new development of specific containers)*

↪ **ZrF_4-MF**

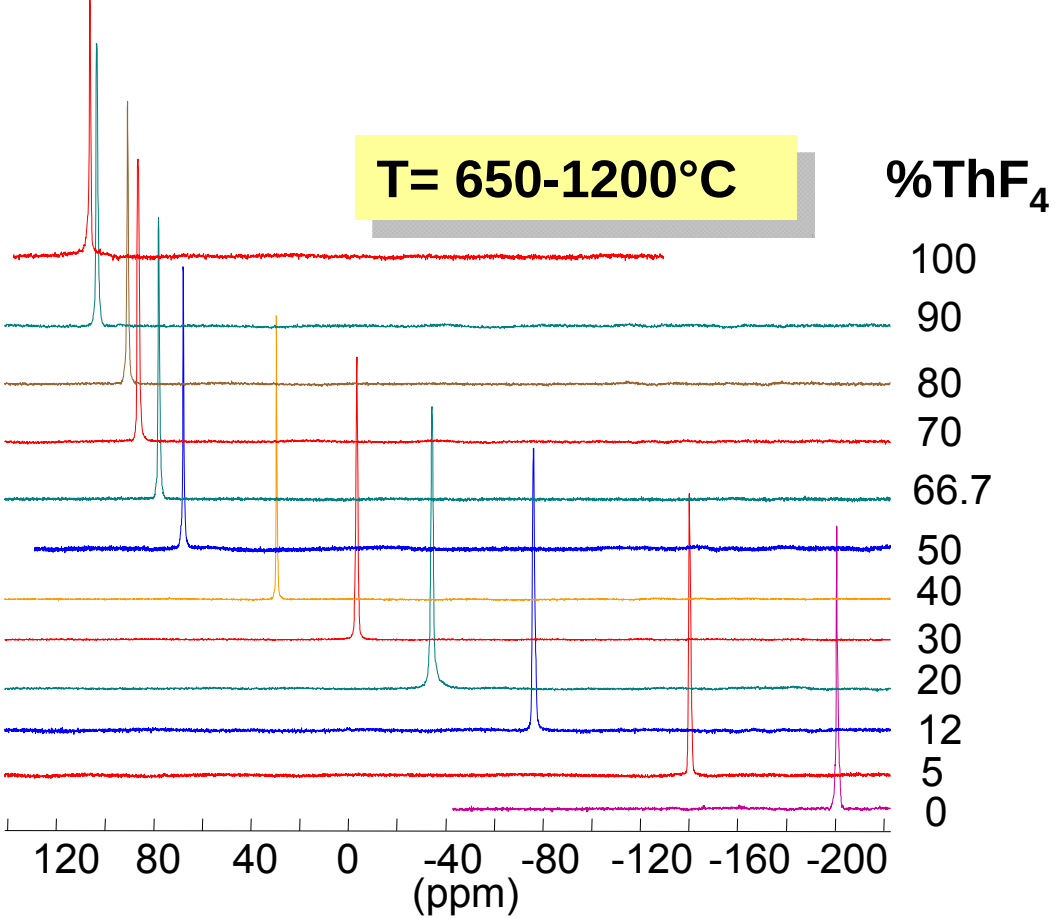
$LiF\text{-}ThF_4$

^{19}F

$LiF\text{-}ThF_4$ Phase diagram

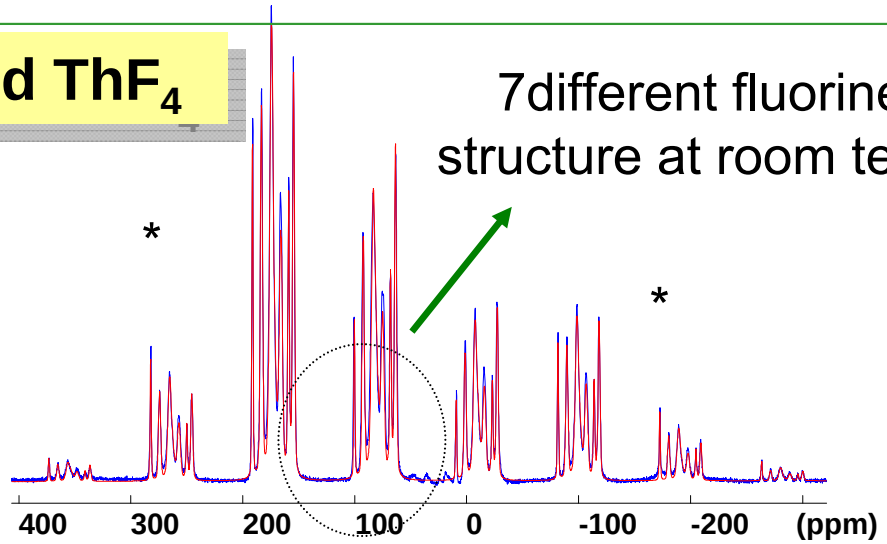


T= 650-1200°C

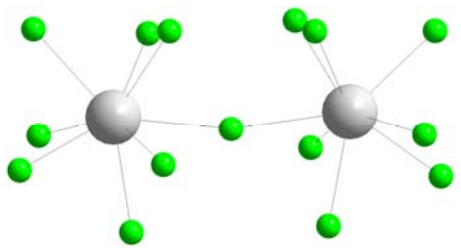


solid ThF_4

7different fluorines in the structure at room temperature

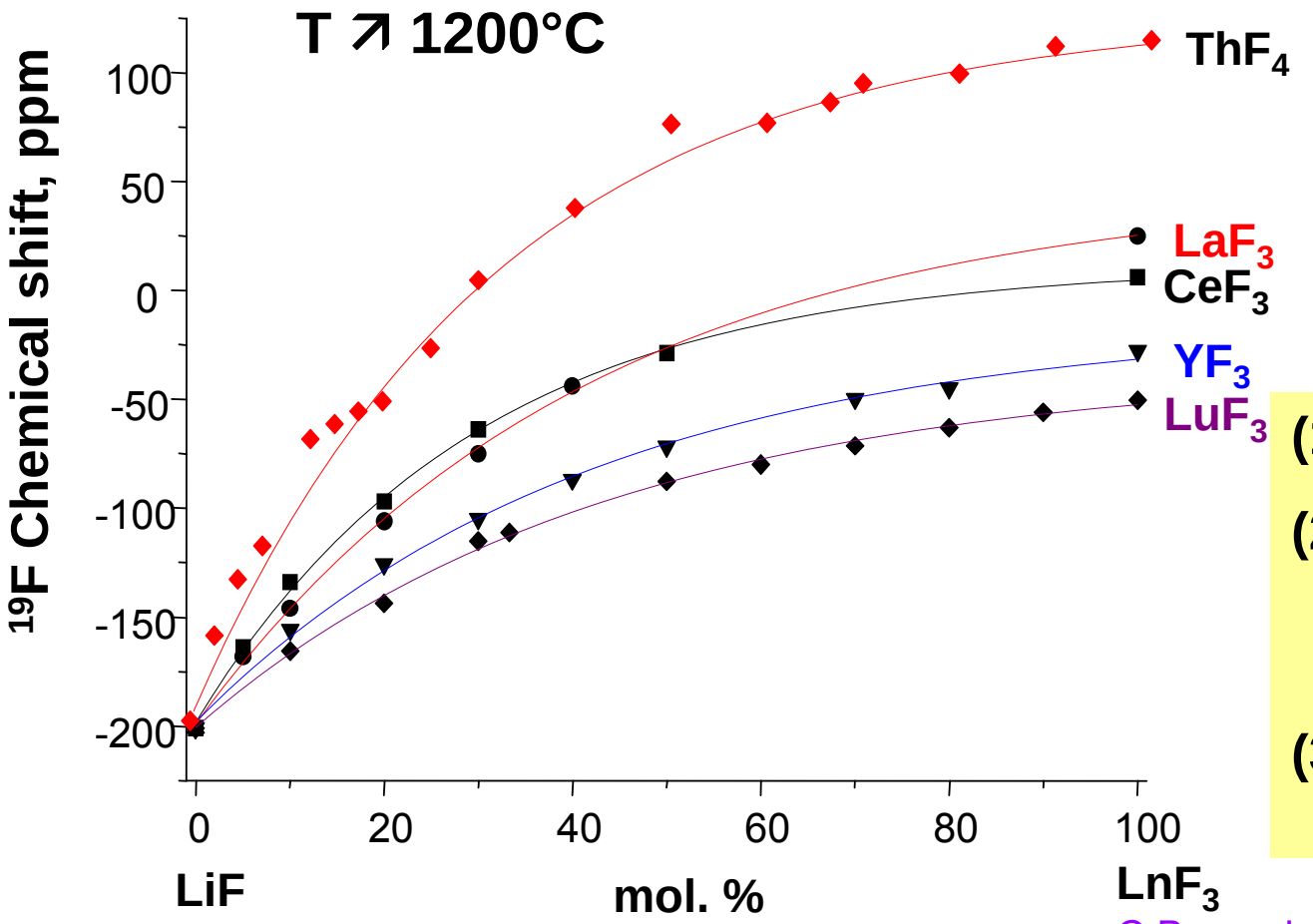


$\delta^{19}F$: 53 to 101 ppm



Comparison of ^{19}F chemical shifts evolutions in $LiF\text{-}ThF_4$ and $LiF\text{-}LnF_3$ (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

%ThF_4

C.Bessada et al. JNM 2007, J.Fluor.Chem. 2008
A.L.Rollet et al. PCCP, 2008

Application to ZrF_4-MF systems (M=Li, Na, K)

zirconium

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)

750 MHz spectrometer (Bruker)

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

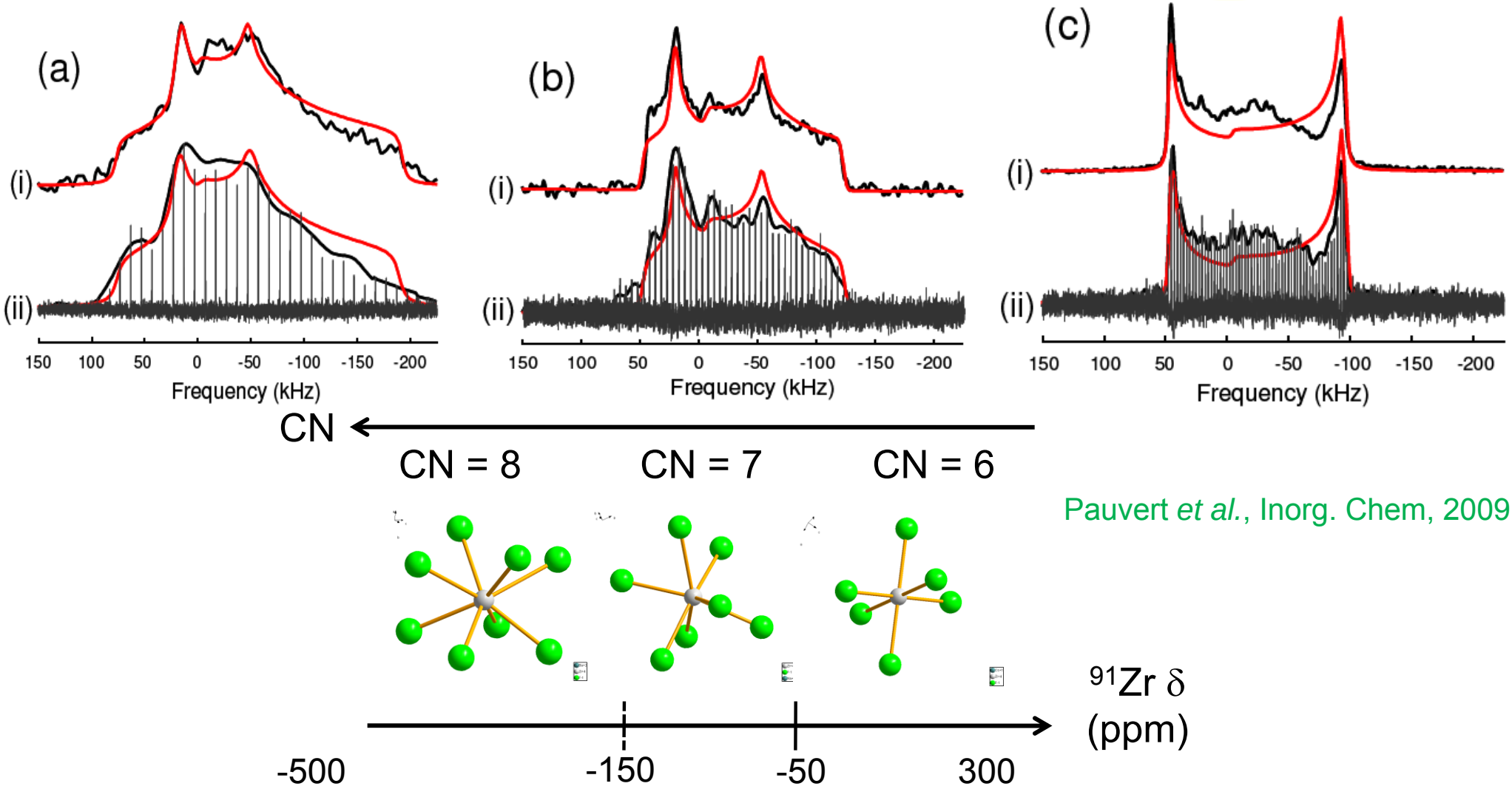
^{91}Zr solid-state NMR at 17.6 and 30.0 Tesla

Zirconium halides (ZrF_4, $ZrCl_4$, $ZrBr_4$, ZrI_4), Alkali and alkaline earth fluorozirconates (Li_4ZrF_7, $Li_3Zr_4F_{19}$, $Na_7Zr_6F_{31}$, $Na_5Zr_2F_{19}$, Li_2CaZrF_8, K_2ZrF_6, Cs_2ZrF_6, Ba_2ZrF_8…)

Ba_2ZrF_8 – CN = 8

$Na_5Zr_2F_{13}$ – CN = 7

Cs_2ZrF_6 – CN = 6

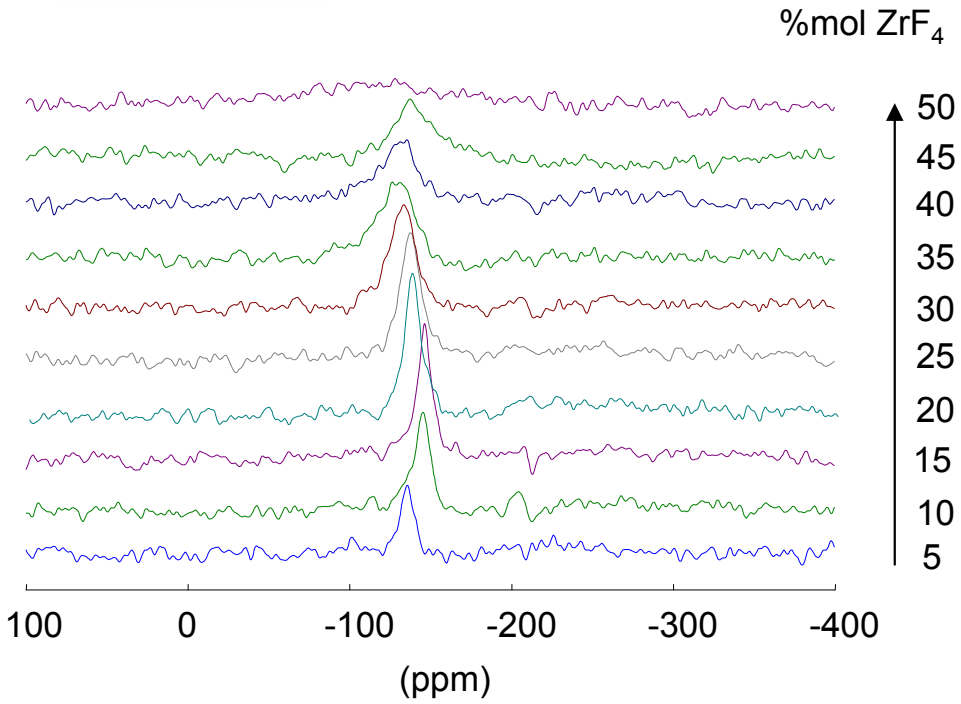


Pauvert *et al.*, Inorg. Chem, 2009

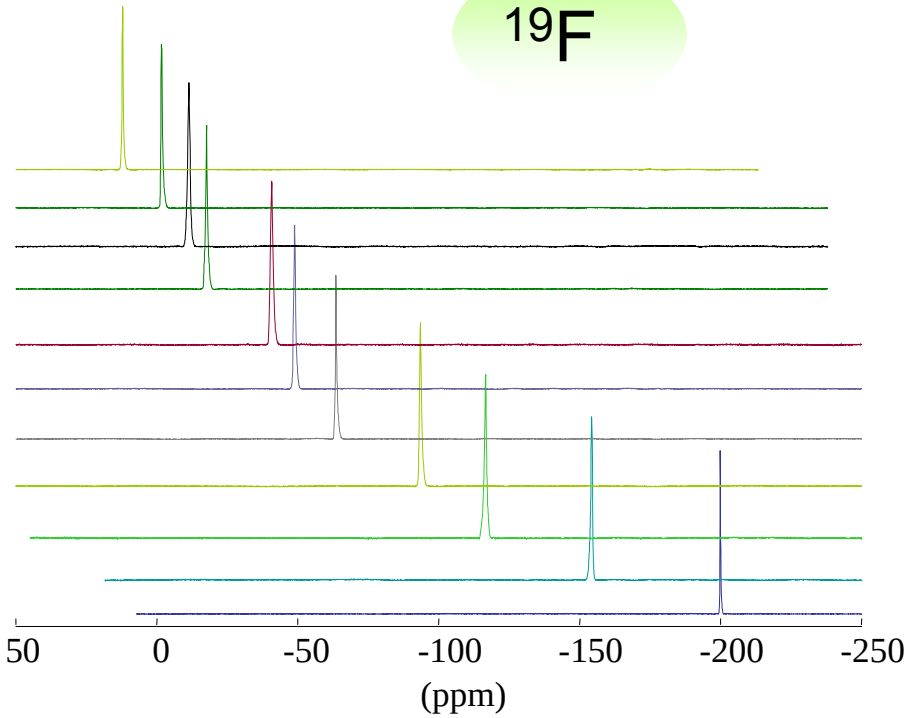
HT ^{91}Zr and ^{19}F NMR in molten $LiF\text{-}ZrF_4$

(600 - 880 °C)

^{91}Zr (9.6 T) $LiF\text{-}ZrF_4$



^{19}F



^{19}F : same evolution as in Ln systems:

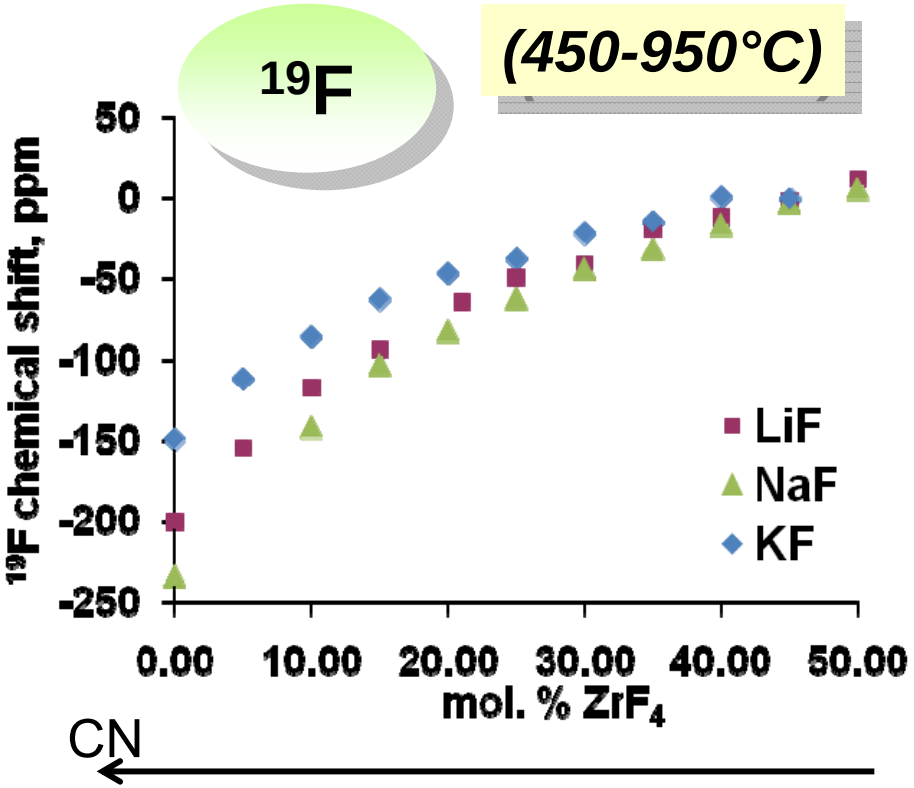
Evolution of $\delta^{91}Zr$ with ZrF_4 content:

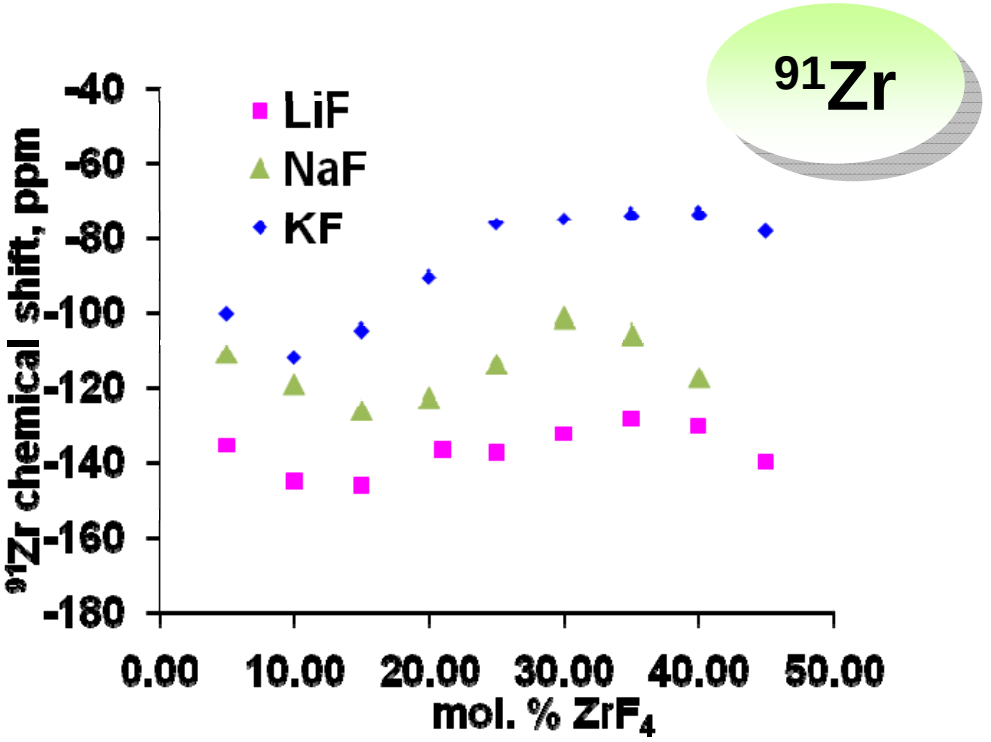
Different kinds of Zr complexes with concentrations depending on %mol ZrF_4

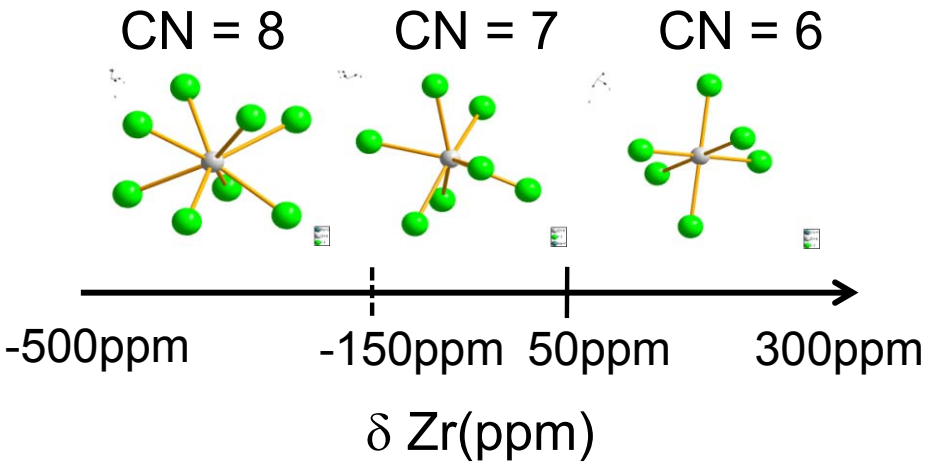
MF → ZrF_4

F free
F in $[ZrF_x]^{4-x}$
F bridging $[ZrF_x]^{4-x}$

^{19}F & ^{91}Zr NMR in MF-ZrF_4 (M = Li, Na, K)







^{91}Zr Chemical shifts measured in molten MF-ZrF_4 mixtures between -70 and -145ppm

CN(Zr) = 7

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

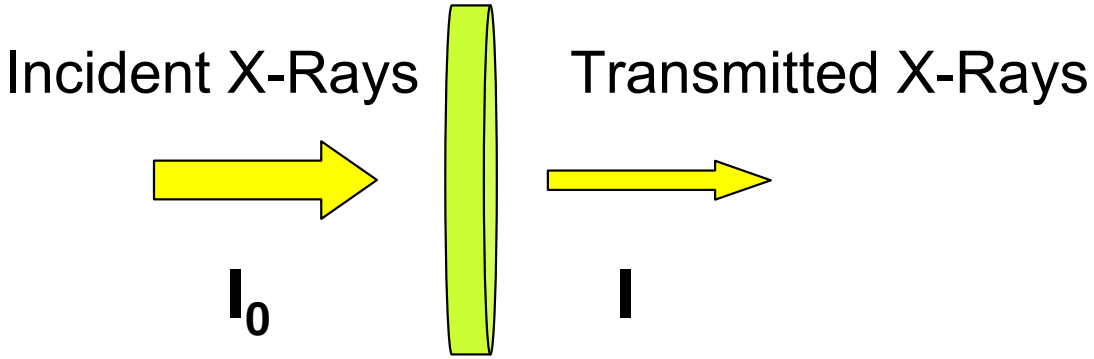
Observability I $\neq 0$

Paramagnetic lanthanides : Ce, Nd, Gd…

Actinides : Th, U, …

➡ XAFS

XAFS experiments in molten fluorides

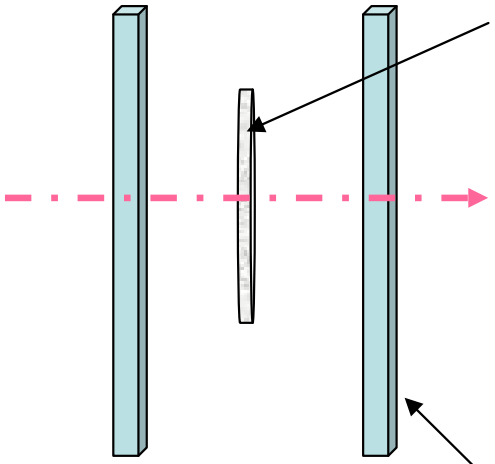


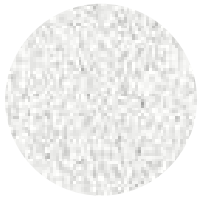
EXAFS

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

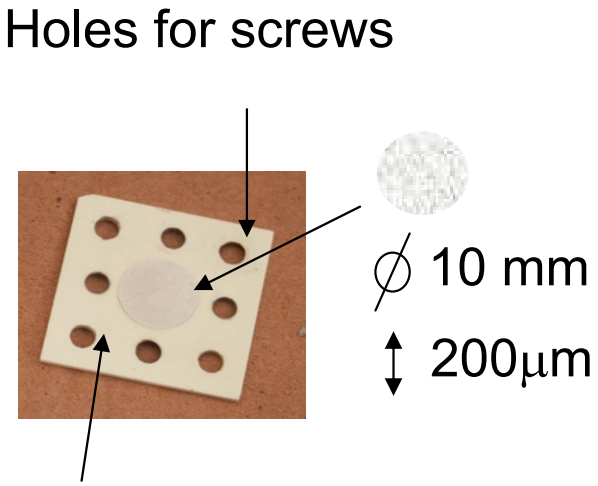
Boron Nitride : > 16KeV $\Delta \sim 8mm$

‘Double barrier cell'

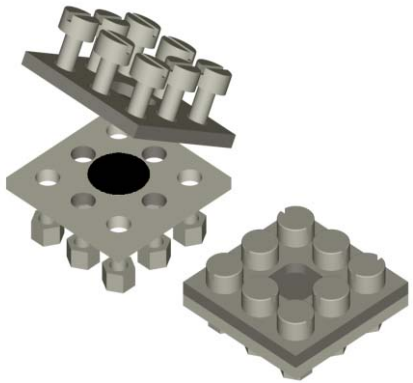




- Pressed in a gloves box under dried argon (6Tons : 200µm)
- Proportion BN/ salt set by the total XRays absorption coeft
- The salt is « fixed » in a matrix of boron nitride



cell

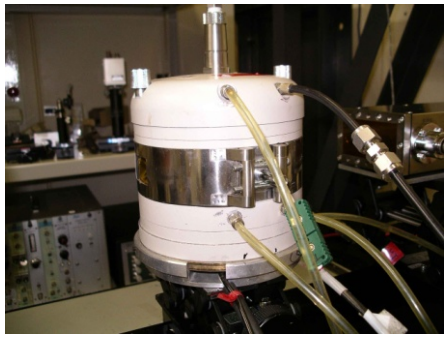


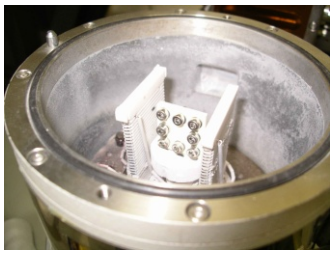
25 mm

XAFS experiments in molten fluorides

Zr K edge (17.9 KeV)

BL27B, PF - KeK (Tsukuba, Japon)

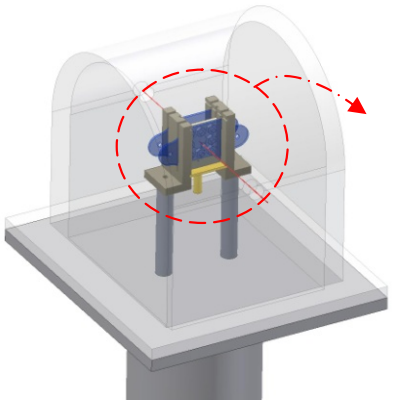




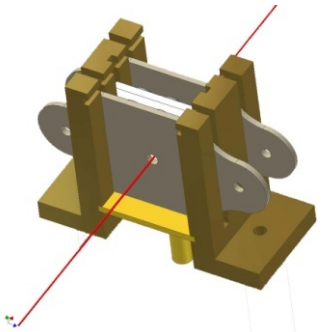
H.Matsuura
H.Akatsuka Tokyo Institute of Technology
A. Nezu

Y.Okamoto
M.Numakura JAEA

Diffabs (Gif Sur Yvette, France)

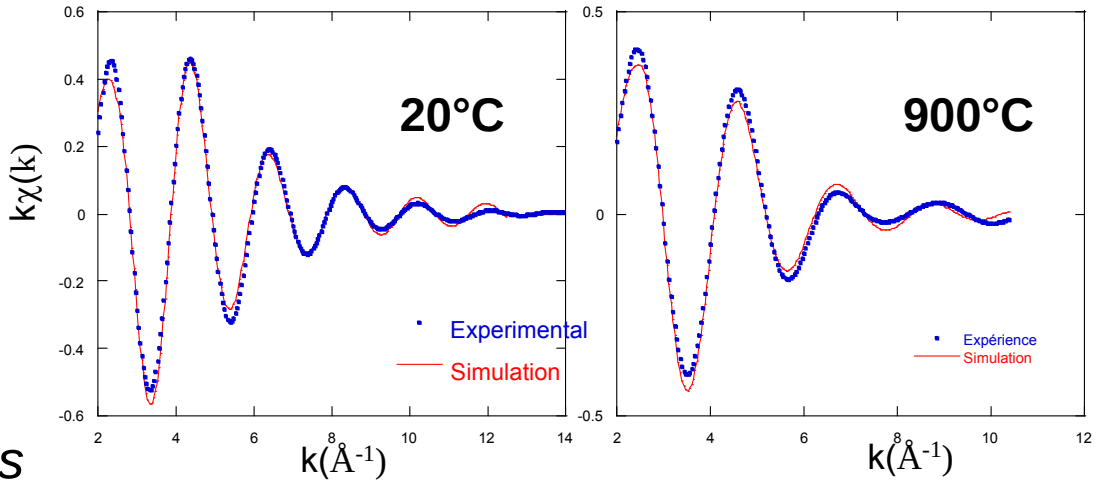


Vaccum chamber
He



Heating elements
(1500°C)

ZrF_4 – LiF (15 – 85 mol %)



Molecular dynamics and XAFS calculations

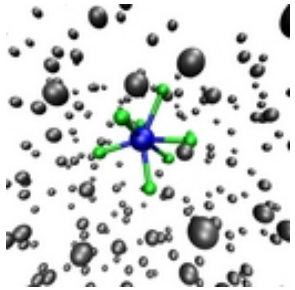
Disordered systems:

Y. Okamoto, NIM A (2004)

Molecular Dynamic (calculation of atomic positions)

+

Feff Code (calculation of XAFS oscillations)



PIM code

Polarizable Ion Model – **Ionic liquids**

Classical potential is the sum of 4 terms:

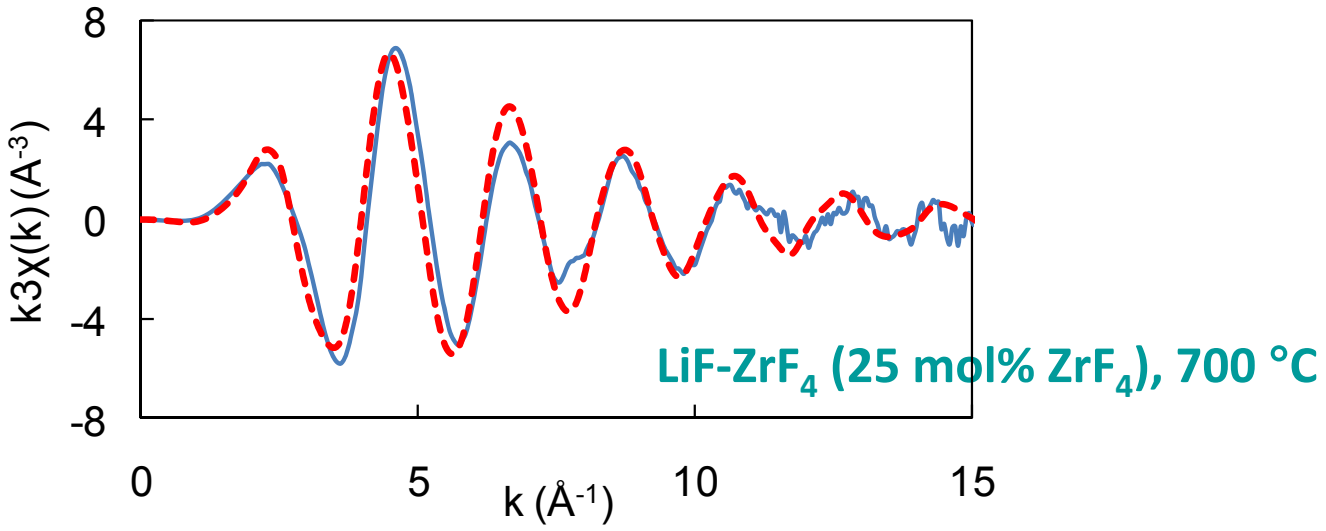
charge-charge/dispersion/ overlap repulsion/ polarization

Feff code

χ (k)

EXAFS oscillations calculated from calculated positions

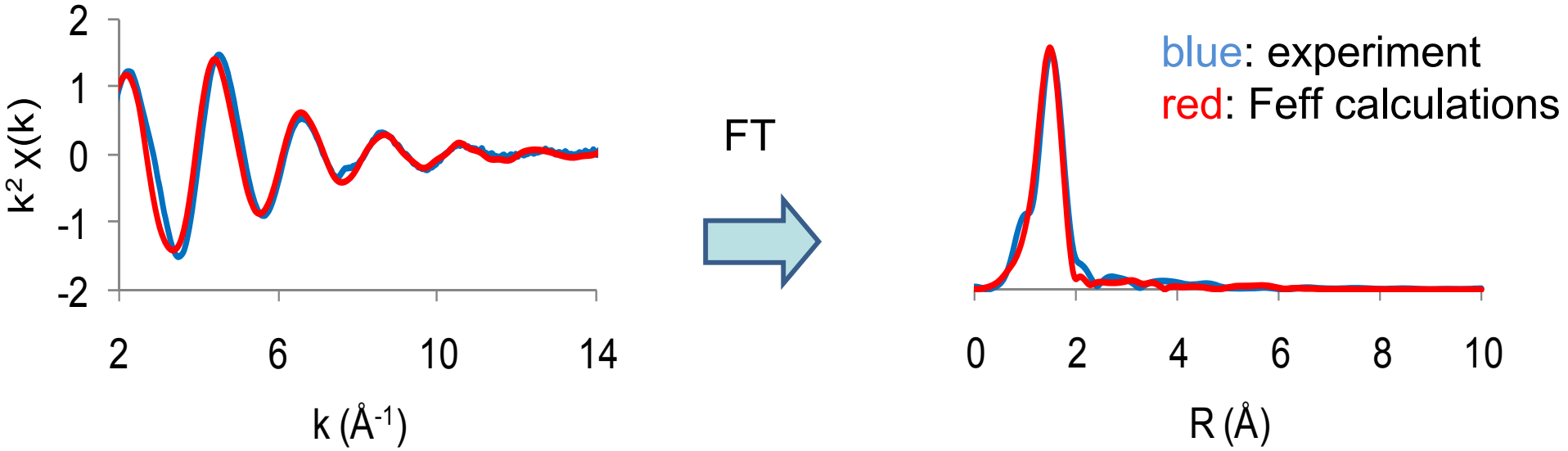
Comparison with experimental data

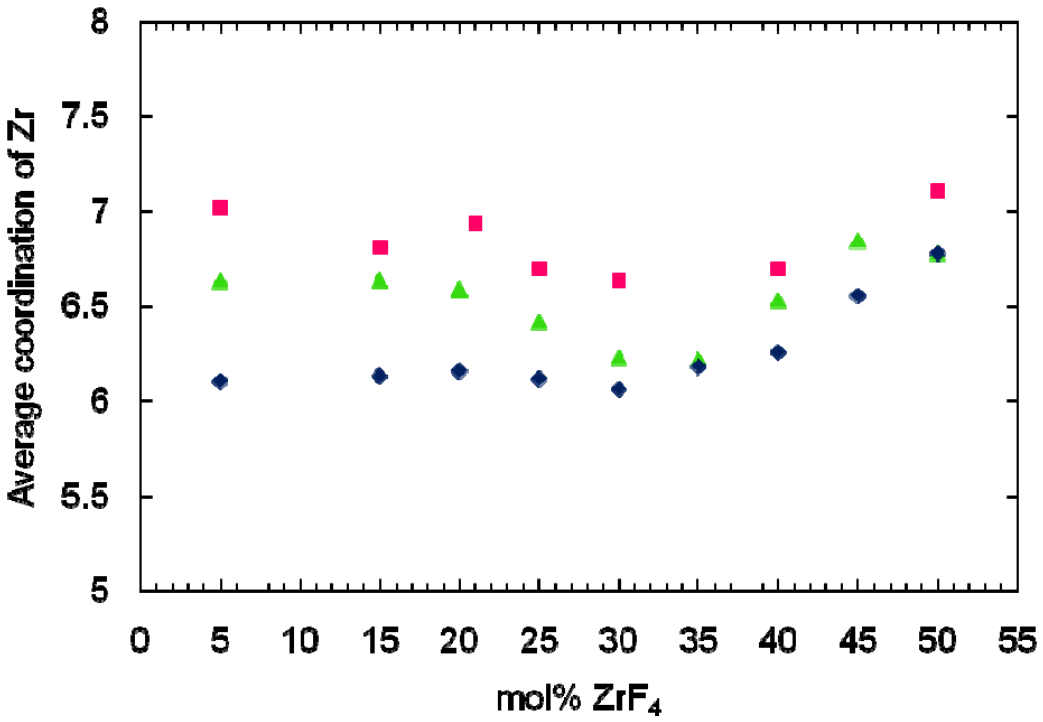


X-ray absorption in MF-ZrF_4

Zr K-edge (17998 eV)

$LiF-ZrF_4$ (21 mol% ZrF_4), 700 °C

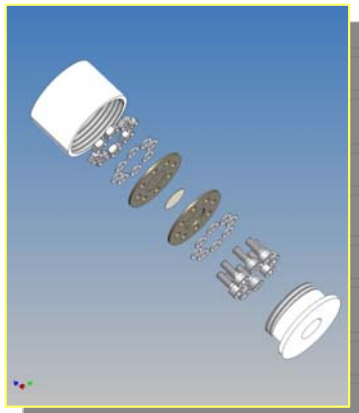


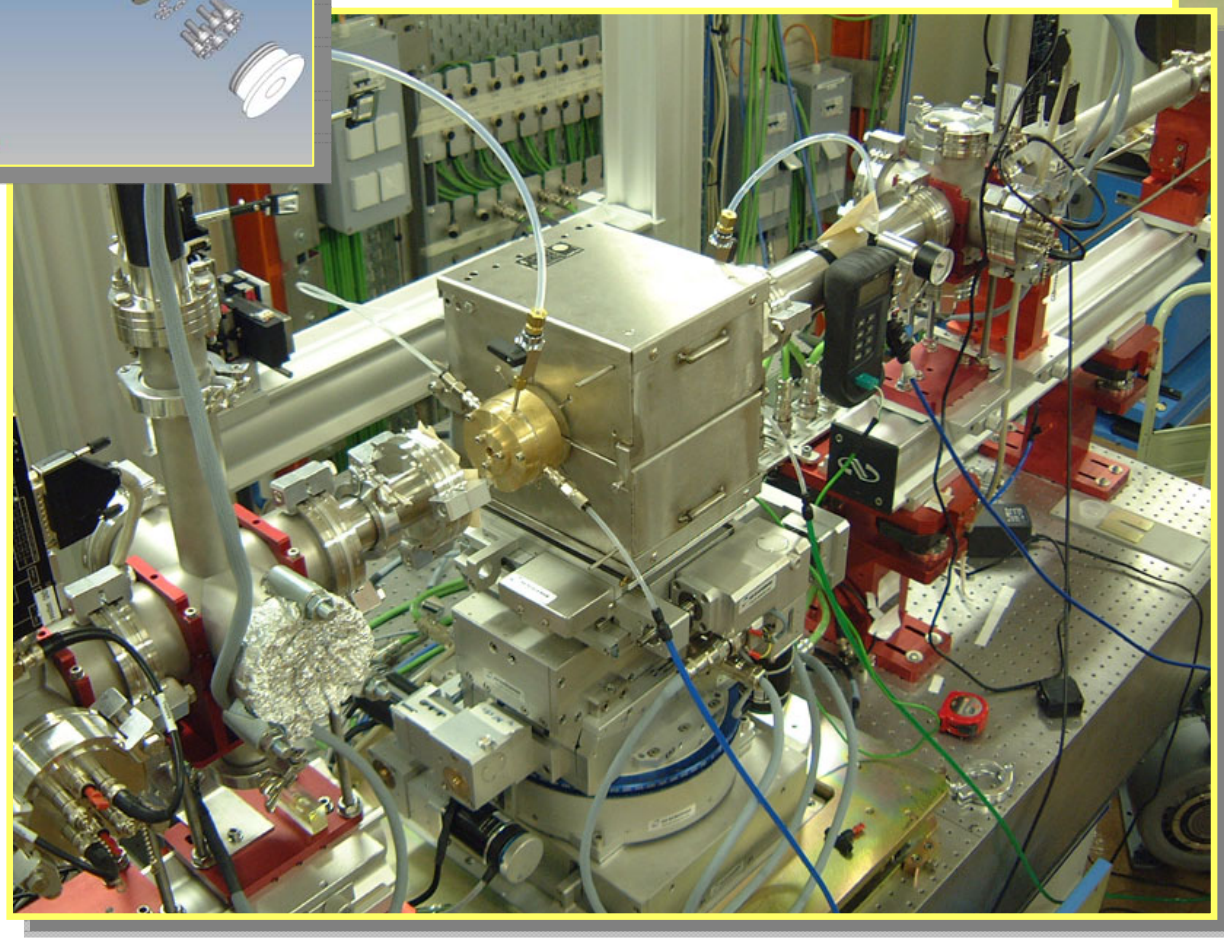


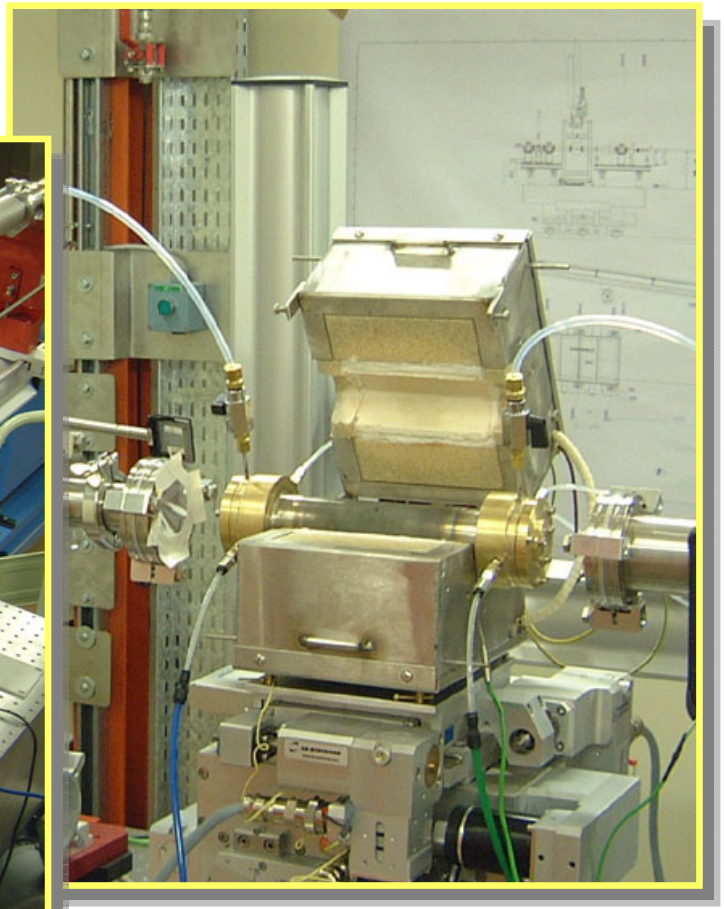
- $LiF-ZrF_4$
- $NaF-ZrF_4$
- $KF-ZrF_4$

System	$\overline{CN}$	$\overline{d_{Zr\_F}}$ (Å)
$LiF-ZrF_4$	6.8 ± 0.2	2.050
$NaF-ZrF_4$	6.5 ± 0.2	2.038
$KF-ZrF_4$	6.3 ± 0.2	2.026

First tests on MARS beam line (SOLEIL Synchrotron)







Th, U

Conclusion

Structure / Dynamics

Diffusion coefficients measurements
up to 1500K in molten fluorides

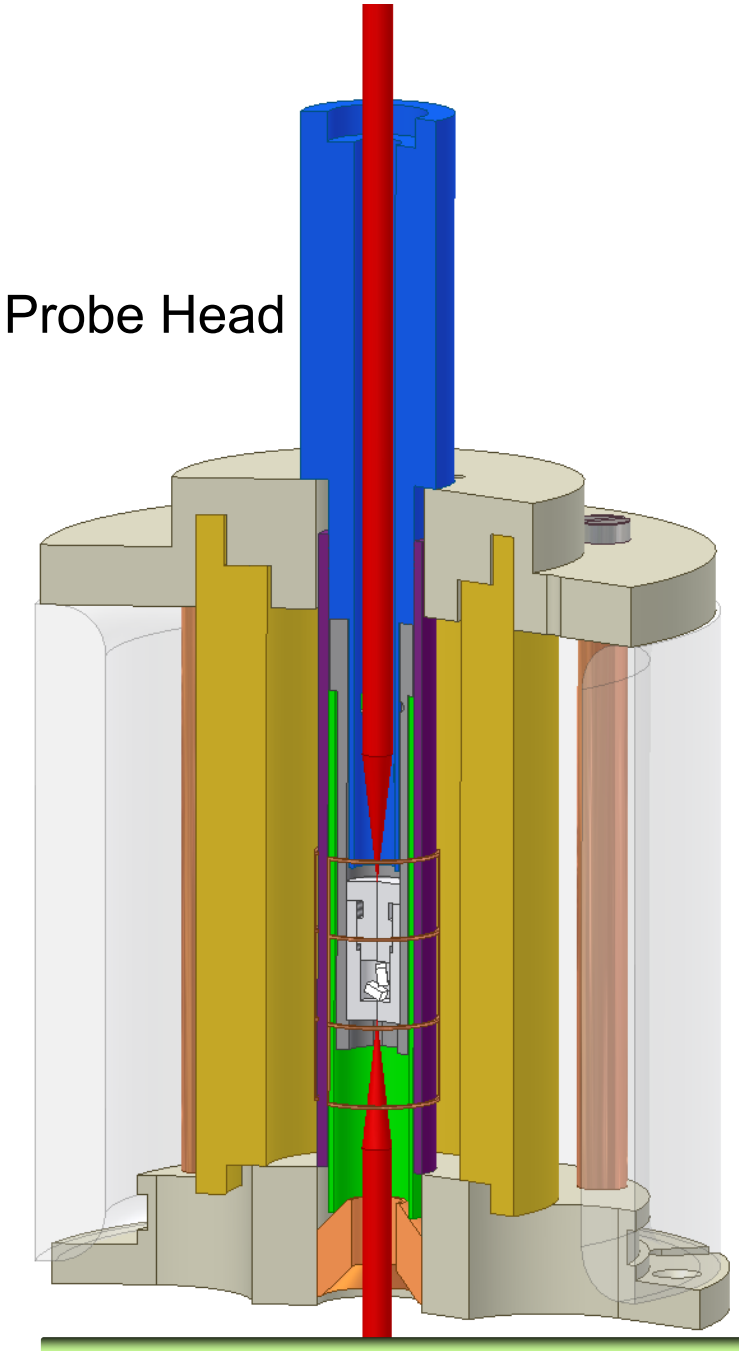
PFG NMR + Laser heating

BRUKER

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

E. Naumann, F. Engelke – Bruker Karlsruhe

High Temperature Pulse Field Gradient NMR



A.-L. Rollet et al.Inorg.Chem (2009)
V.Sarou-Kanian et al PCCP (2009)

Constraints :

- geometry : d(crucible– rf coil) ≈ 2mm)
- Temperature / gradients/ convection

crucible

Thermal shield #1

Thermal shield #2

Thermal shield #3 (silica tube)

Rf coil

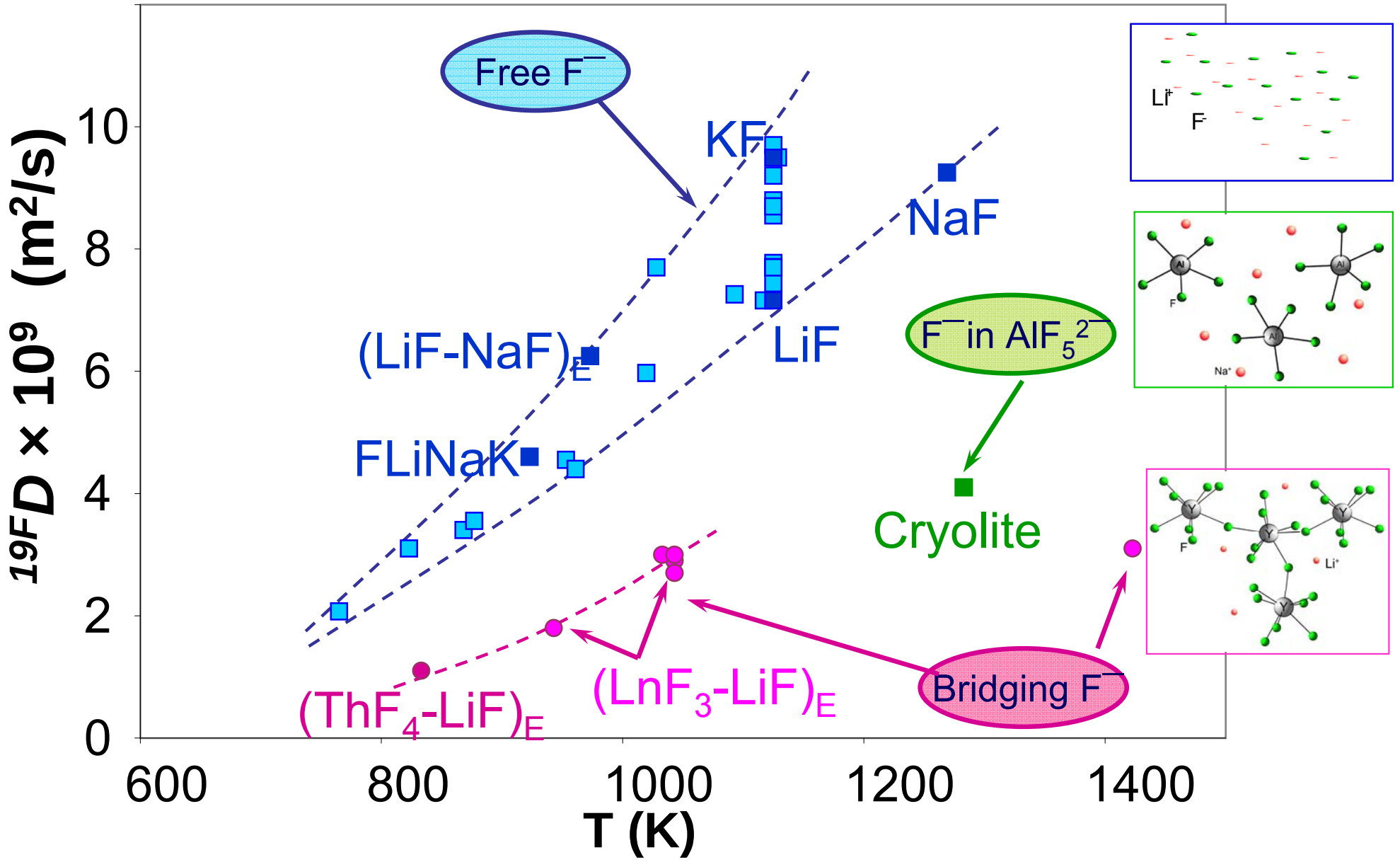
Gradients coil

↑ 1200°C

<150°C

<40°C

High Temperature Pulse Field Gradient NMR



Acknowledgments

Aydar Rakhmatullin

Vincent Sarou-Kanian

Olivier Pauvert

Didier Zanghi

Mallory Gobet

Dominique Massiot

Franck Fayon

(CEMHTI, Orléans)

Anne Laure Rollet

Mathieu Salanne

Christian Simon

(PECSA, UPMC, Paris)

Paul Madden
(Dept Mater, Oxford)

Haruaki Matsuura

Masahiko Numakura

(RLNR, Tokyo Inst Tech Japan)

Yoshiro Okamoto
(JAEA, Japan)