Mesures de Coefficients de Diffusion par Résonance Magnétique Nucléaire

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Atelier diffusion dans les oxydes amorphes solides et liquides
13 Septembre 2018, Orléans

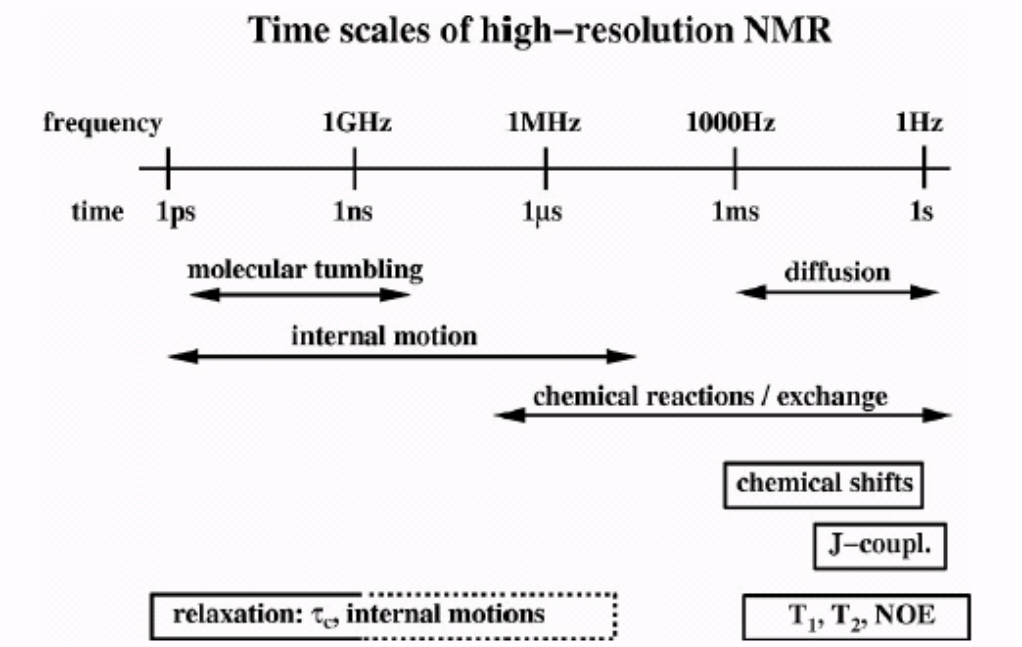
Résonance Magnétique Nucléaire

→Matériaux liquides et solides / ordonnés ou désordonnés
→ Structure locale à l'échelle atomique (Å-nm)
→ La dynamique (Å-mm)
→ Imagerie (IRM)

+Non invasive
+Non destructive
+Sélectivité isotopique
+Volumique
−Peu sensible (mMol)
−Echantillon généralement diamagnétique (~ ~~métaux de transition~~)

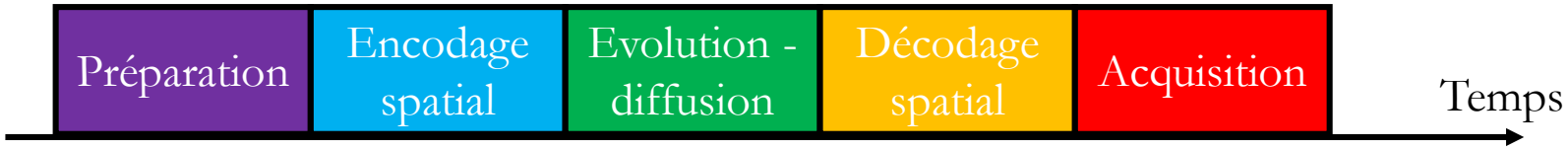
Dynamique par RMN

- **Relaxométrie** (mesures des temps de relaxation RMN – T_1, T_2, $T_{1\varrho}$)
  - Sonde les échelles de temps caractéristiques des mouvements atomiques, moléculaires (intra/inter)
- **Expérience d'échange**
  - Sonde le changement d'environnement structural d'atomes entre deux instants
- Mesures du **coefficient d'auto-diffusion**
  - Sonde la dynamique translationnelle des atomes/molécules

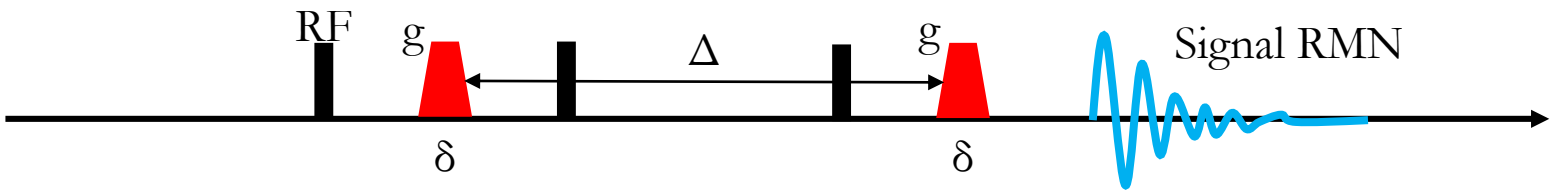


… et bien d'autres

Expérience de diffusion par RMN



Impulsions radiofréquences : manipulation de l'aimantation
Impulsion de champ gradient : encodage spatial de l'aimantation



Un exemple de séquence RMN pour la mesure du coefficient de diffusion

Obtention du coefficient de diffusion *D*

L'expression analytique de l'atténuation de l'écho S(2τ) est telle que:

$$S(2\tau) = S(0)\cdot\exp(-2\tau/T_2)\cdot\exp\left(-\gamma^2 D\, g^2\,\delta^2\,(\Delta-\delta/3)\right)$$

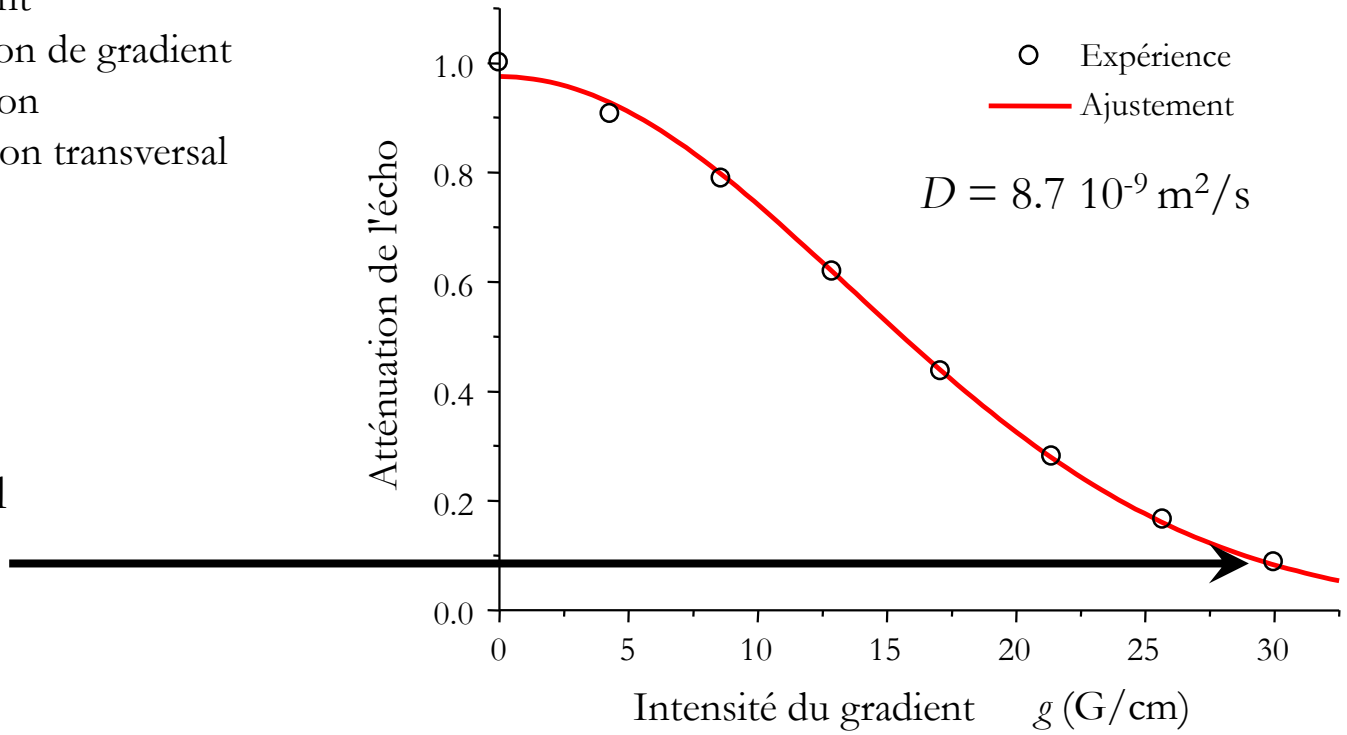
S(0) : Signal de l'écho sans gradients
D : coefficient d'auto-diffusion (m^2/s)
γ : rapport gyromagnétique
g : intensité du gradient
δ : durée de l'impulsion de gradient
Δ : période de diffusion
T_2 : temps de relaxation transversal

Expérimentalement

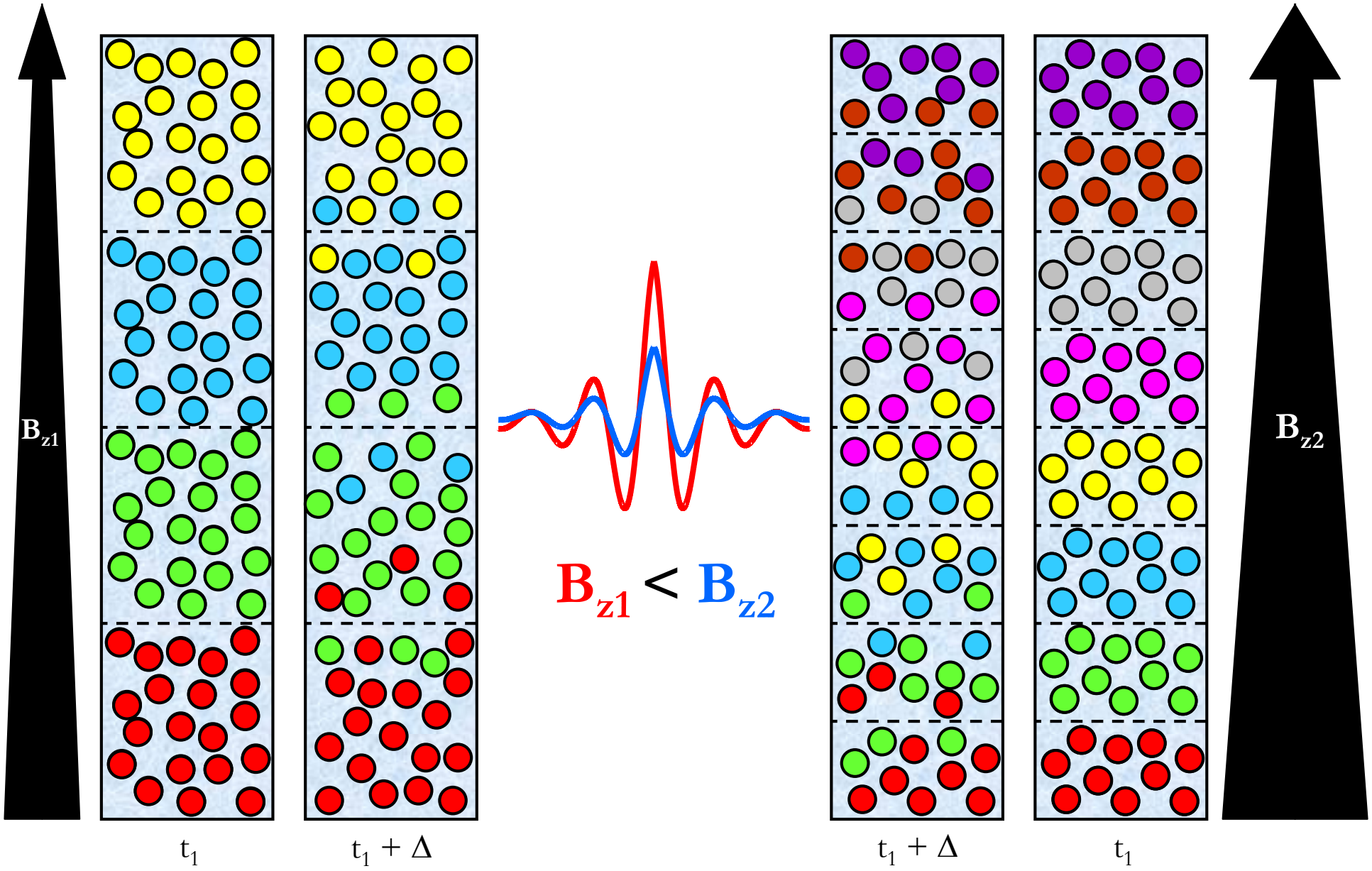
✓Mesure l'atténuation de l'écho pour plusieurs valeurs de gradients (≥ 8)

✓Le gradient le plus élevé atténue le signal d'un facteur 10

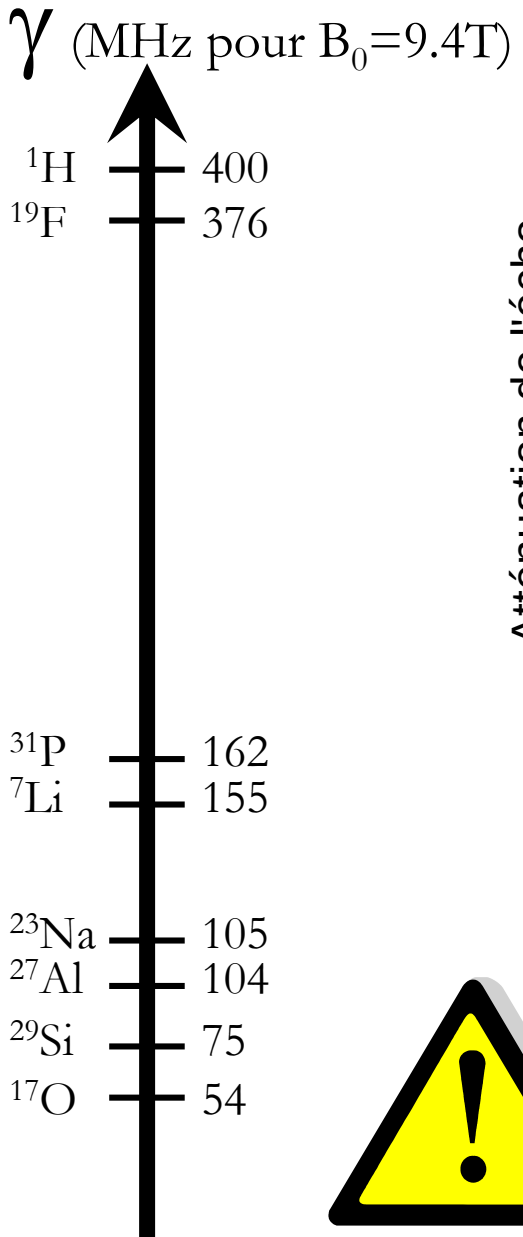
✓Calcul de *D* par ajustement

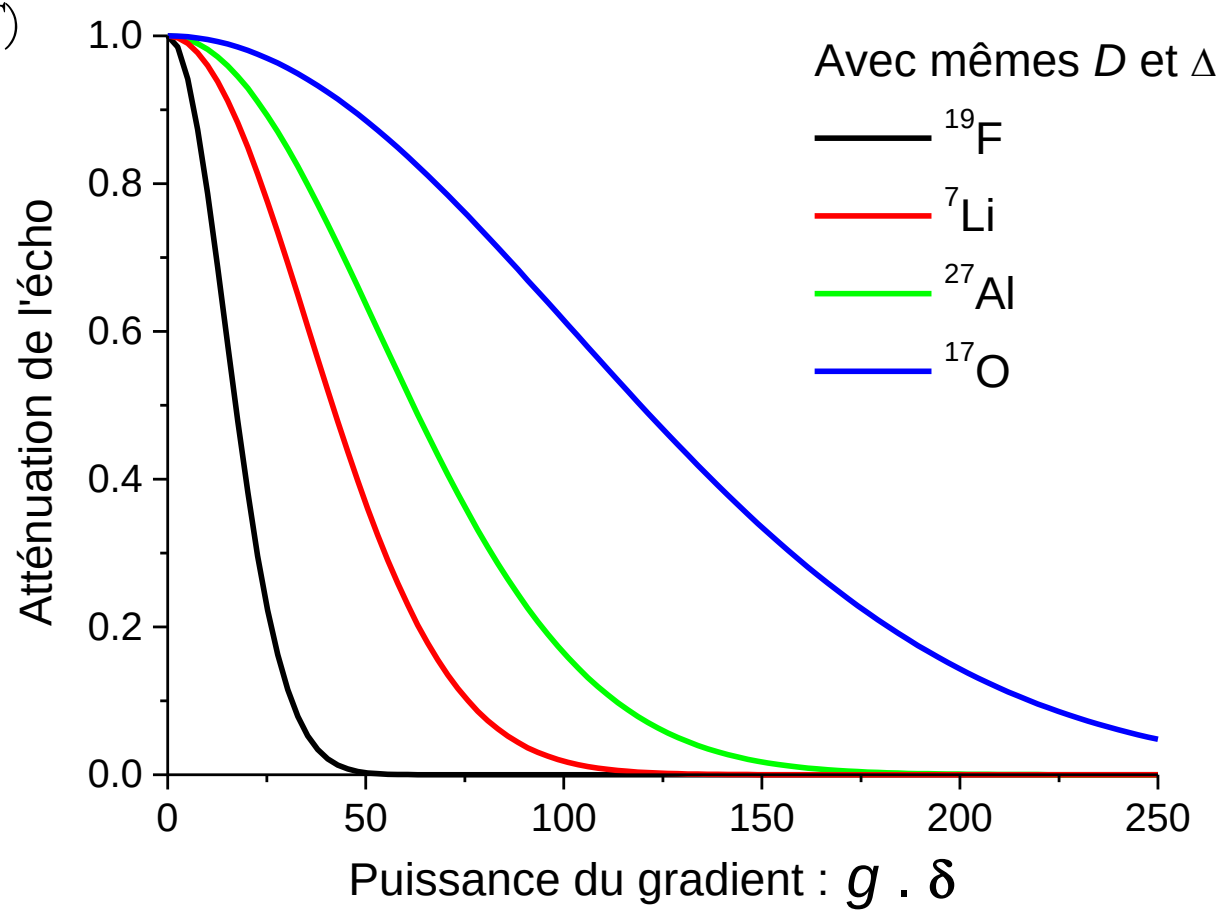


Importance de l'intensité du gradient *g*



Importance de γ





Le signal détecté dépend également:

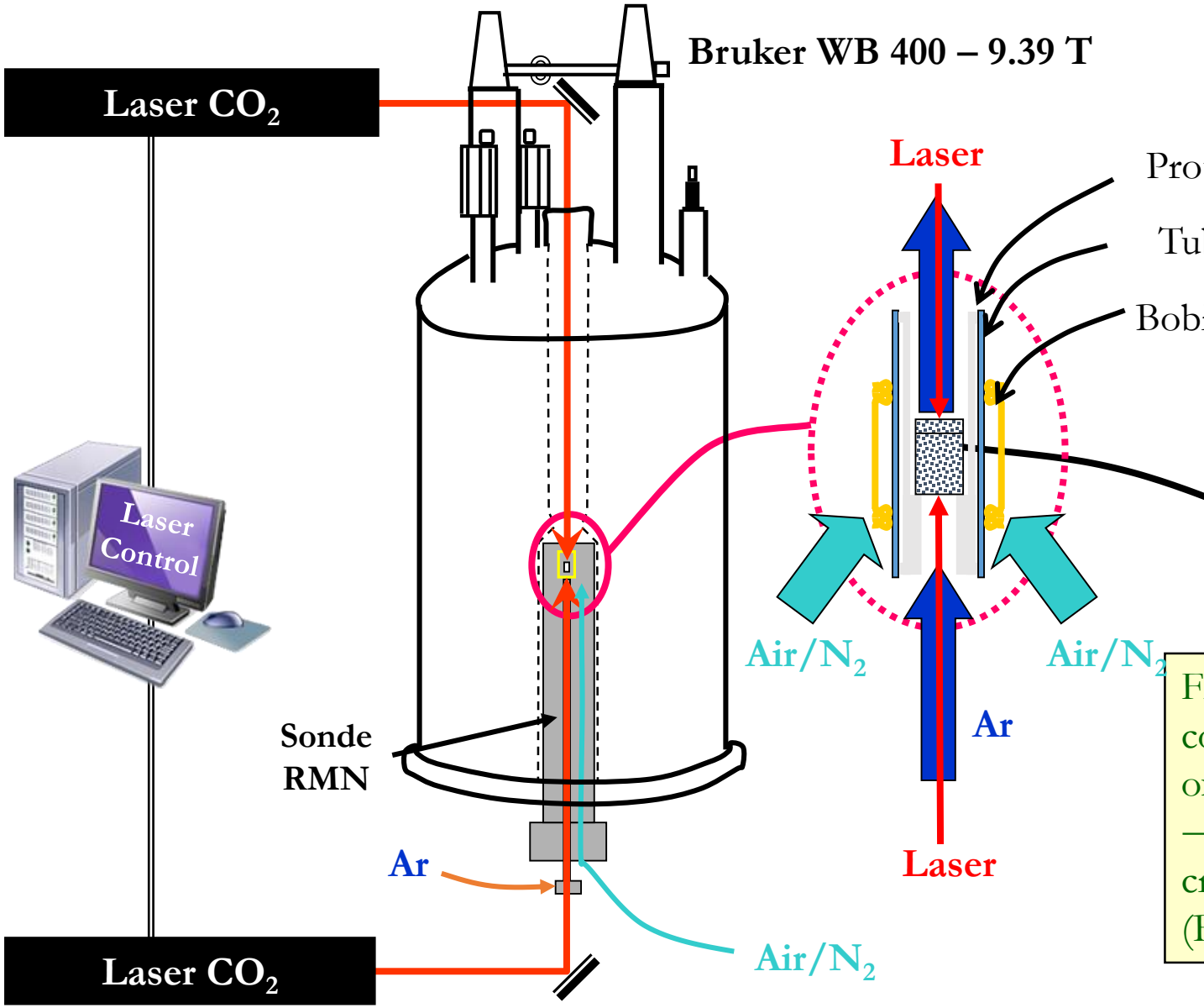
- de l'abondance (^{29}Si=4.7%, ^{17}O=0.04%)
- de la relaxation du noyau: I>1/2, $T_{1,2}$ peuvent devenir du même ordre que Δ.

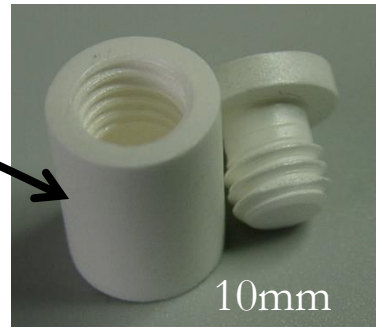
Noyaux observables en diffusion RMN

• Group	I	II		IIIa	IVa	Va	VIa	VIIa	VIIIa	VIIIb	VIIIc	IB	IIB	III	IV	V	VI	VII	VIII
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanides			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinides			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Nuclear Spins	1/2	1	3/2	5/2	7/2	9/2

RMN Haute Température





Fluorures fondus sont corrosifs (dissolvent les oxydes) et volatils.
→ Confinement dans des creusets en nitrure de bore (BN)

Lacassagne et al., J. Phys. Chem. B, 106, 1862, (2002)

High temperature diffusion NMR: probes @ CEMHTI

Bruker probe (diff-5) modified in CEMHTI (with Bruker)
z-gradients: up to 55 G/cm
2 RF channels:
- ^{1}H - ^{19}F
- X Broad band (^{17}O - ^{31}P)

⇨ ***D*** **range: 10^{-10} to 10^{-8} m²/s**

$$I = I_0 exp\left[-D(\gamma g \delta)^2\left(\Delta + \frac{2\delta}{3} + \frac{3\tau}{4}\right)\right]$$

Low *D*
and/or **Low γ nuclei**
and/or **Short delays (relaxation)**

⇨ ***Higher gradients***

Bruker probe (diff-30/50) modified in CEMHTI
z-gradients: up to 2400 G/cm
RF inserts ^{1}H, ^{7}Li, ^{17}O, ^{19}F, ^{23}Na - ^{27}Al

⇨ ***D*** **range: 10^{-12} to 10^{-8} m²/s**

Molten fluorides: cryolitic melts

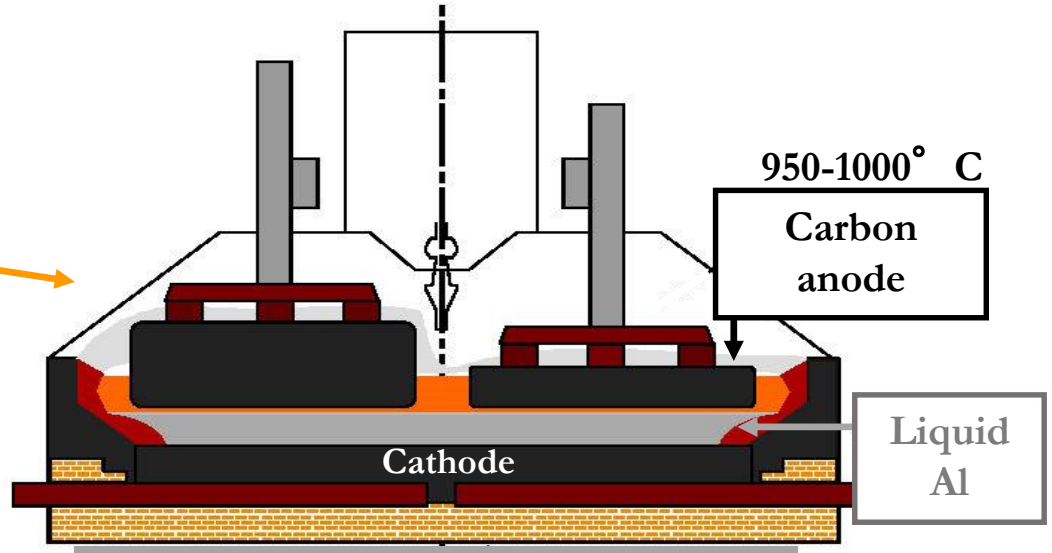
Molten fluorides: used in various technologies (pyroprocessing, electrolysis, fluxing…) to dissolve oxides.

Particular chemistry: can contain free, complexed or connected ions.
Speciation and acidity need better understanding

Aluminium production: alumina (Al_2O_3) dissolved in cryolite(Na_3AlF_6)-based bath and reduced by electrolysis at T~1000° C

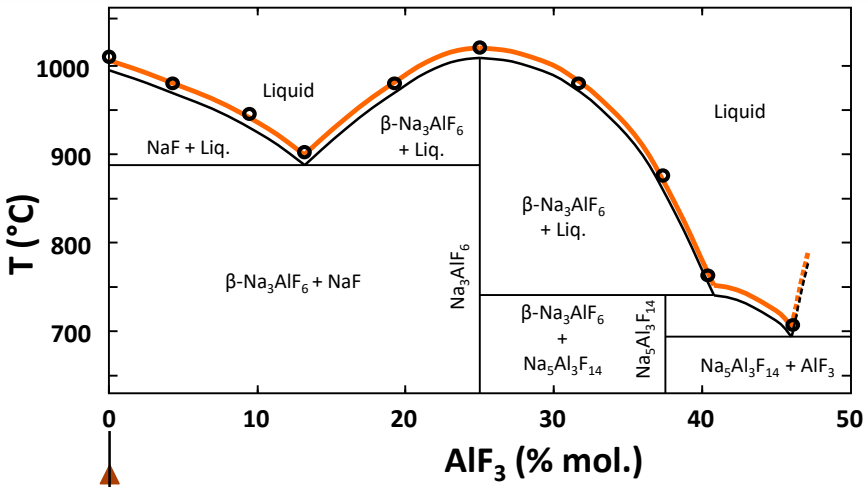
Bath = Al_2O_3 + Na_3AlF_6 + fluorides additives

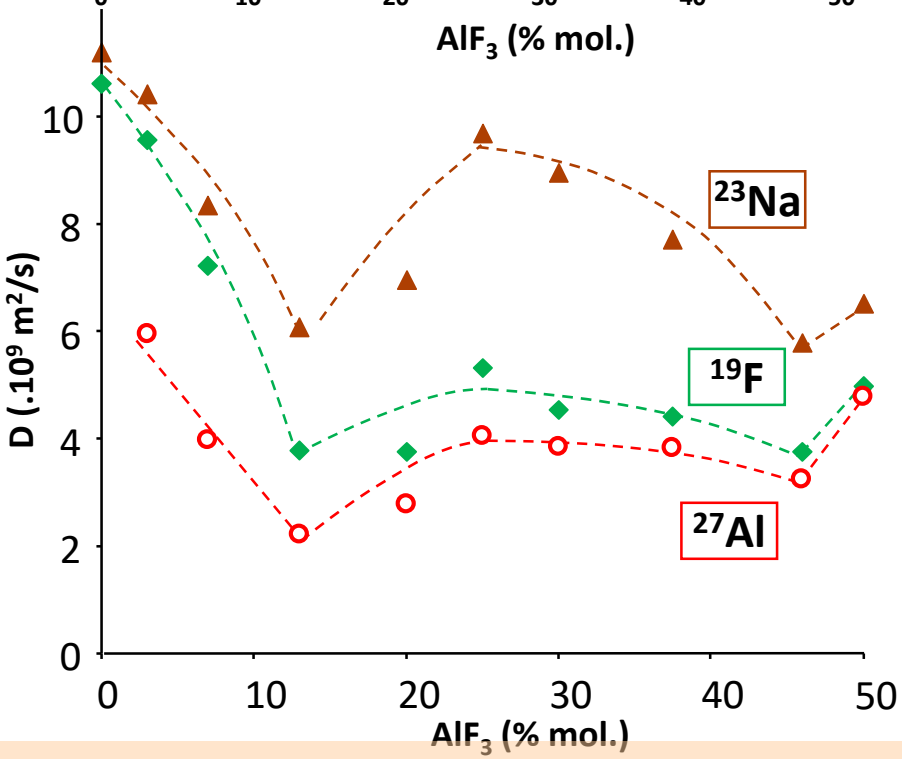
- Free ions: F^-, Na^+
- Al complexes : AlF_4^-, AlF_5^{2-} , AlF_6^{3-} , $Al_2O_2F_4^{2-}$



Simplified scheme of an electrolysis cell

Self-diffusion in NaF-AlF3





M. Gobet, V. Sarou-Kanian, A.L. Rollet, M. Salanne, C. Simon, C. Bessada *ECS Transactions 2010*, 33, 679

Na: D_{Na} follows the phase diagram. The diffusion of Na is mainly affected by T

⇨ **Monoatomic cations diffusing "freely"**

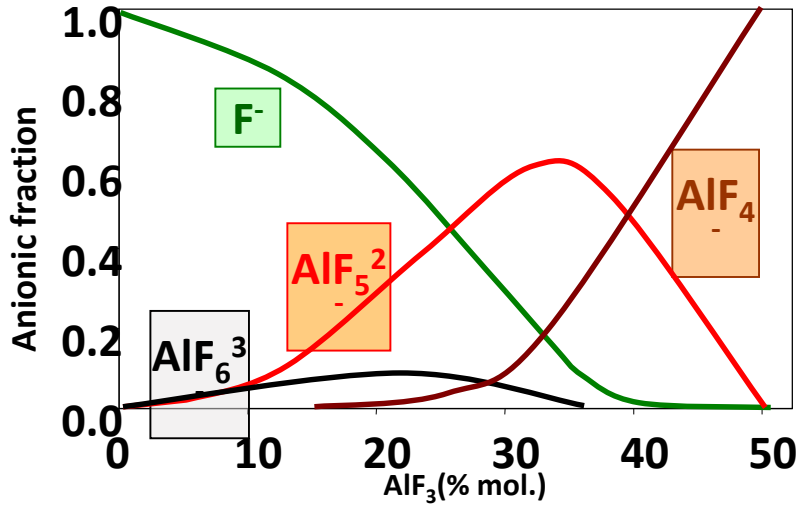
Al: D_{Al} is much lower than D_{Na}. Al is involved in larger entities

⇨ **AlF_n^{3-n} anionic units**

F: $$D_F = x_{F^-} . D_{F^-} + x_{AlF_n^{3-n}} . D_{AlF_n^{3-n}}$$

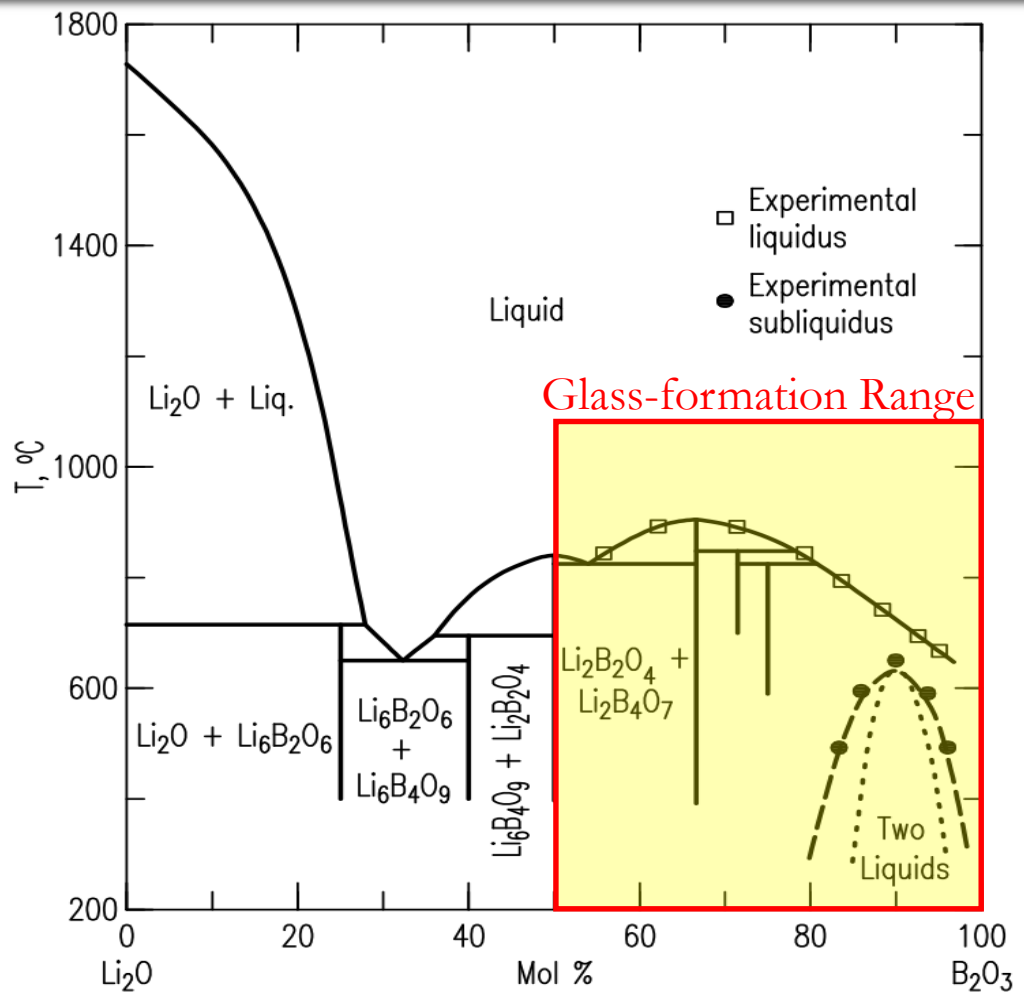
$D_F \sim D_{Na}$ at low $[AlF_3]$ then converges towards D_{Al}

⇨ **The content of F^- decreases with $[AlF_3]$**



Robert *et al.*, *Inorg. Chem. 1999*, 38, 214
Lacassagne *et al.*, *J. Phys. Chem. B 2002*, 106, 1862

Oxides: Li diffusion in lithium borates



Kim & Sanders, Ceram. Int. v26, p769

xLi$_2$O-(1-x)B$_2$O$_3$

→ionic conducting glasses

Our study:
7 crushed glass samples

x=0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50

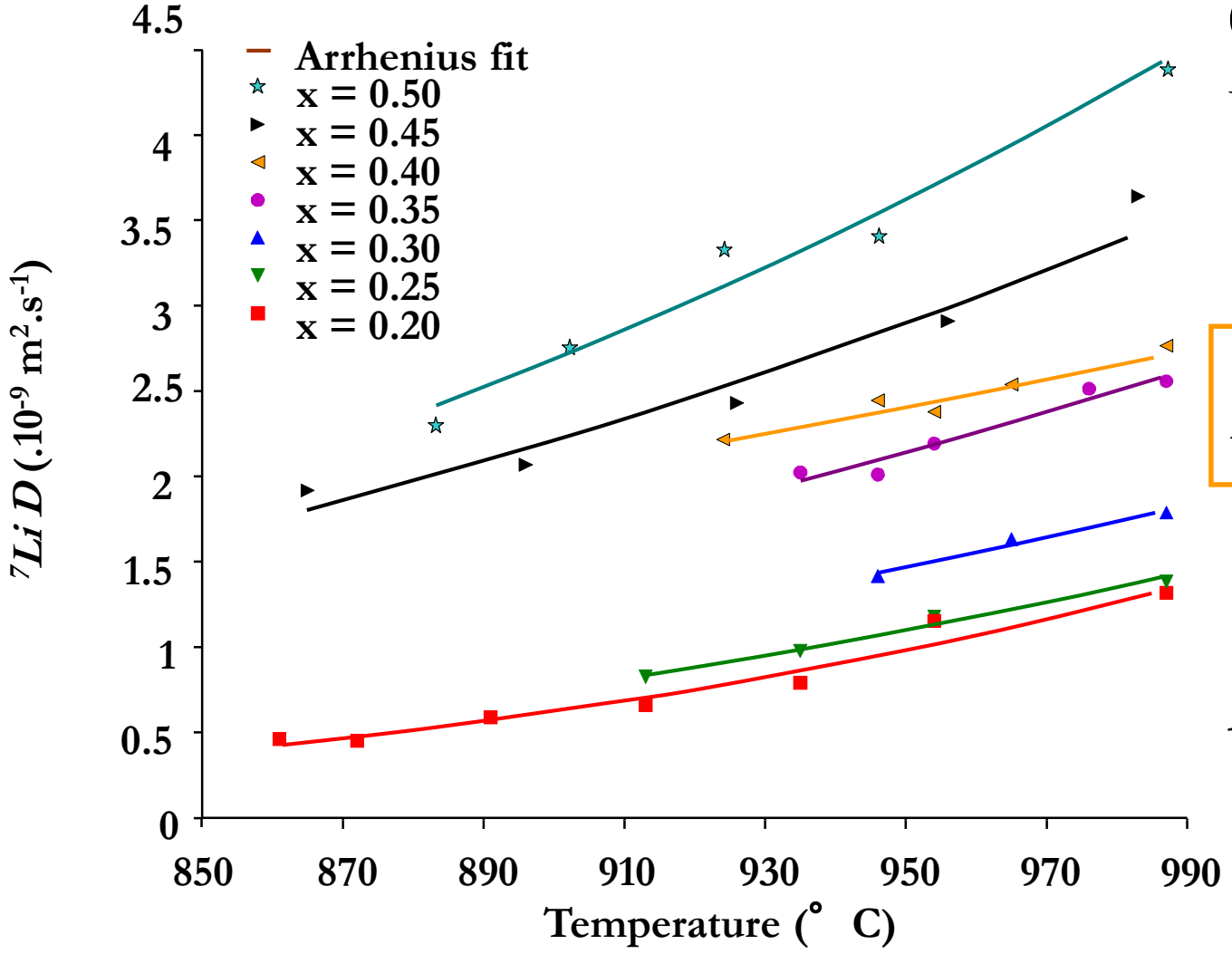
Molten state
850° C ≤ T ≤ 1000° C
Glasses around Tg
450° C ≤ T ≤ 600° C

Collaboration with **T. Ohkubo, M. Nozawa & Y. Iwadate**

Graduate School of Engineering, Chiba University, Japan

Chiba University

Li diffusion in molten state as a function of temperature



$0.5 \leq D \leq 4.5\ 10^{-9}\ m^2.s^{-1}$

Viscosity range:
1000 to 7000 mPa.s
($0.17 \leq x \leq 0.29$ 820-920°C)

⇨Fast diffusion of Li through B-O network

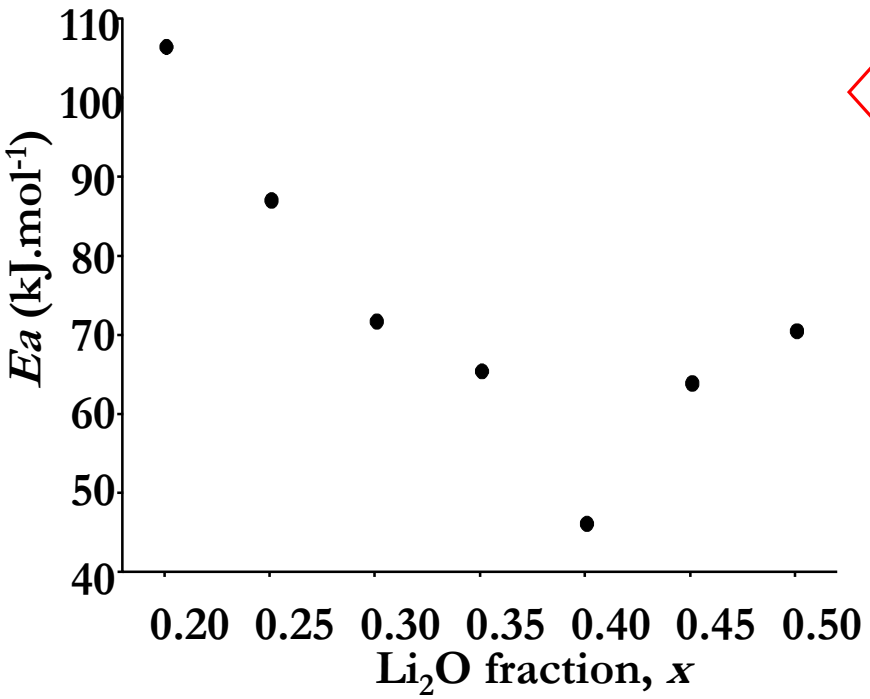
D* increases with *x

Arrhenius behaviour
⇨Activation energy *Ea*

T.Ohkubo, M.Gobet, V.Sarou-Kanian, C.Bessada, M.Nozawa, Y.Iwadate *Chem. Phys. Lett. 2012*, 530, 61

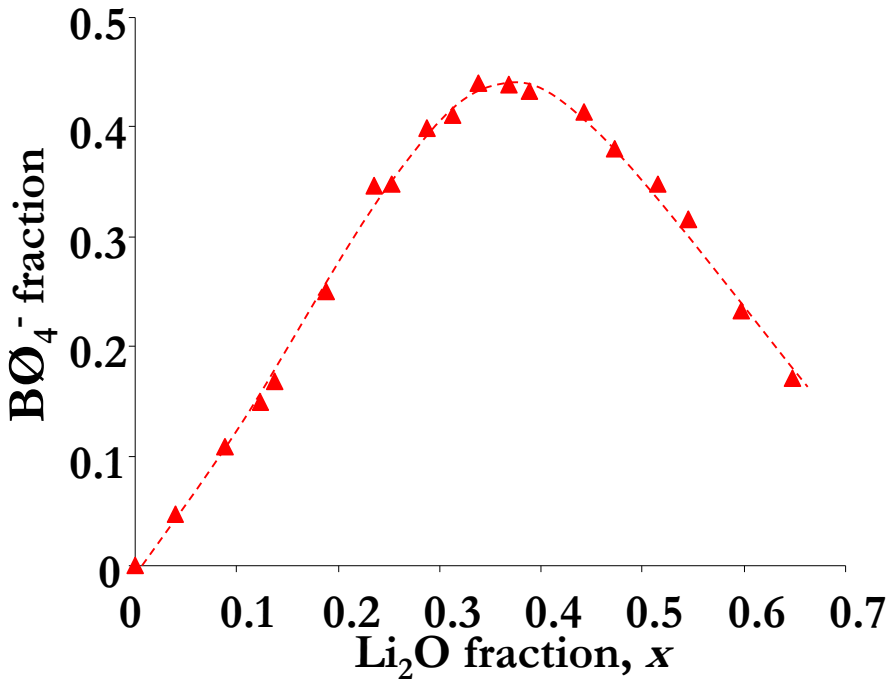
Activation energy in Li_2O-B_2O_3 melts

Non-monotonous trend for *Ea:* minimum for x≈0.4



Boron speciation **in glasses**

MAS ^{11}B NMR: **$B\varnothing_4^-$ fraction**

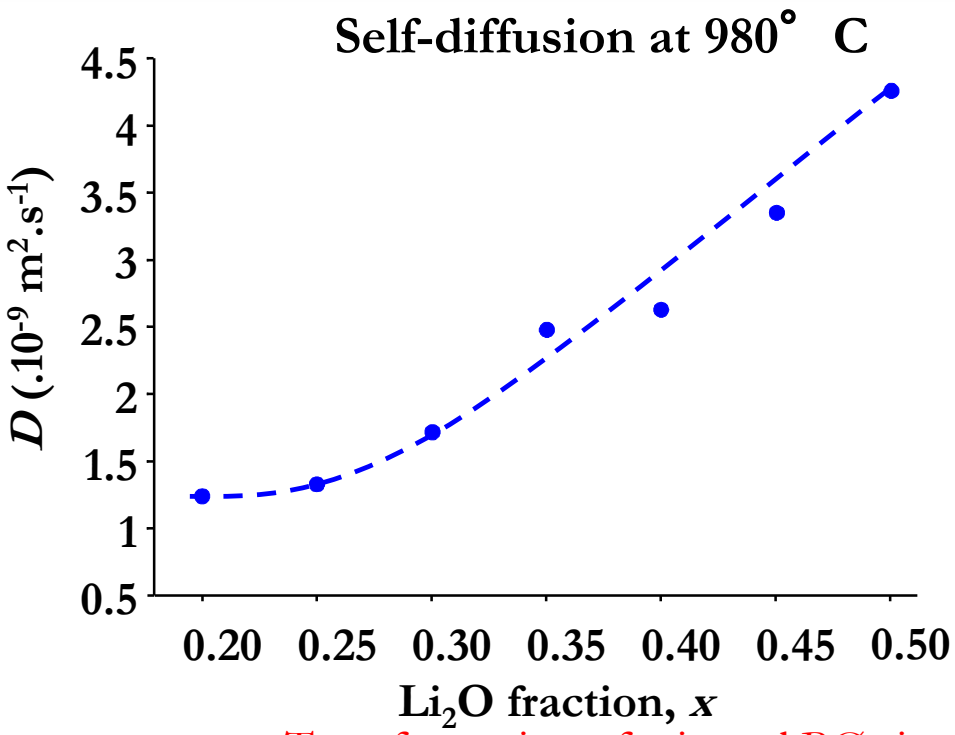


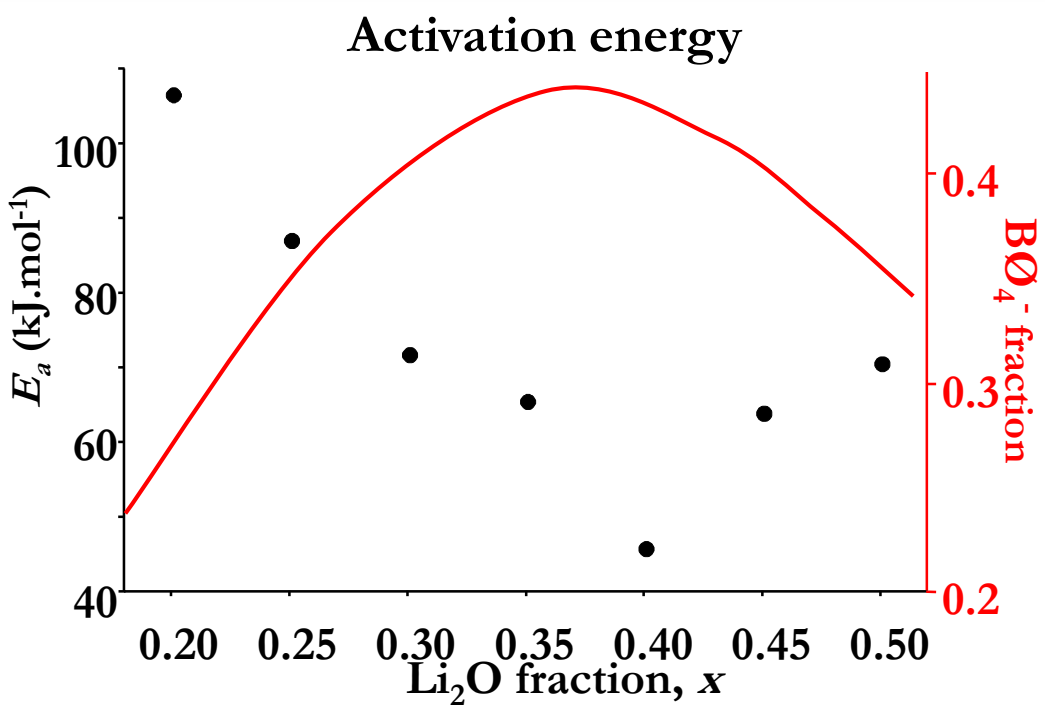
Shibata et al. *J. Non-Crystal. Solids 1986*, 85, 29

Boron oxide: trigonal $B\varnothing_3$ Ø = bridging O atom

Lithium is a **network modifier: $B\varnothing_3$ → tetragonal $B\varnothing_4^-$**

Diffusion vs. structure

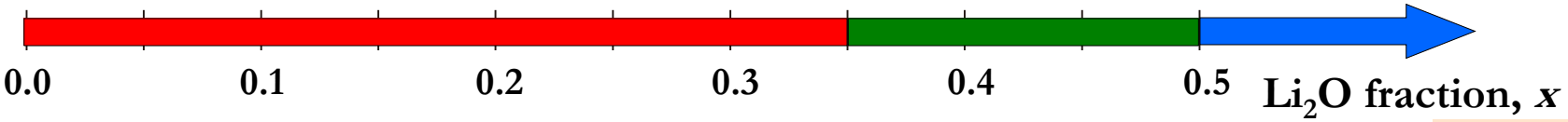




Transformation of trigonal $BØ_3$ into charged tetragonal $BØ_4^-$

Breaking of B-Ø and creation of terminal O^-

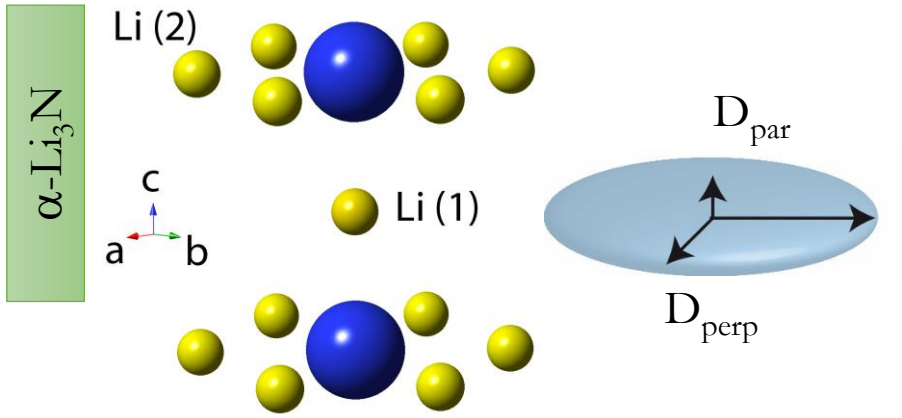
Depolymerization of network isolated units with terminal O^-



Effect on diffusion = competition between different processes

- **« Network » destructuring with increasing [Li]**: greater D
- **[$BØ_4^-$] increasing** = shorter distance between negative sites: lower Ea, greater D
- Li^+ - B^- interaction weaker than Li^+ - O^-. **Non-bridging O = « Li^+ trap »**: greater Ea

Balkanski & Elliot, 1998 "Atomic diffusion in disorded materials"



Sample is a powder: distribution of orientations

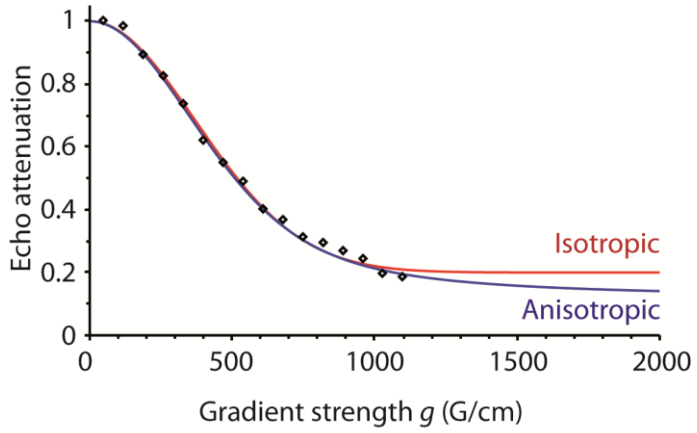
Cylindrical symmetry

⇨ D along the axis (D_{par}) ≠ D within the plan (D_{perp})

$$\langle z^2(\Delta)\rangle = 2D_{\mathrm{par}}(\Delta)\Delta\cos^2\Theta + 2D_{\mathrm{perp}}(\Delta)\Delta\sin^2\Theta$$

$$\Psi(\delta g,\Delta) = \frac{1}{2}\int_0^{\pi}\exp\{-(\gamma\delta g)^2\Delta(D_{\mathrm{par}}\cos^2\Theta + D_{\mathrm{perp}}\sin^2\Theta)\}\sin\Theta\, d\Theta$$

Isotropic + ψ_0 or anisotropic+ ψ_0 ?



From XRD: 90% Li_3N - 10% of Li_2O

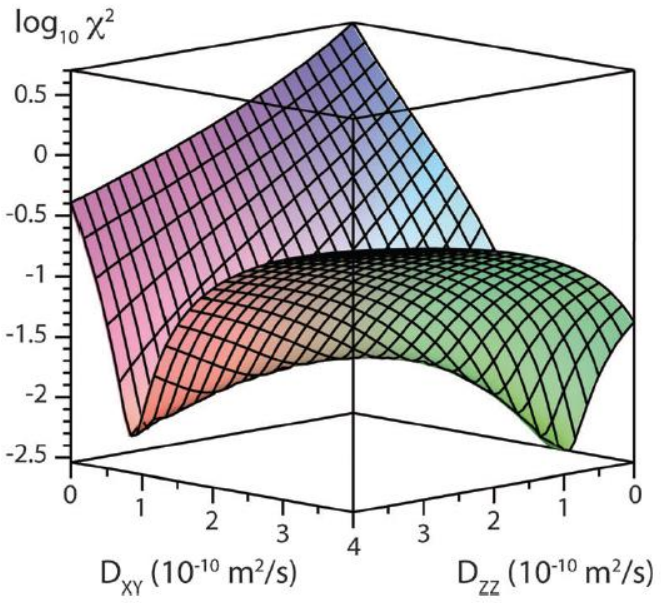
T = 431°C
D_{ab} = 3.0.10^{-10}m^2/s
D_c = 0
Non-diffusing part:
Ψ_0 = 12%

OR
D = 2.0.10^{-10}m^2/s
Ψ_0 = 20%

Z.Wang, M.Gobet, V.Sarou-Kanian, D.Massiot, C.Bessada, M.Deschamps
Phys. Chem. Chem. Phys. **14,** 13535-13538 2012

Anisotropic diffusion in lithium nitride

X^2 plot vs D_{perp} and D_{par}



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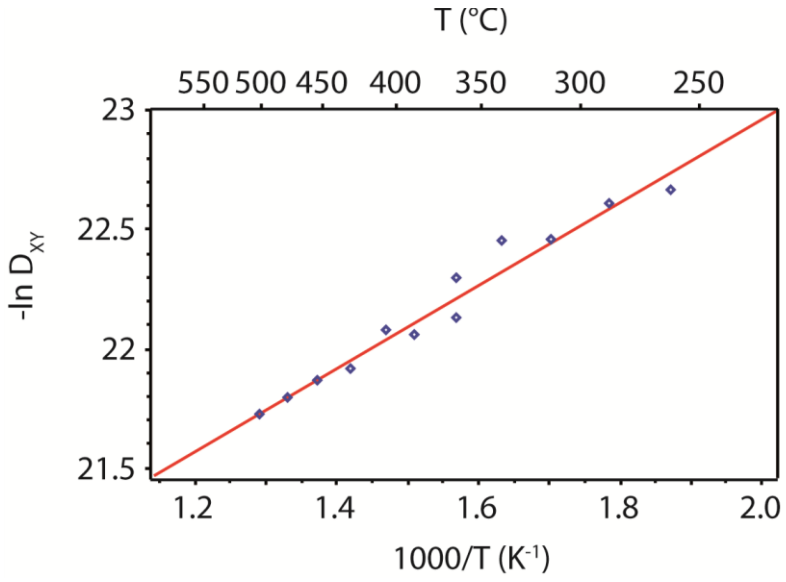
Phys. Chem. Chem. Phys. **14,** 13535-13538 2012



E_a = 14,5 kJ/mol
= **0,15 eV** for D_{ab}

Good agreement with
E_a = 0,17 eV for D_{ab} using linewidths and T_1

K. Nishida, T. Asai and S. Kawai
Solid State Commun. **48** 701-704 (1983)

Measured by PFG-NMR

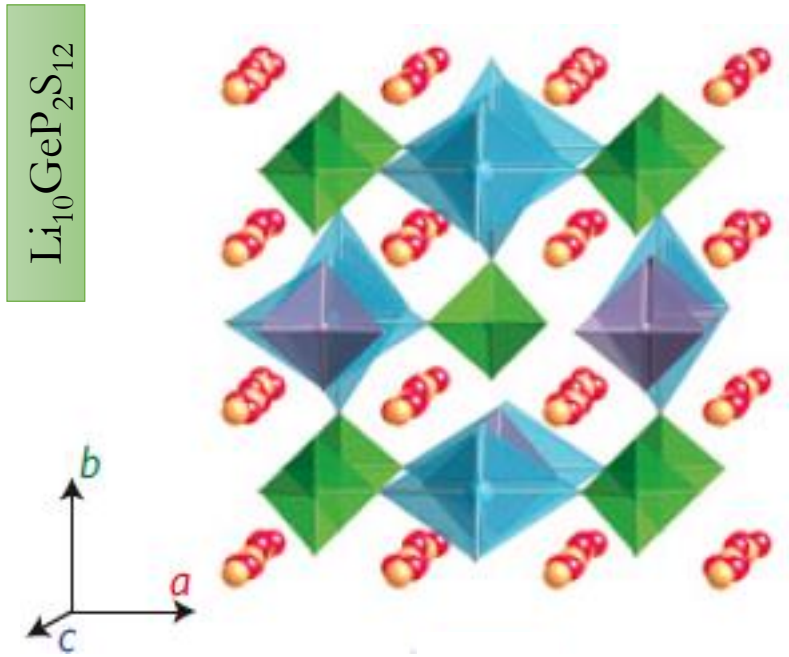
$$\tau_{XY} = \frac{(x^2) + (y^2)}{4D_{XY}}$$

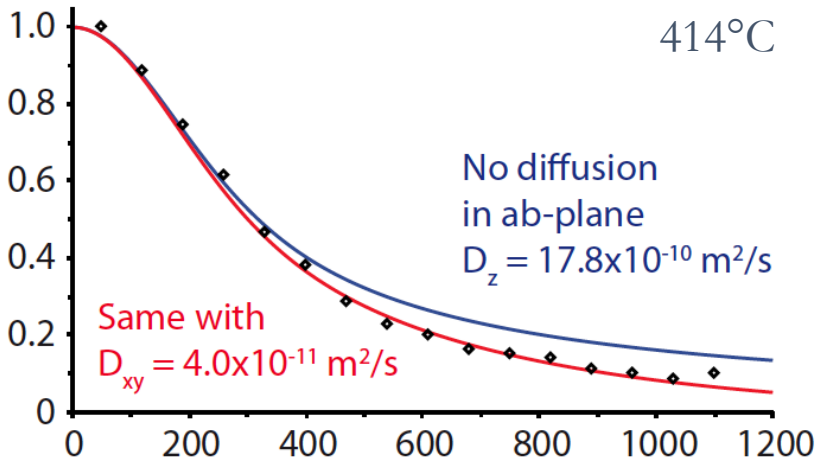
T (K)	D_{XY} (x 10^{-10} m^2/s)	τ_{XY} (ps)	Calculated from (1) τ_Z (ps)
534	1.438	78	20828
560	1.522	73	10685
587	1.770	63	5880
612	1.779	63	3434
637	2.457	46	2112
637	2.079	54	2112
662	2.638	42	1358
680	2.587	43	1001
704	3.042	37	687
728	3.195	35	486
751	3.433	33	354
774	3.682	30	264

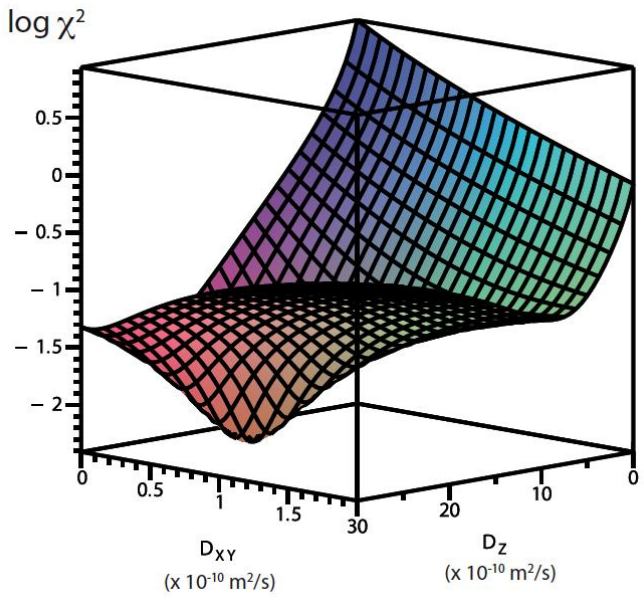
(1) NMR on **monocristal** / SAE sensitive to change in H_Q:
E_a = 0,65 eV pour D_c
M. Wilkening, D. Gebauer and P. Heitjans
J. Phys. Cond. Mat. **20** 022201 (2008)

(2) Calculations: E_a = 0.0065 eV for defect migration
W. Li, G. Wu, C. M. Araujo, R. H. Scheicher et al.
Energy & Environmental Science **3**, 1524-1530 (2010)
-> measure the activation energy for the creation of defects

$Li_{10}GeP_2S_{12}$ from RT to 414°C



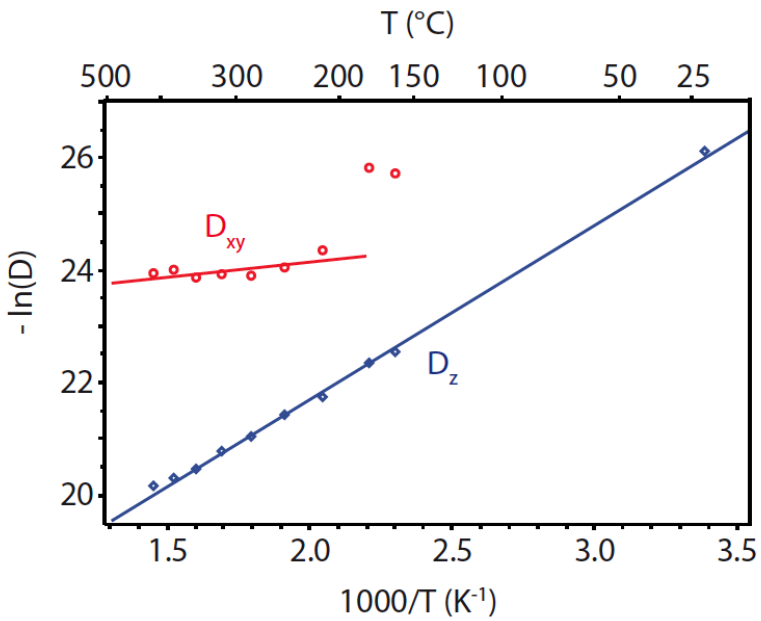




Kuhn, A.; Duppel, V.; Lotsch, B. V.
Energy Environ. Sci. 2013, 6 (12), 3548–5.
Anisotropic diffusion **not detected**
Averaging of quadrupolar interaction
Presence of **orthorhombic modification** of LGPS
Observed by ^{31}P NMR
Size of crystallite vs diffusion delay
Evolution of the sample ?

$Li_{10}GeP_2S_{12}$: comparison with MD and calculations

Experiments



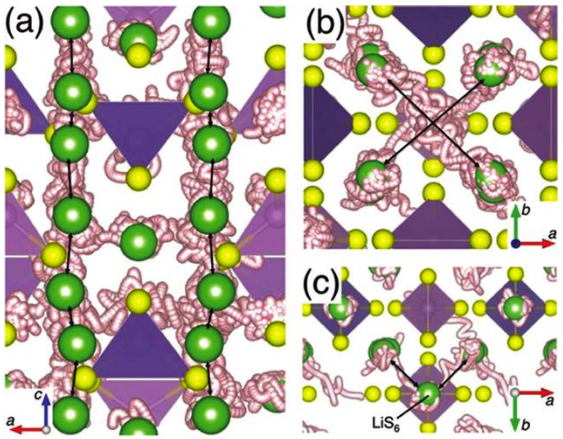
E_{az} = 0.268 eV (compared to 0.22 eV in Kuhn et al.)
E_{axy} = 0.047 eV at higher T -

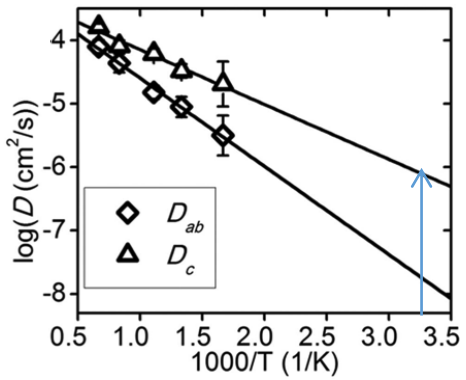
E_a(conductivity) = 0.24 eV

D_z(300K) = 4.6 x 10^{-12} m^2/s

2.1 x 10^{-10} m^2/s in 1M LiTFSI in EC @ RT
1.3 x 10^{-11} m^2/s for 1M LiTFSI in $Pyr_{13}FSI$ @ RT
10^{-13} m^2/s at RT and 4.84 x 10^{-12} at 60°C in LiTFSI/PEO

MD and Calculations





E_{az} = 0.17 eV
E_{axy} = 0.28 eV

D_c(300K) = 10^{-6} cm^2/s
= **10^{-10} m^2/s**

D_{ab}(300K) = 10^{-8} cm^2/s
= **10^{-12} m^2/s**

Y.Mo, S.P.Ong, G.Ceder
Chem. Mater. **24** 15−17 (2012)

Conclusions

- Mesure des coefficients d'auto-diffusion
- Multi nucléaire → structure
- Isotropie /anisotropie
- ↓$10^{-12,13}$ m²/s