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La chimie de Coordination, un outil pour la conception de Matériaux Magnétiques Moléculaires

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Sommaire

1- Matériaux moléculaires: pourquoi et comment ?

- Intérêts / limitations
- Propriétés / spécificités…
- Exemples (molécules aimants ou SMM)

2- La transition de spin des complexes du Fe^{II}

- Synthèse rationnelle
- Correlation magneto-structurales
- Spectroscopie Mössbauer
- Photomagnétisme…

1- Matériaux moléculaires: pourquoi et comment ?

Chimie Moléculaire ?

Synthèse organique: préparation de nouveaux ligands organiques (C, H, N, S, O)

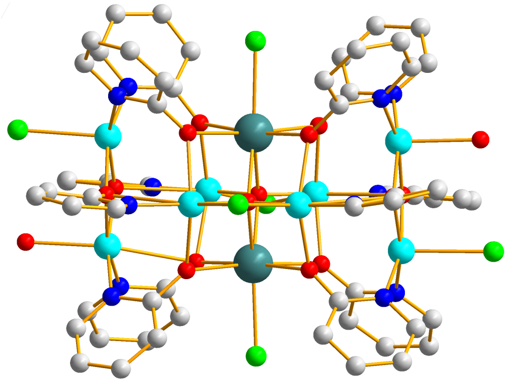
+

Chimie « inorganique »: sels de métaux de transition (3d, 4d, 5d, lanthanides)

Chimie de coordination (douce)

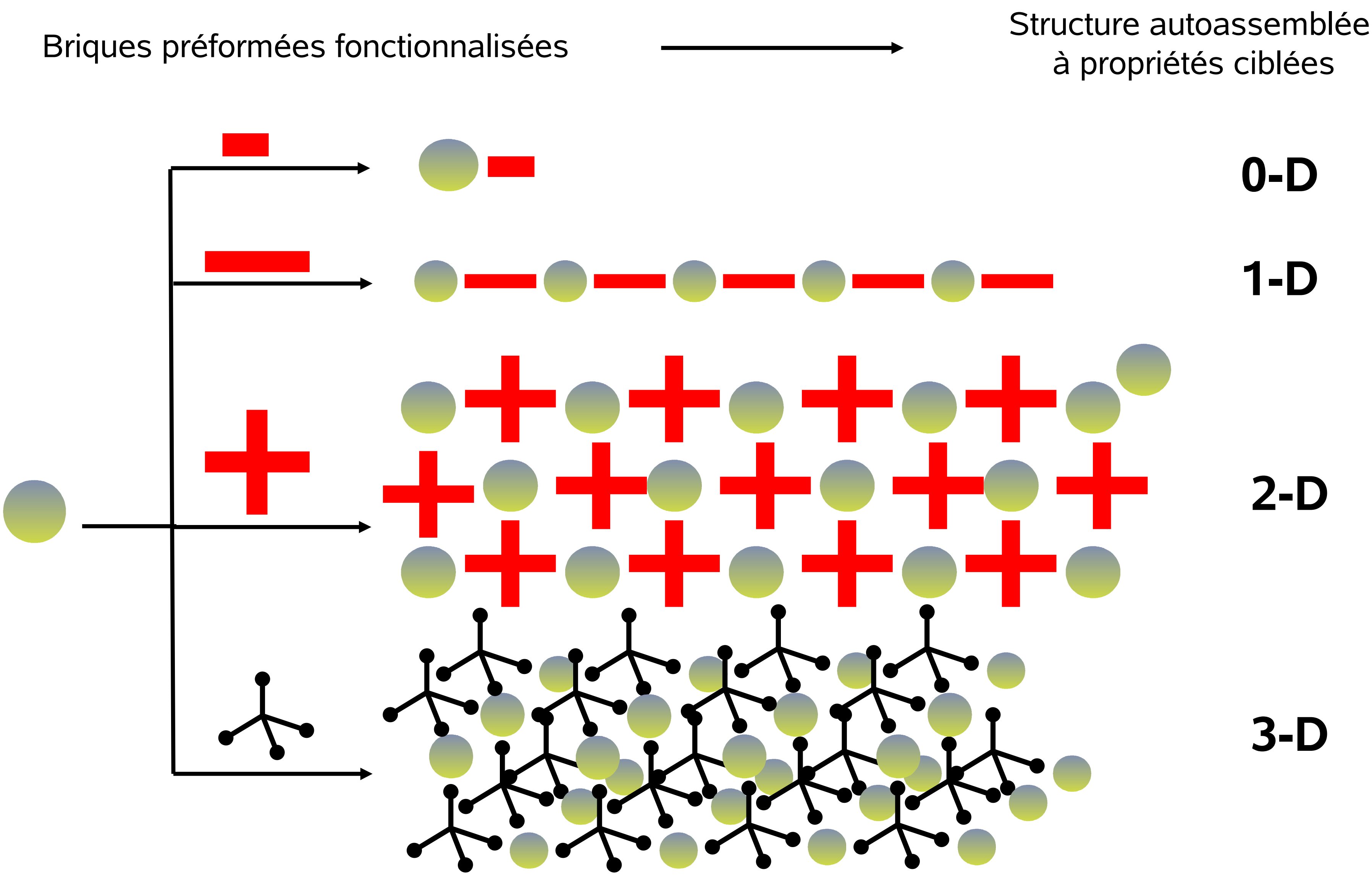
Matériaux Moléculaires

Poudre microcristalline, amorphe



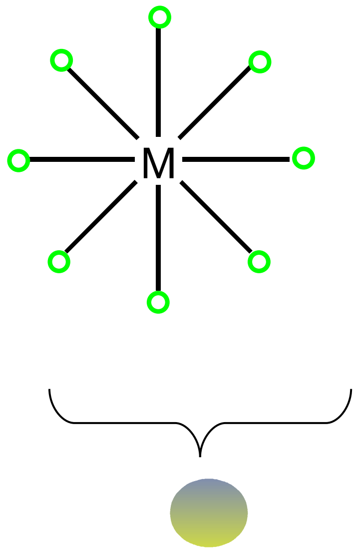
Monocristaux

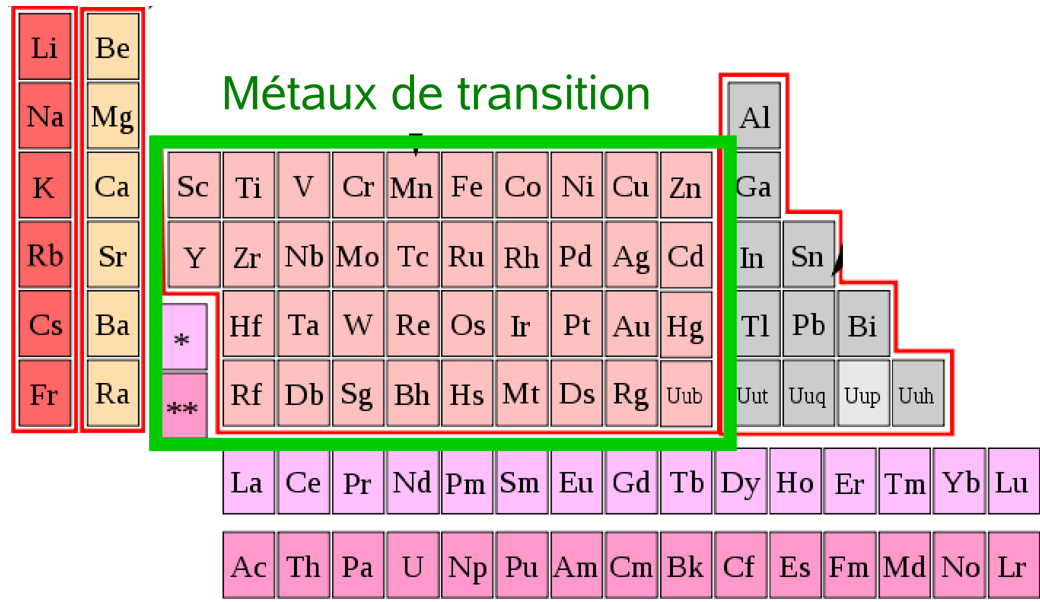
« De la molécule au matériau »



Synthèse Rationnelle d'architectures moléculaires

Brique « Complexe de coordination »





<u>Paramètres ajustables:</u>

- Degré d'oxydation du centre métallique
- Nature de l'ion métallique (3d, 4d, 4f, 5d…)
- Coordinence (tétra, hexa, octacoordinné…)
- Nature du ligand: mono, bi, tridente…

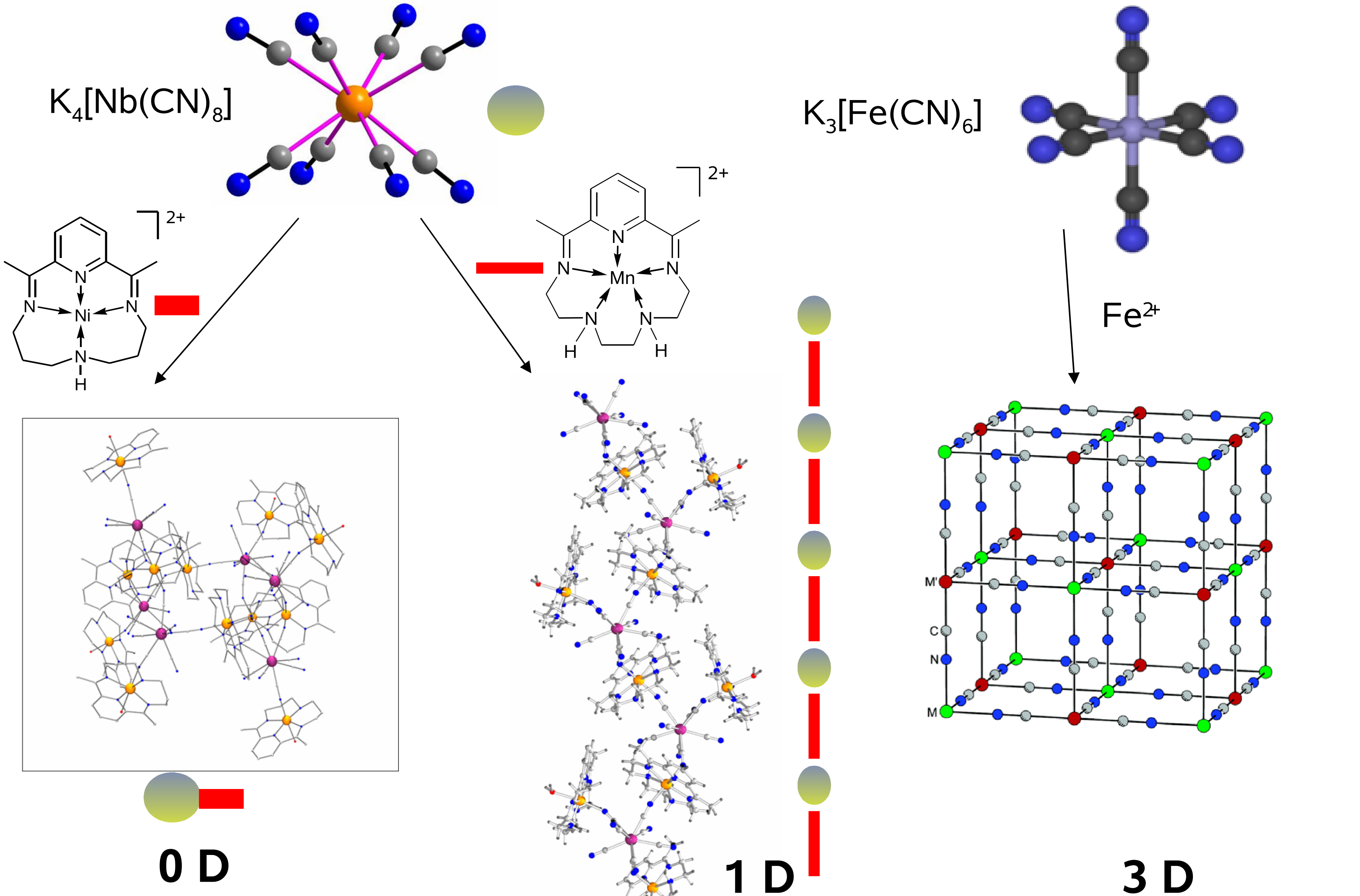
<u>Auto-assemblage:</u>

Structure auto-assemblée fonctionnelle

Quelles interactions ?

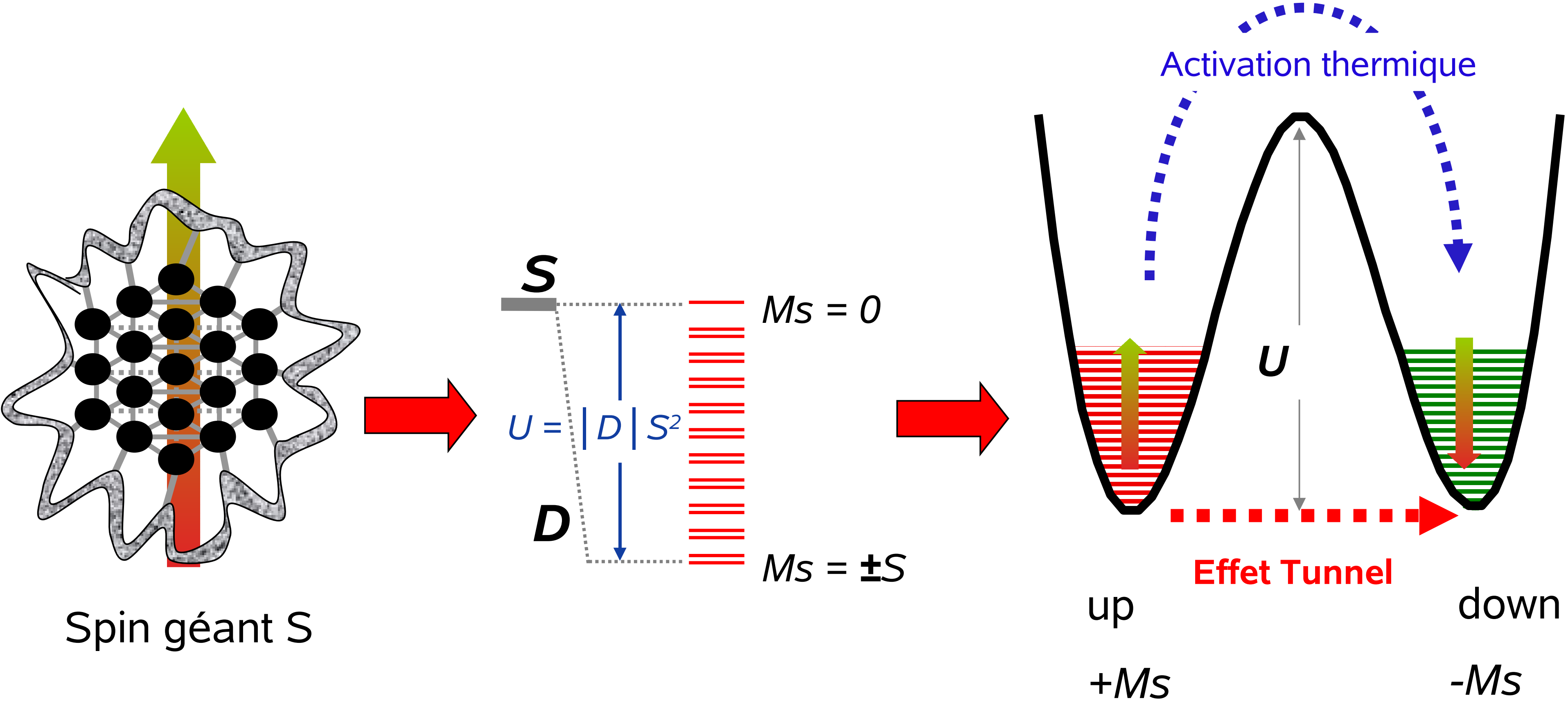
- Liaison de coordination (fortes)
- Interactions faibles (liaisons hydrogène, interactions π-π…)

Quelques exemples issus de la chimie des cyanures…



Sutter, *Inorg. Chem* **2003**

Molécules Aimants



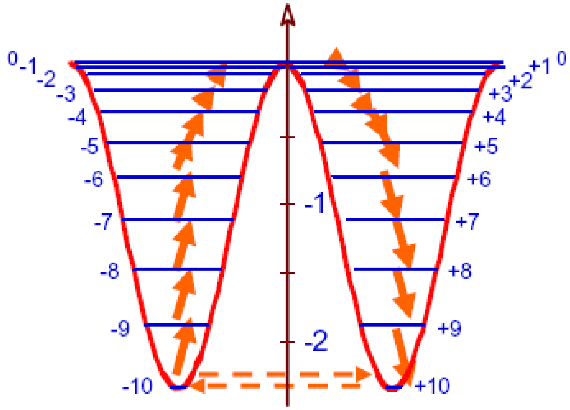
Conditions:

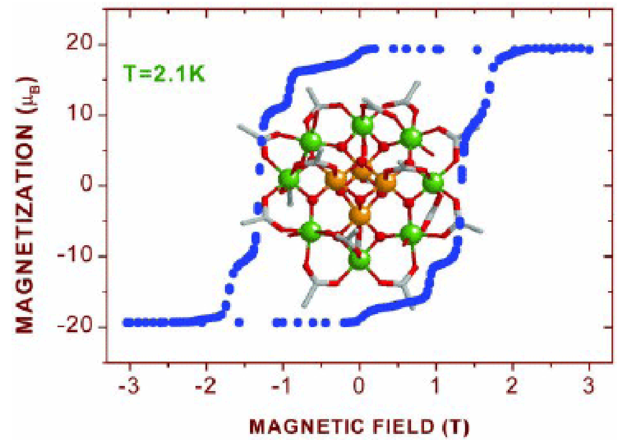
- Fort Moment Magnétique
- Forte anisotropie magnétique axiale

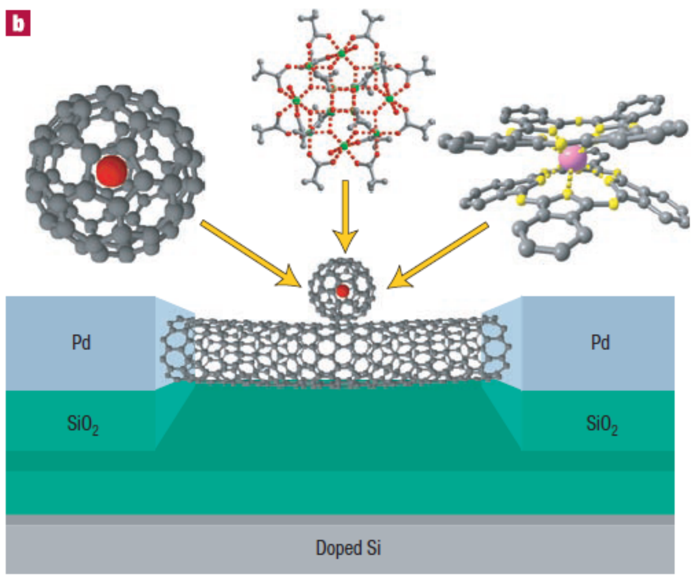
SMM (Single Molecule Magnet) et **SCM** (single Chain Magnet) [nano amants et nano fils]

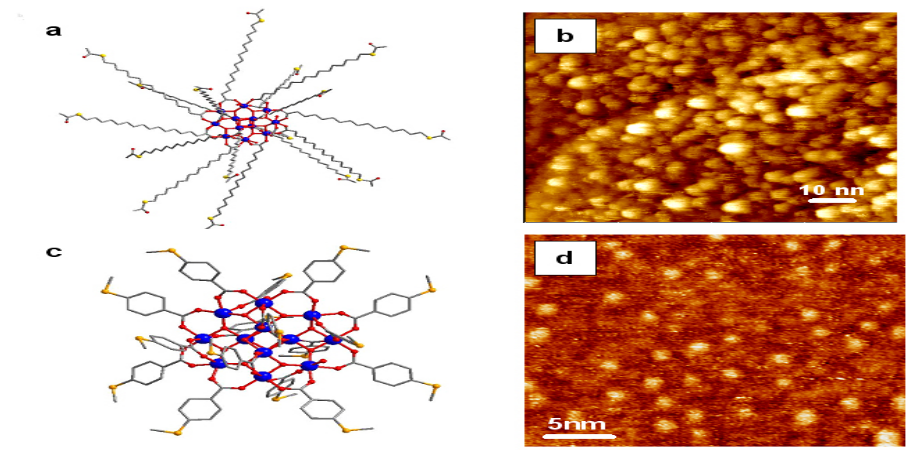
Vers la miniaturisation de la taille des éléments de mémoire…

Le cluster Mn_{12}









Spintronique Moléculaire

Wolfgang Wernsdorfer

NÉEL institut

Groupe Nanospintronique et Transport Moléculaire

Déposition couches minces

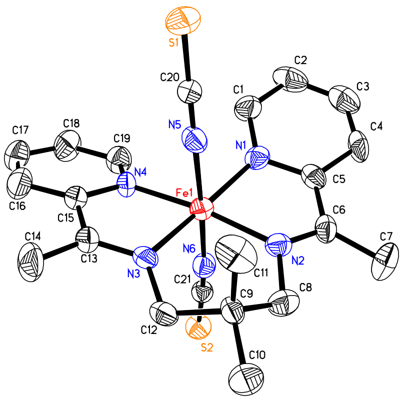
Andrea Cornia

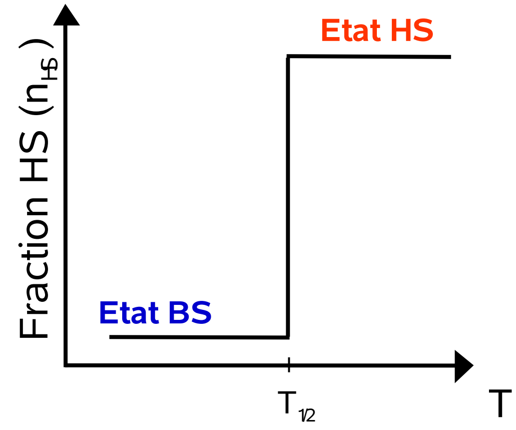
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

2- Les complexes à transition de spin

La transition de spin (TS)

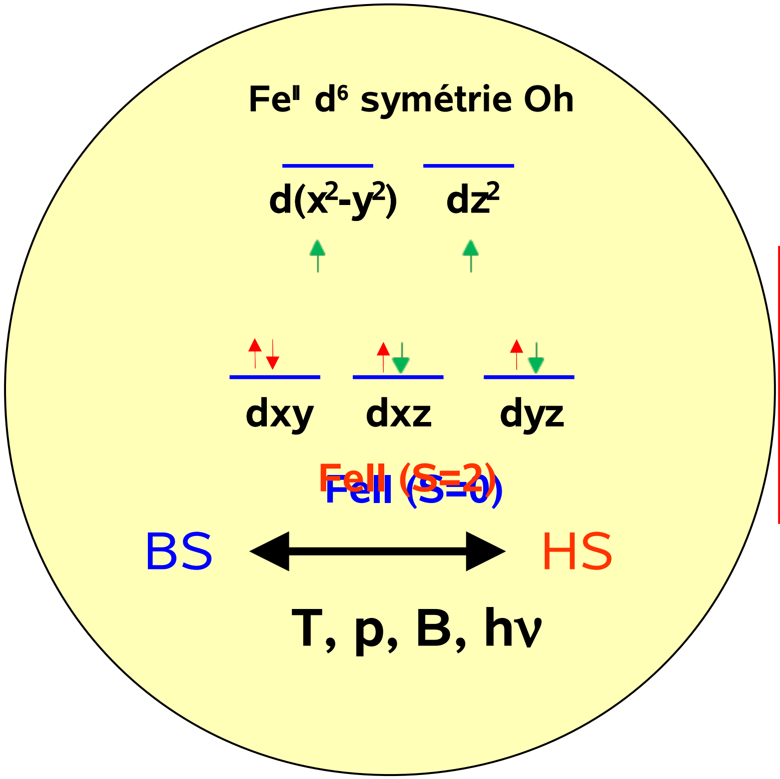




Etat diamagnétique (S=0)

Bas Spin (BS)

Champ de ligand fort



Etat paramagnétique (S=2)

Haut Spin (HS)

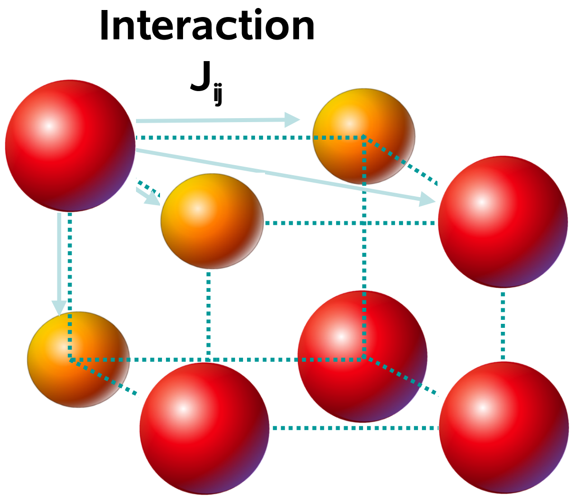
Champ de ligand faible

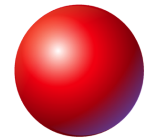
Thermochromisme
Photochromisme

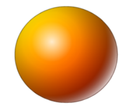
Magnétochromisme
Piézochromisme

P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **(1994)**
A. Bousseksou, G. Molnar, G. Matouzenko, *Eur. J. Inorg. Chem.* **(2004)**

A l'état solide….

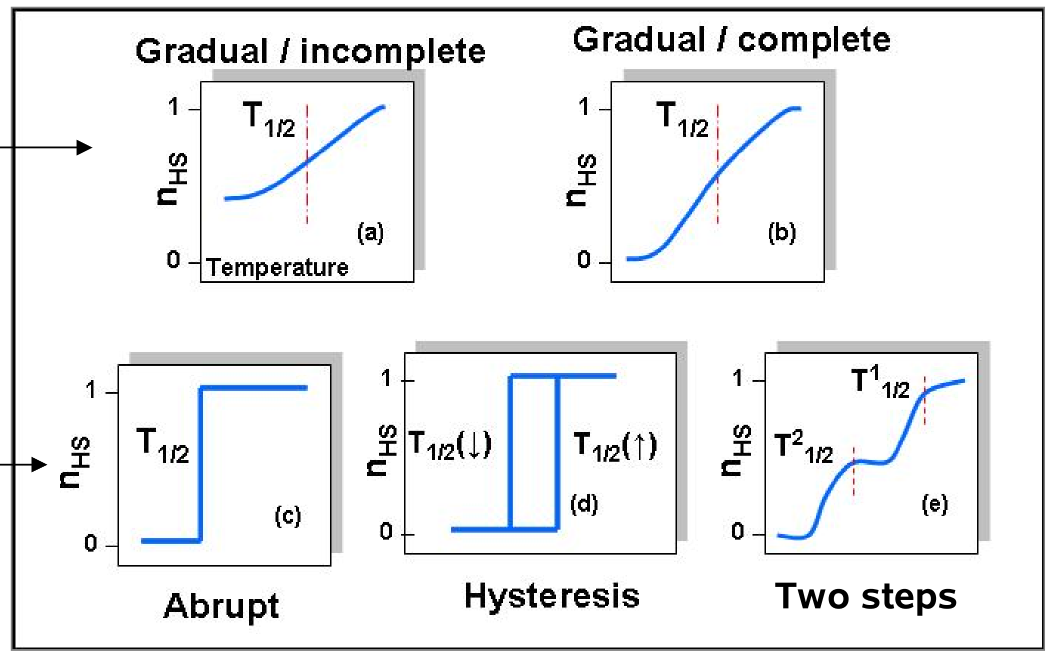


 : Site Fe^{II} HS

 : Site Fe^{II} BS

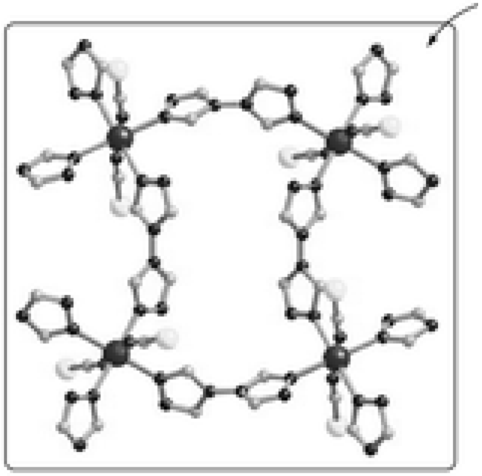
(n_{HS} = fraction HS)

- Interactions faibles →
- Interactions fortes →

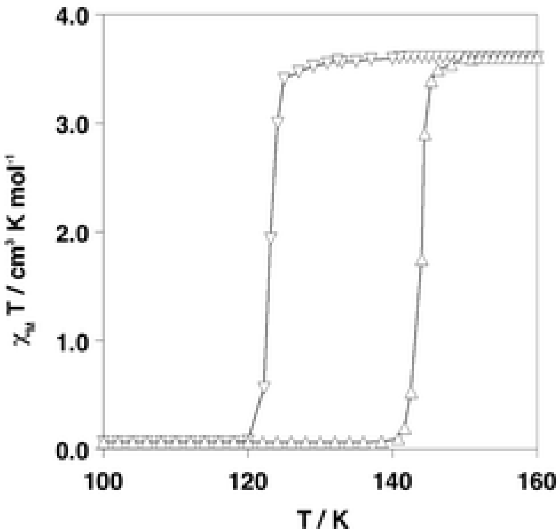


Boucle d'Hysteresis: $\Delta T = T_{1/2}\uparrow - T_{1/2}\downarrow$

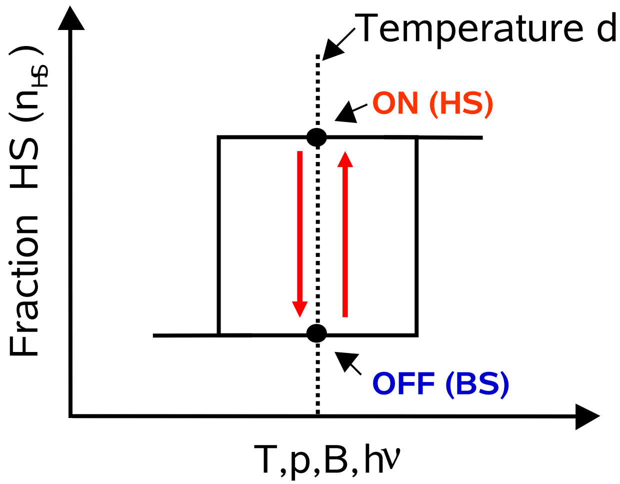
Thermochromisme / Détection Optique



$[Fe(btr)_2(NCS)_2].H_20$



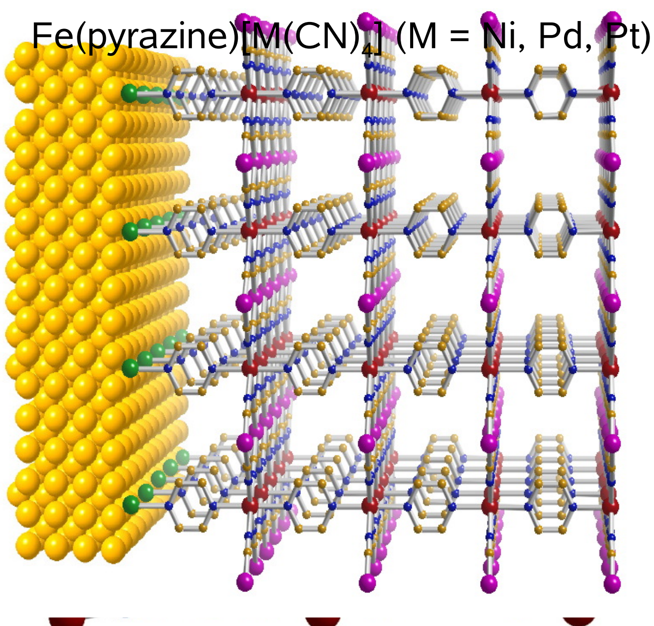
Haasnoot et al. *Polyhedron* **1985**

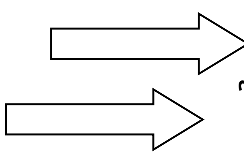


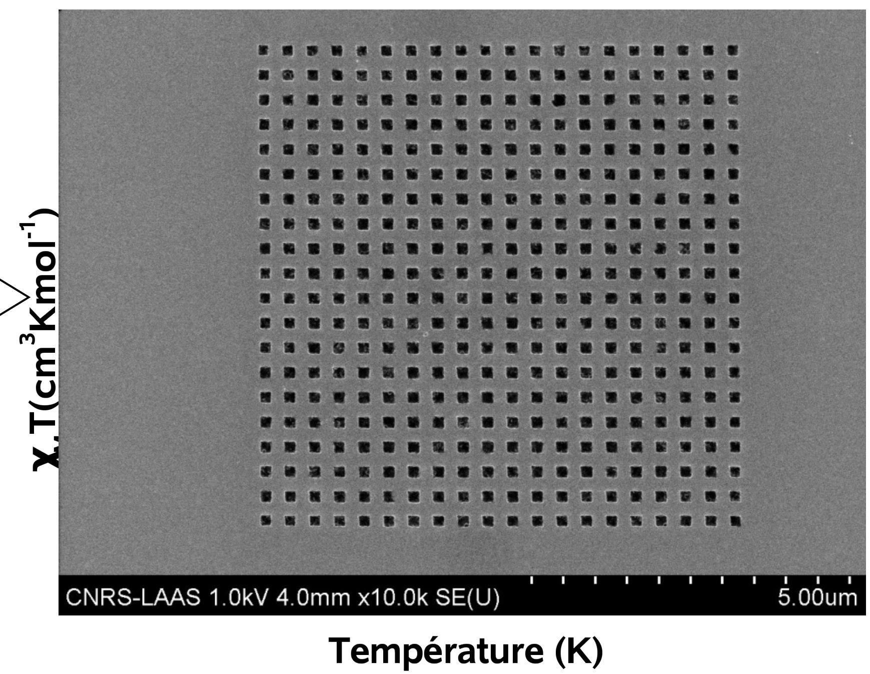
Bistabilité Moléculaire	=	**Interrupteur commutable**

Conditions pour applications potentielles :
- $T_{1/2} \approx 300$ K
- $\Delta T = T_{1/2}\uparrow - T_{1/2}\downarrow > (30\text{ K})$

Fe(pyrazine)[M(CN)$_4$] (M = Ni, Pd, Pt)



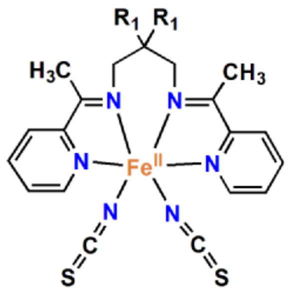




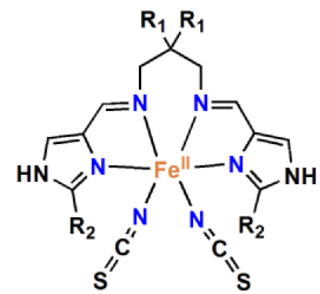
S. Cobo et . *Angew. Chem.* **(2006)**
V. Niel et al. *Inorg. Chem.* **(2001)**
G. Molnar et al. *Adv. Mat.* **(2007)**

Complexe cible: ligand tetradente + 2 anions pseudohalogénures NCX^-

Ligand **Bis-pyridine**
Champ fort
→ Complexe **BS**



$[FeL^A(NCS)_2]$
Low-Spin



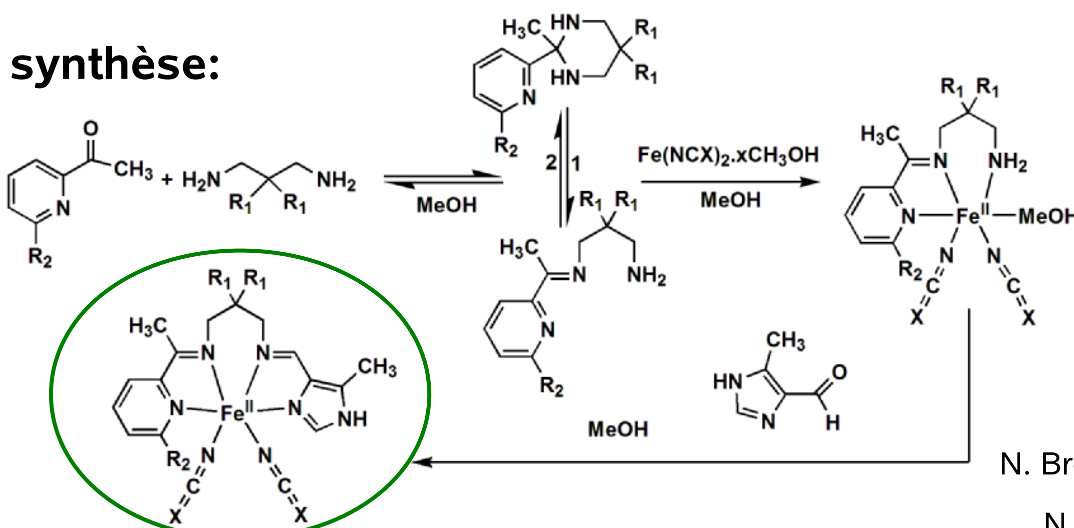
$[FeL^B(NCS)_2]$
High-Spin

Ligand **Bis-imidazole**
Champ faible
→ Complexe **HS**

?

Un **Ligand Tetradente Asymétrique** peut-il générér une TS ?

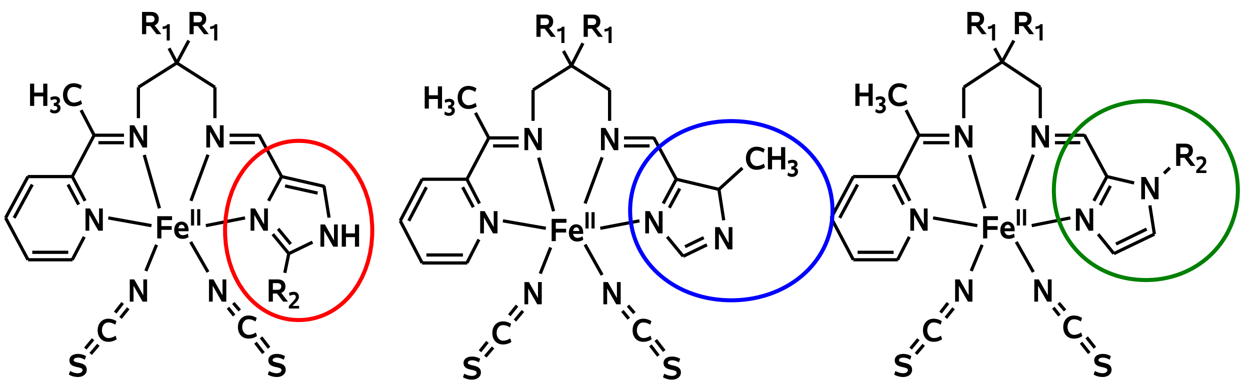
Stratégie de synthèse:



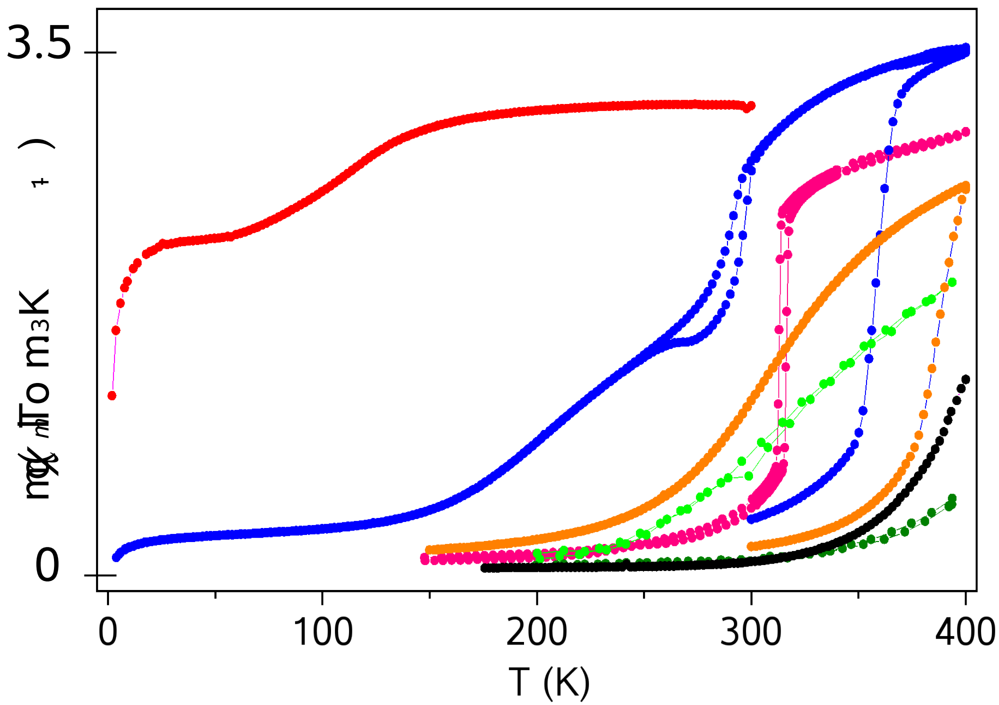
N. Bréfuel et al., *Chem Comm.* **(2007)**

N. Bréfuel et al. *Polyhedron* (**2007)**

Propriétés Magnétiques de la famille [FeL(NCS)$_2$]



FeL^{Cx}(NCS)$_2$ **FeL^{Dx}(NCS)$_2$** **FeL^{Ex}(NCS)$_2$**



R_1 = H, CH_3

R_2 = H, CH_3, C_6H_5

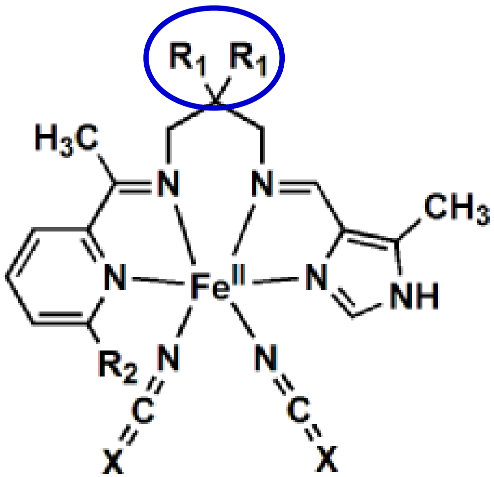
NCS^-, $NCSe^-$

Modulation du champ de ligand
(nature et position des substituants)

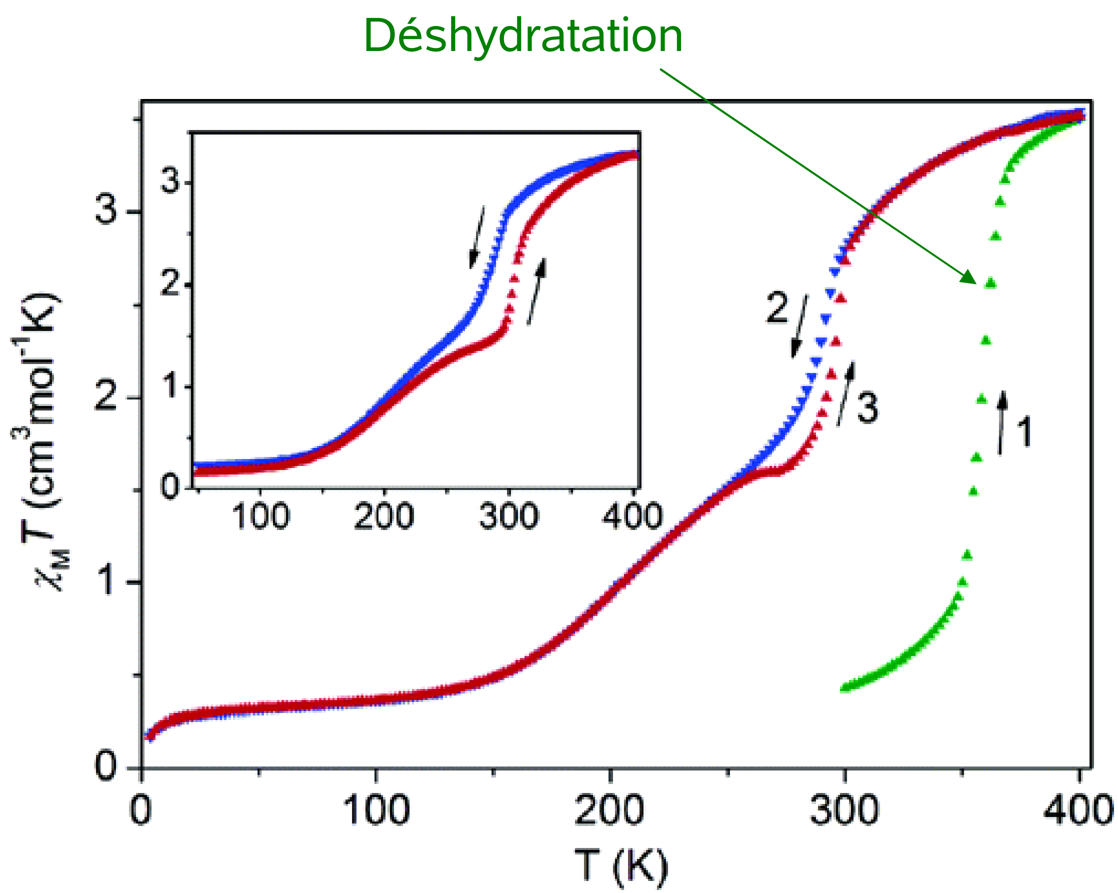
N. Bréfuel et al., *Chem Mat.* **(2006)**

N. Bréfuel et al., *Eur. J Inorg. Chem.* **(2007)**

*Propriétés Magnétiques de [FeL^{D2} (NCS)$_2$].H$_2$O (R$_1$ = H) (**1**)*

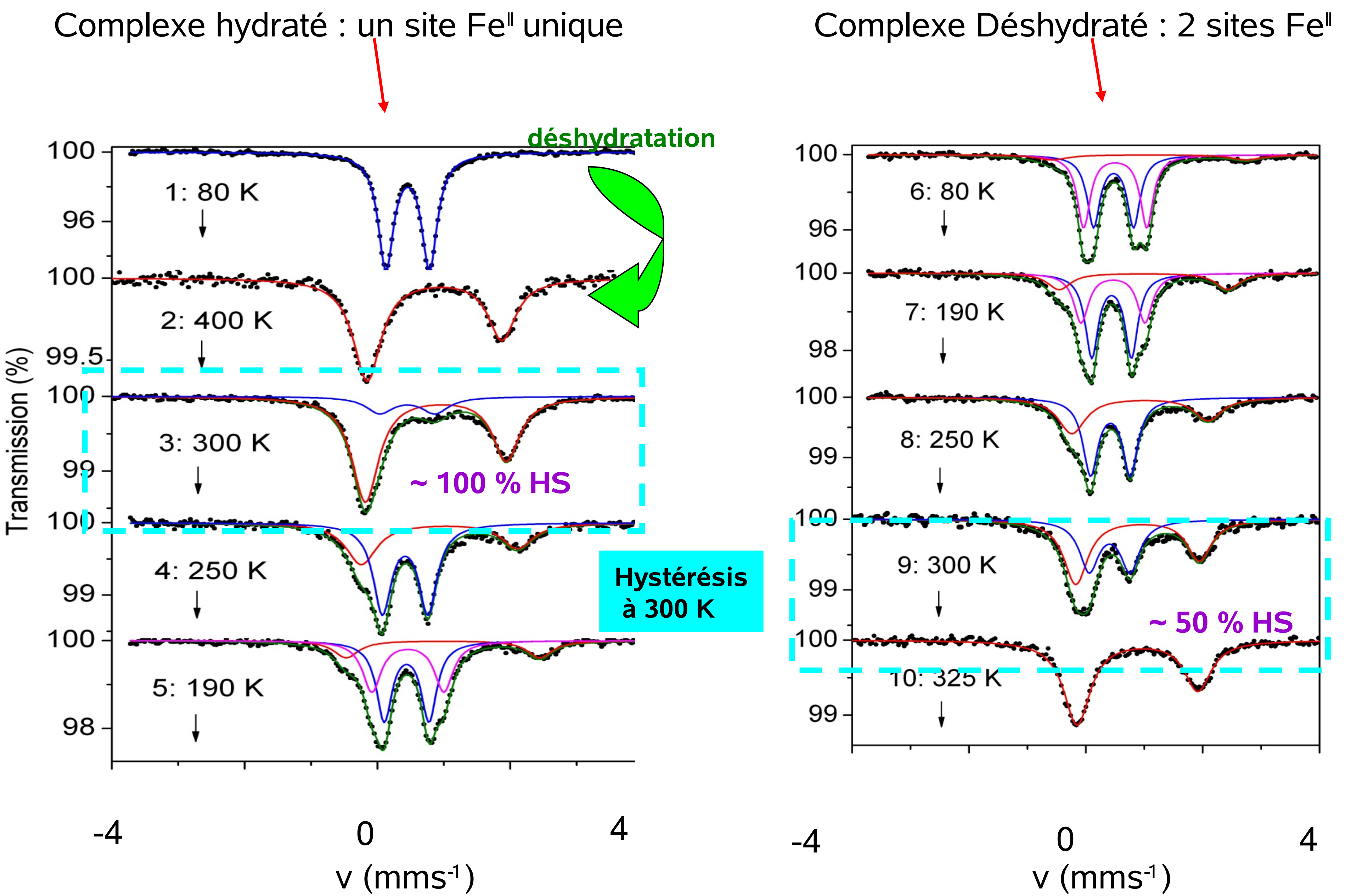


<u>1^{ière} étape:</u>
$T_{1/2}$ = 202 K
<u>2^{ième} étape:</u>
Hystérésis $T_{1/2}$ ↑ = 304 K,
$T_{1/2}$ ↓= 293 K

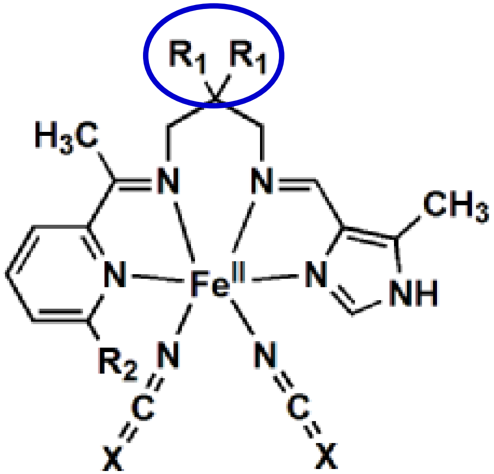


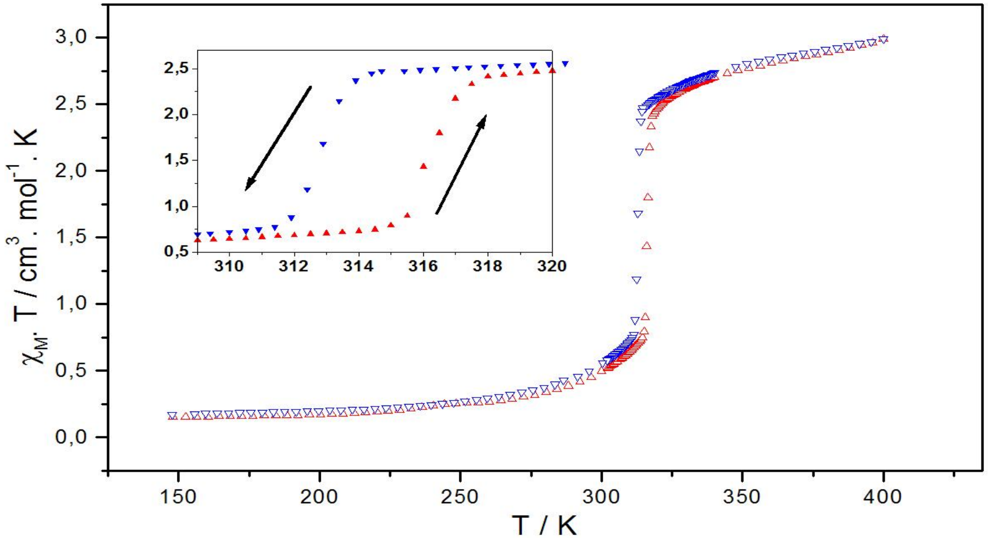
- Transition en **deux étapes** (espèce déshydratée)
- 2nde étape avec **hystérésis** (11 K) at ~ 300 K
- **Deux sites Fe^{I} distinguables** ?

*Spectres Mössbauer de $[FeL^{D2}(NCS)_2].H_2O$ (**1**)*

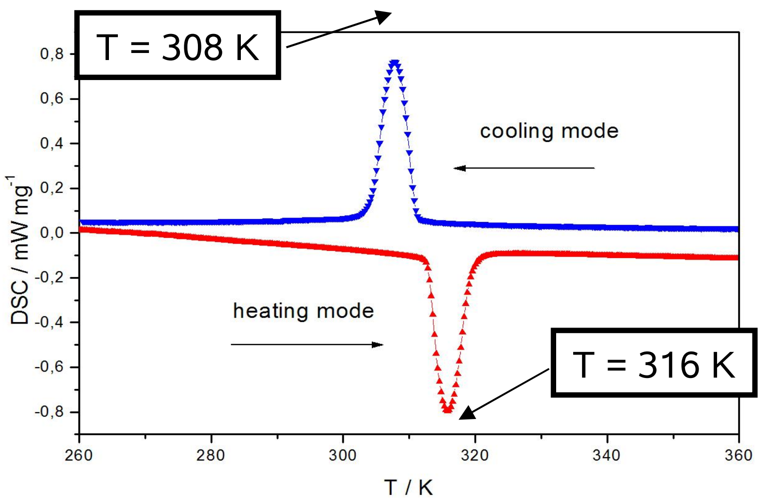


Propriétés Magnétique de [FeL^{D1} (NCS)$_2$] (R$_1$ = CH$_3$) (2)

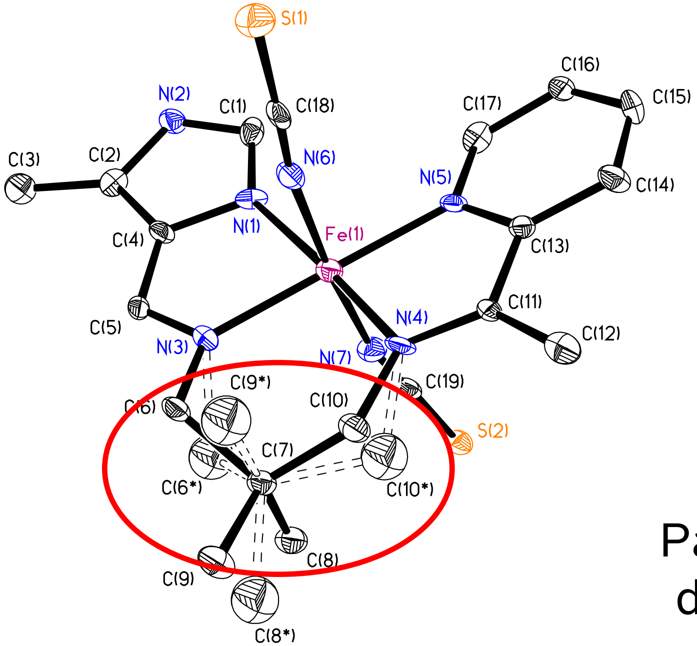




- TS du **1er ordre,** T$_{1/2}$ **=** 315 K
- **Boucle d'hystérésis** de 4K
- Transition de phase structurale ?

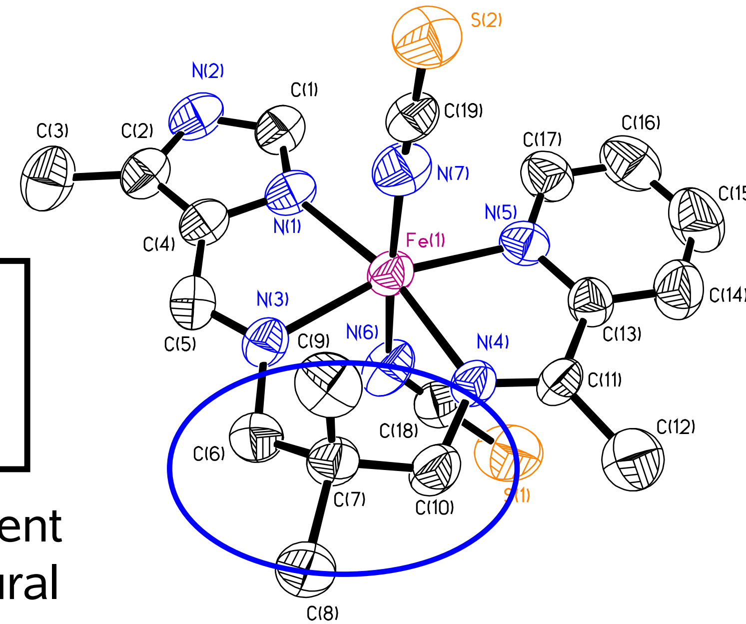


Structure Moléculaire de $[FeL^{DI}(NCS)_2]$ (**2**)



$C_{19}H_{23}N_7S_2Fe$
Triclinique, P_{-1}
Z = 2

Pas de changement de phase structural



T = 300 K (BS) ⟷ T = 350 K (HS)

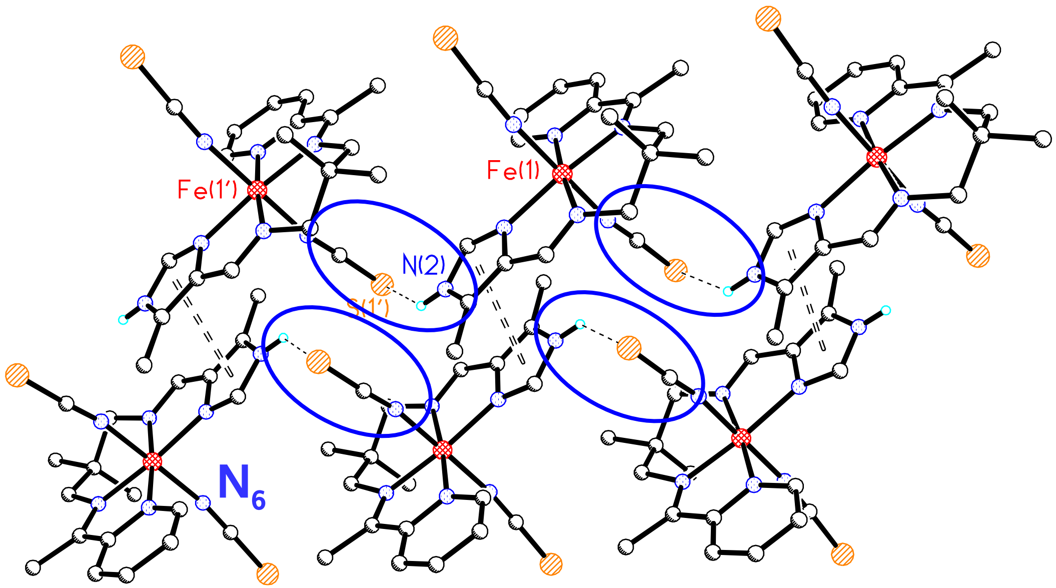
Deux positions statistiques du fragment C_6-C_7-C_{10}

Fragment C_6-C_7-C_{10} désordonné

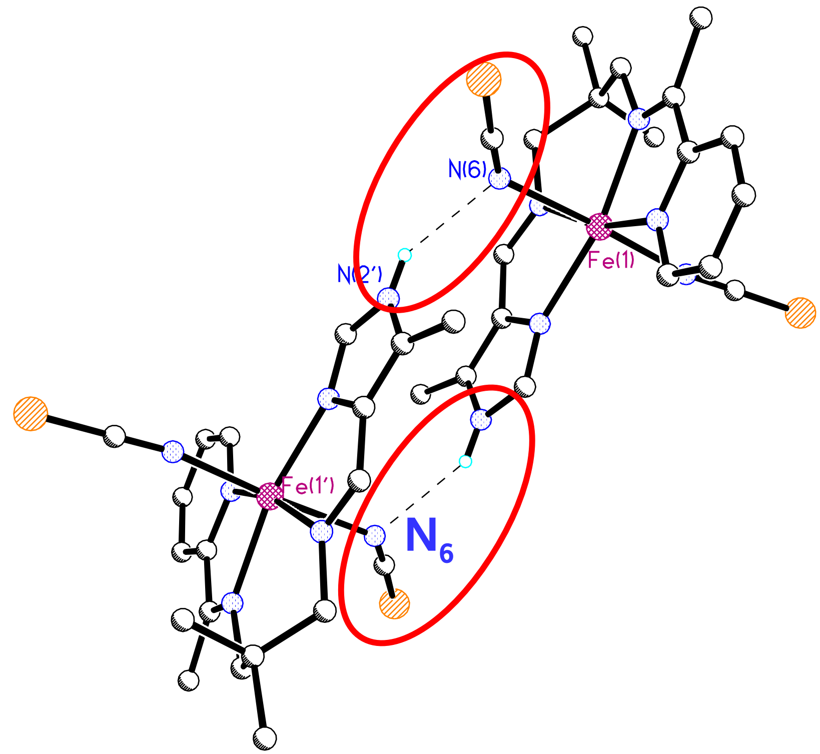
	T = 300 K (BS)	T = 350 K (HS)
Fe(1)-N(6)	1.933(6)	2.370(5)
Fe(1)-N(7)	1.936(6)	2.082(5)
Fe(1)-N(4)	1.958(4)	2.147(3)
Fe(1)-N(3)	1.957(5)	2.116(4)
Fe(1)-N(5)	1.965(4)	2.124(4)
Fe(1)-N(1)	2.046(4)	2.177(4)

Δd/d = 6 à 22 % !! ⟶

*Structure Supramoléculaire de $[FeL^{DI}(NCS)_2]$ (**2**)*



300 K
Contacts **NCS···HN** (imidazole)



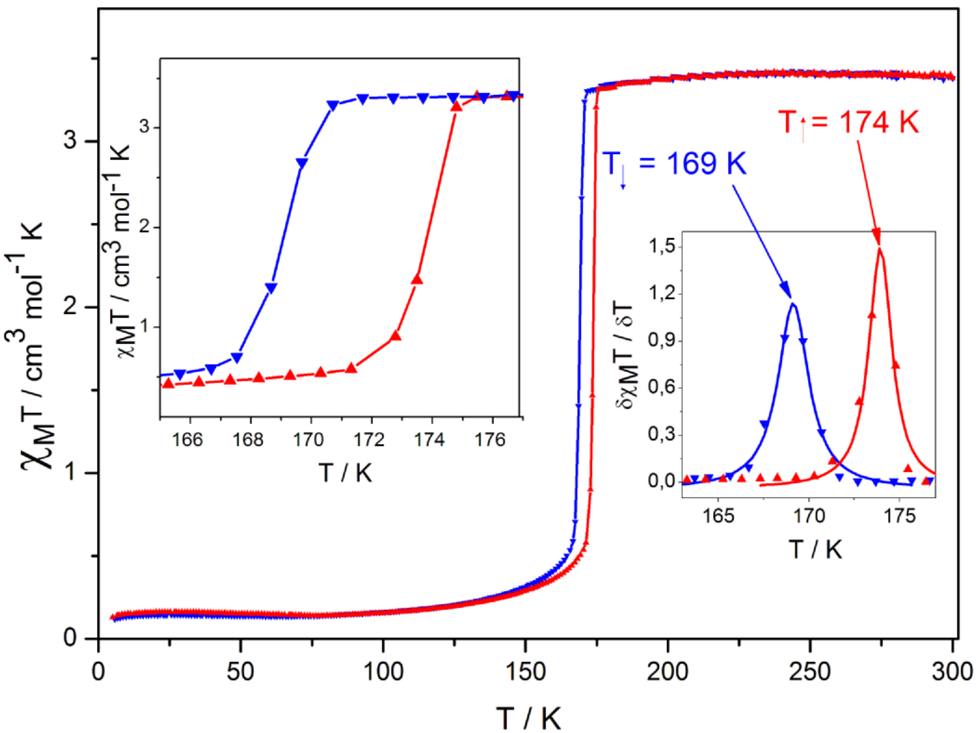
→

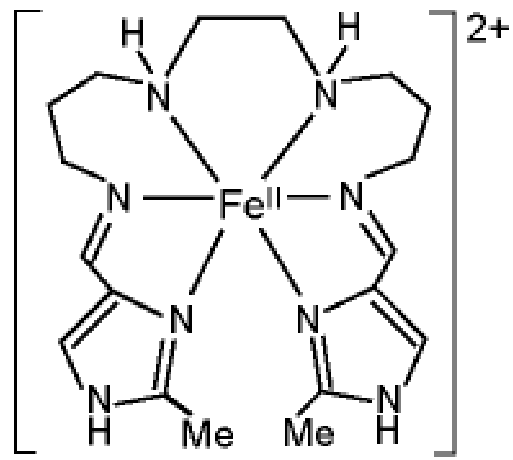
350 K
Contacts **SCN···HN** (imidazole)

➡ Réarrangement du réseau de liaisons hydrogène

Systèmes supramoléculaires: effet du contre-anion

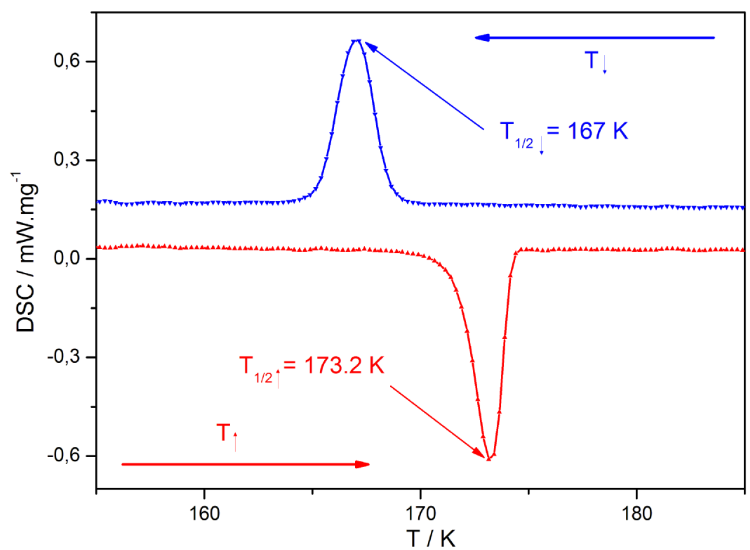
$[FeH_2L^{2Me}](ClO_4)_2$ (**3**)





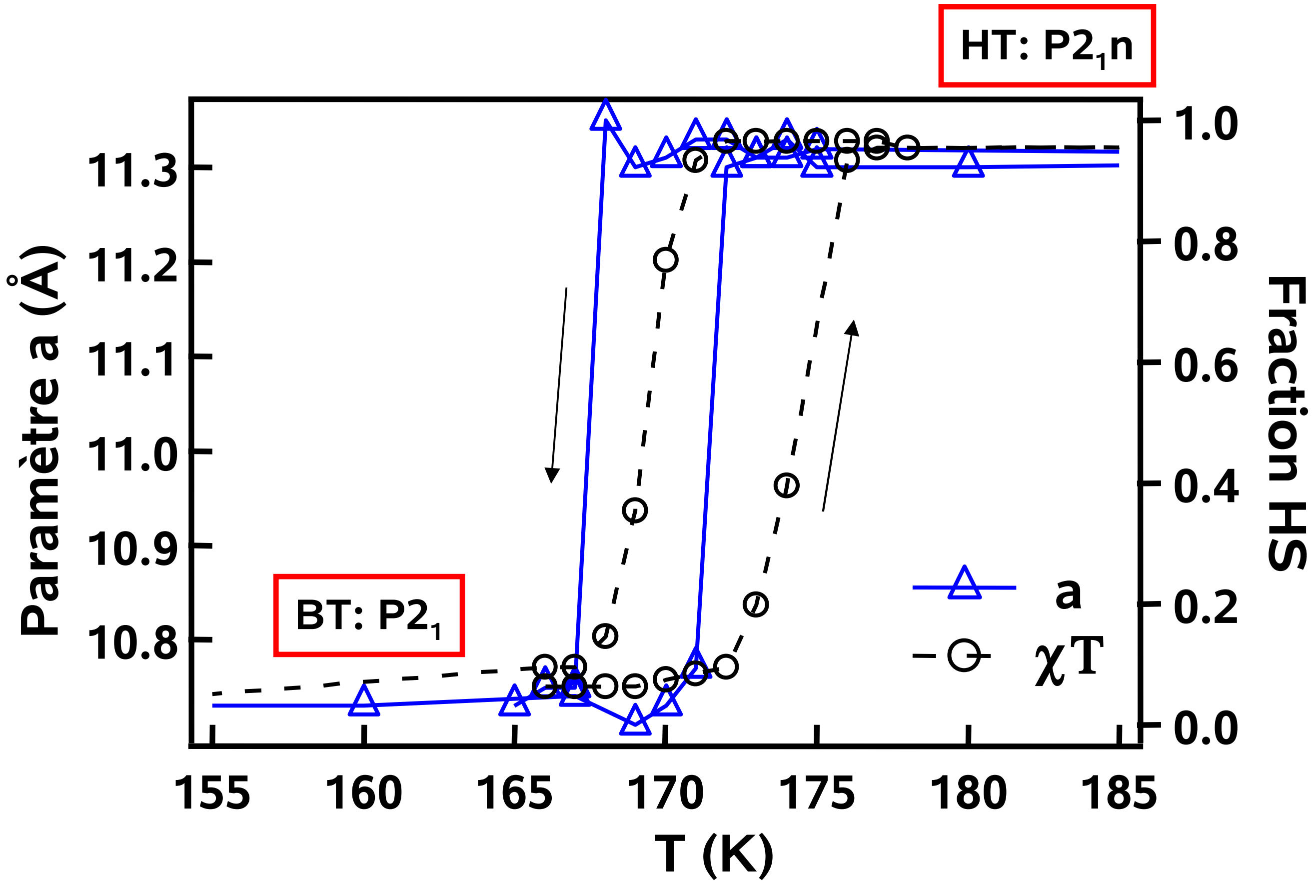
2 ClO_4^-

-Transition du 1er ordre
($T_{1/2}$ = 171 K , hystérésis de 5 K)
- Transition phase structurale ?

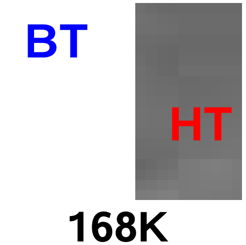


N. Bréfuel et al., *Inorg. Chem.* **(2006)**

*Variation du paramètre de maille a de $[FeH_2L^{2Me}](ClO_4)_2$ (**3**)*



Tâche de Bragg
(2,0,3)



Séparation de Phase

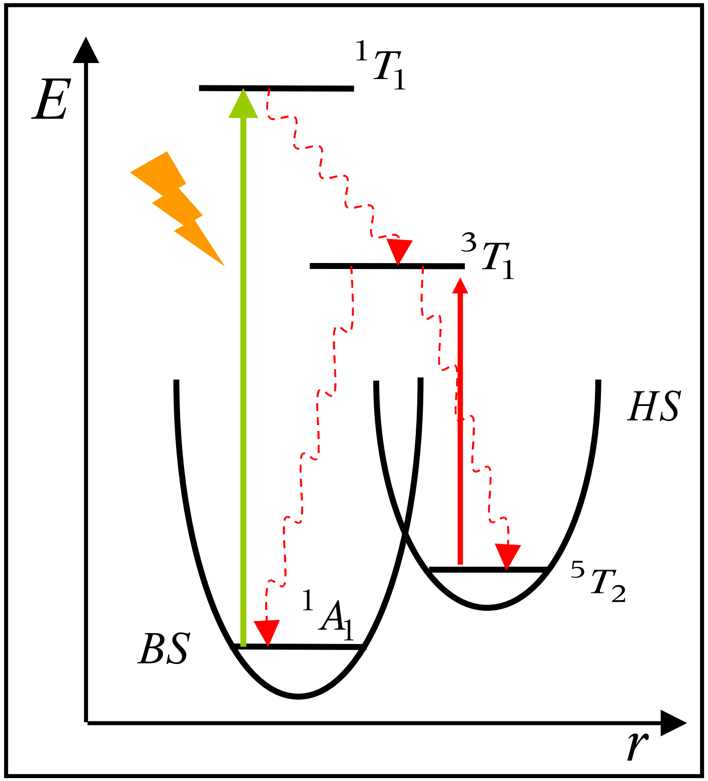
Précision du
jet Cryostat He
:±0.1 K

Maille : $T_{1/2\downarrow}$ =168K, $T_{1/2\uparrow}$ =171K (abrupte)

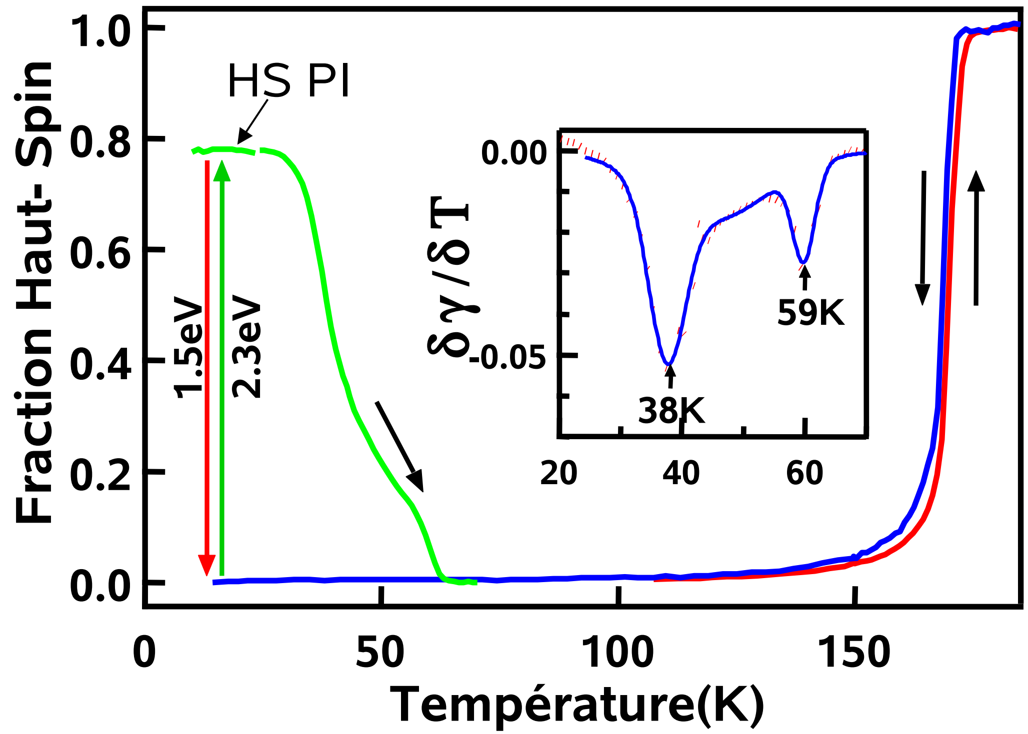
Spin : $T_{1/2\downarrow}$ =169K, $T_{1/2\uparrow}$ =174K (+ graduelle)

- Variation brutale du paramètre de maille avec hystérésis (séparation de phase)
- Transitions de phase magnétique/structurale du 1ier ordre

Effet LIESST pour $Fe[H_2L^{2Me}](ClO_4)_2$ (3)



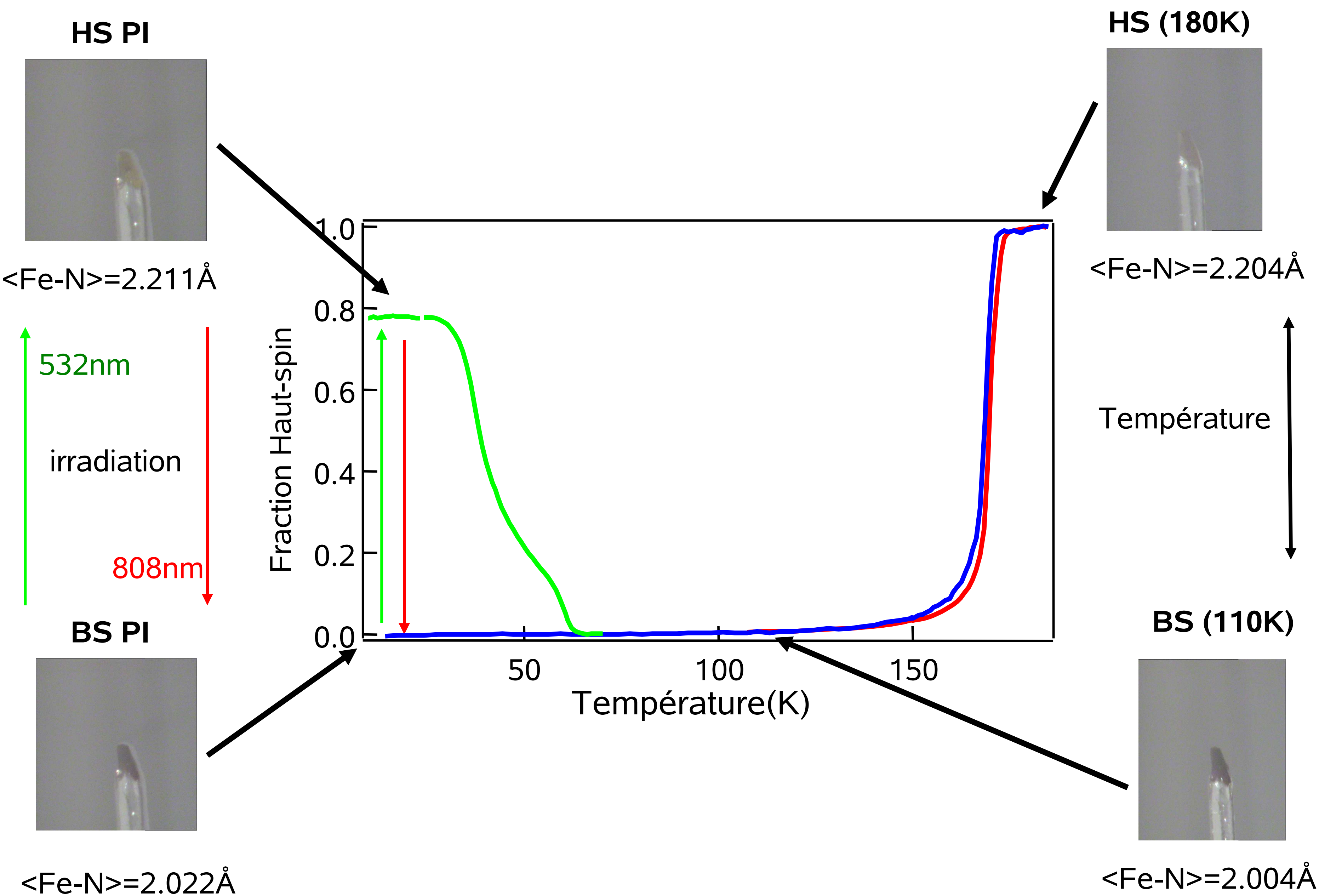
HS PI = état HS photo-induit



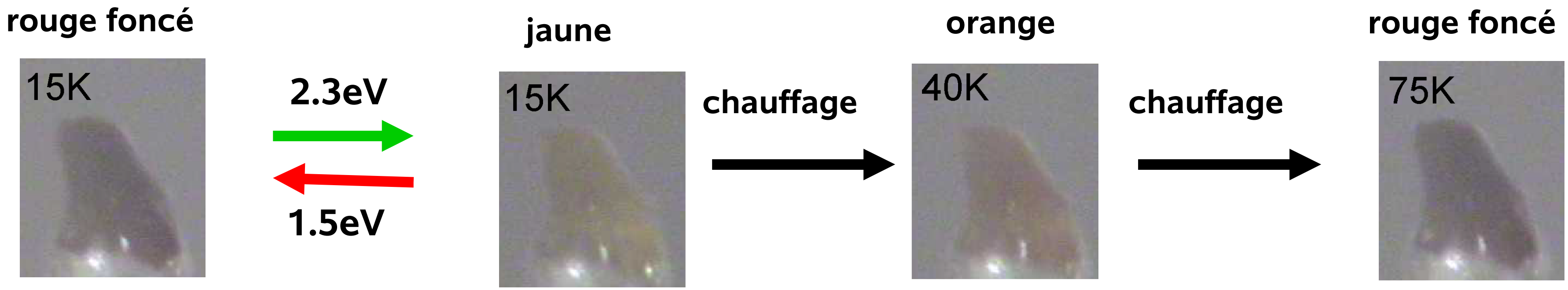
- **Effet LIESST (quasi quantitatif) et reverse LIESST observés**
- **Relaxation du PIHS vers l'état BS en deux étapes (38K et 59K)**

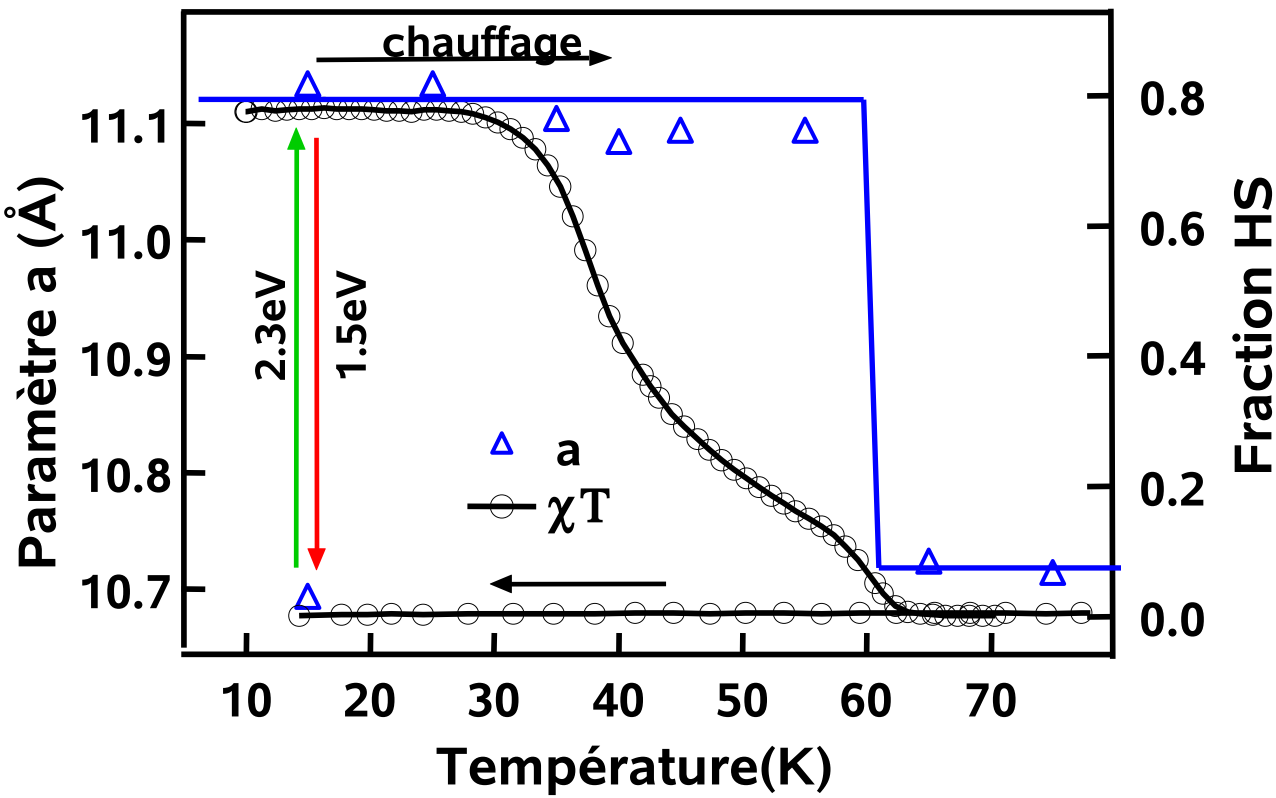
Origine d'un tel processus ?

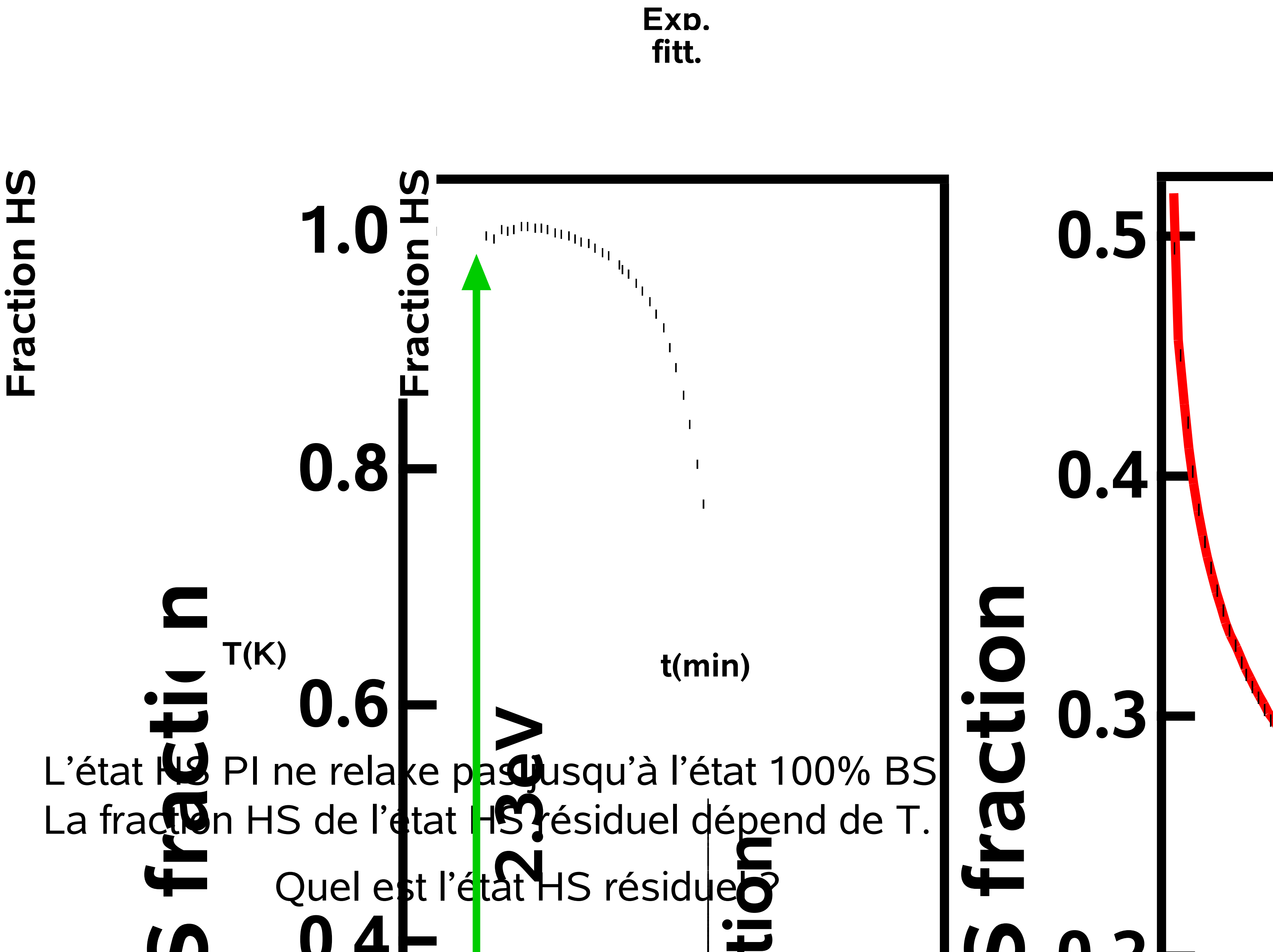
*Photocristallographie de $[FeH_2L^{2Me}](ClO_4)_2$ (**3**)*



Evolution de l'état PIHS en f(T)







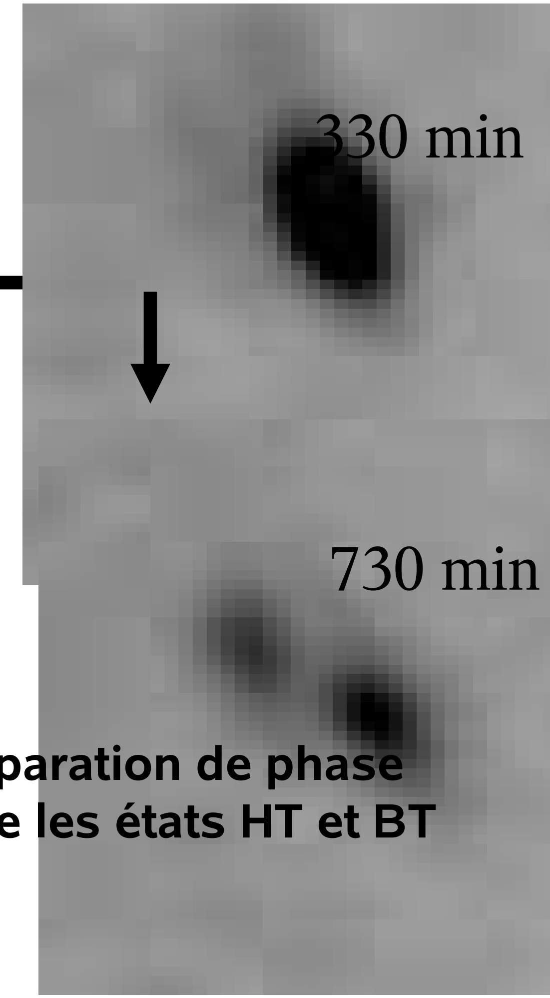
L'état HS PI ne relaxe pas jusqu'à l'état 100% BS

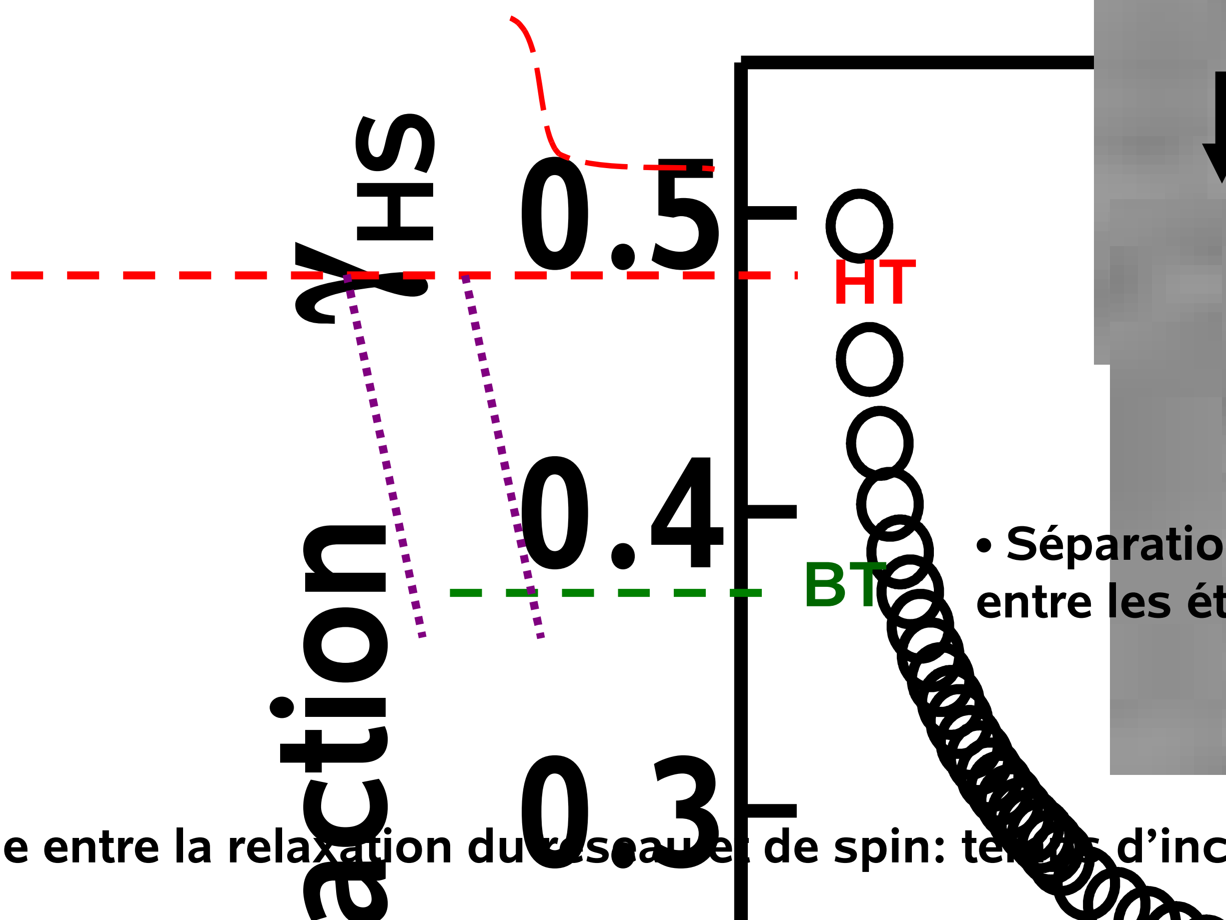
La fraction HS de l'état HS résiduel dépend de T.

Quel est l'état HS résiduel ?

Evolution du paramètre a en f(t) à 45K

Tâche de Bragg (-7,0,3)

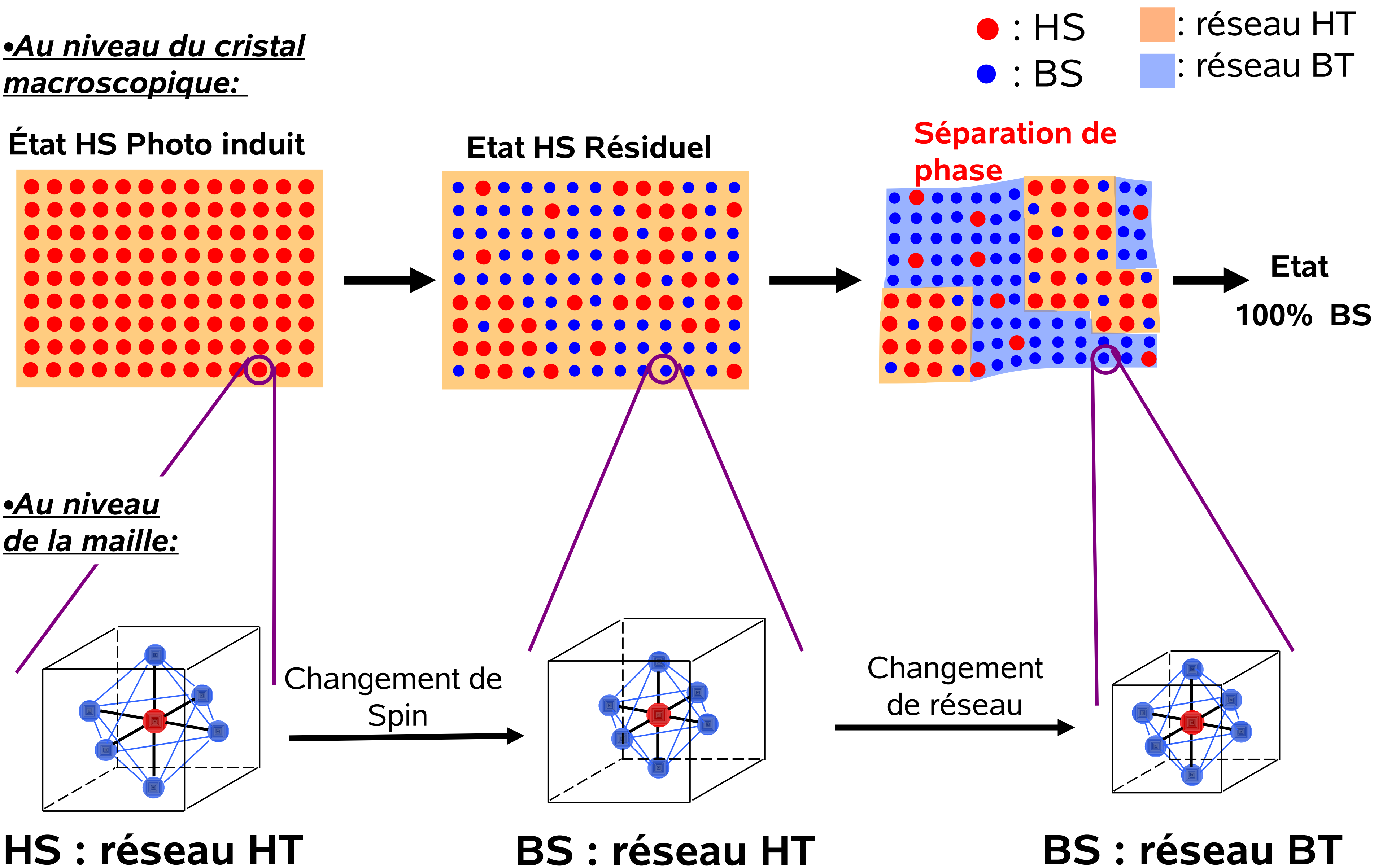




• **Séparation de phase entre les états HT et BT**

• **Décalage entre la relaxation du réseau et de spin: temps d'incubation**

En résumé…

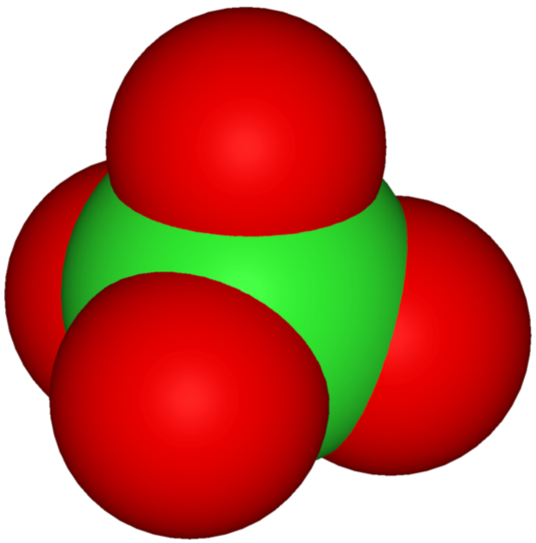


H. Watanabe, N. Bréfuel et al., soumis

Effet du changement du contre-anion

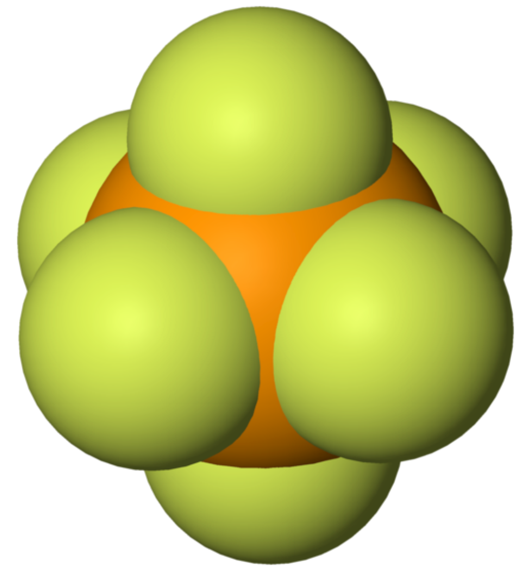
Anion Perchlorate
ClO_4^-

- Monoanionique
- Tetrahédrique



Anion Hexafluorophosphate
PF_6^-

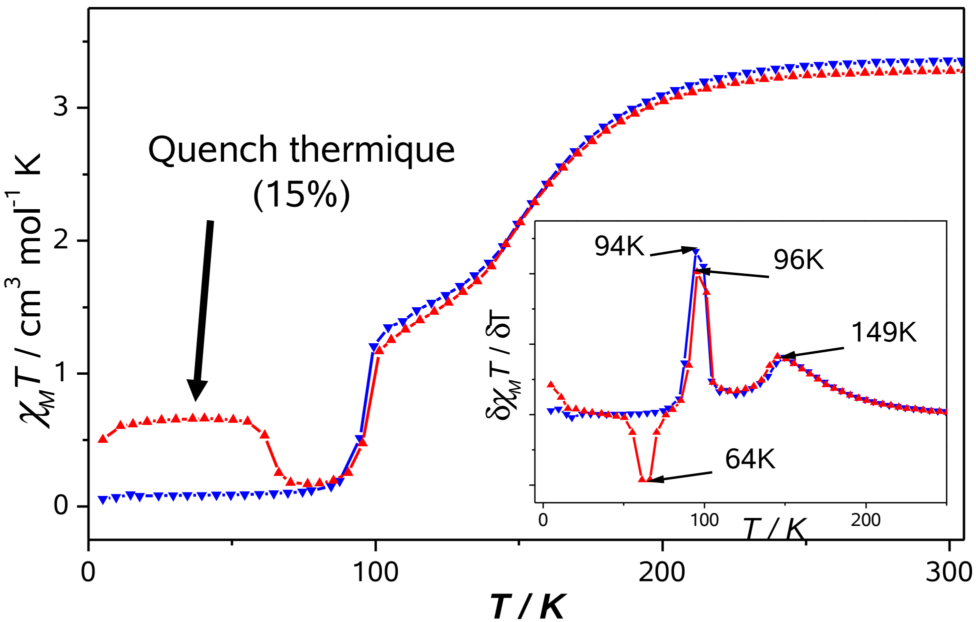
- Monoanionique
- Octahédrique



★ Effets géométriques sur le réseau de liaisons H: conséquences sur la TS ?

★ Remplacer PF_6^- par AsF_6^- ou SbF_6^-: effet de taille sur la TS ?

Etudes magnétiques et Mössbauer de $[FeH_2L^{2Me}](PF_6)_2$ (4)

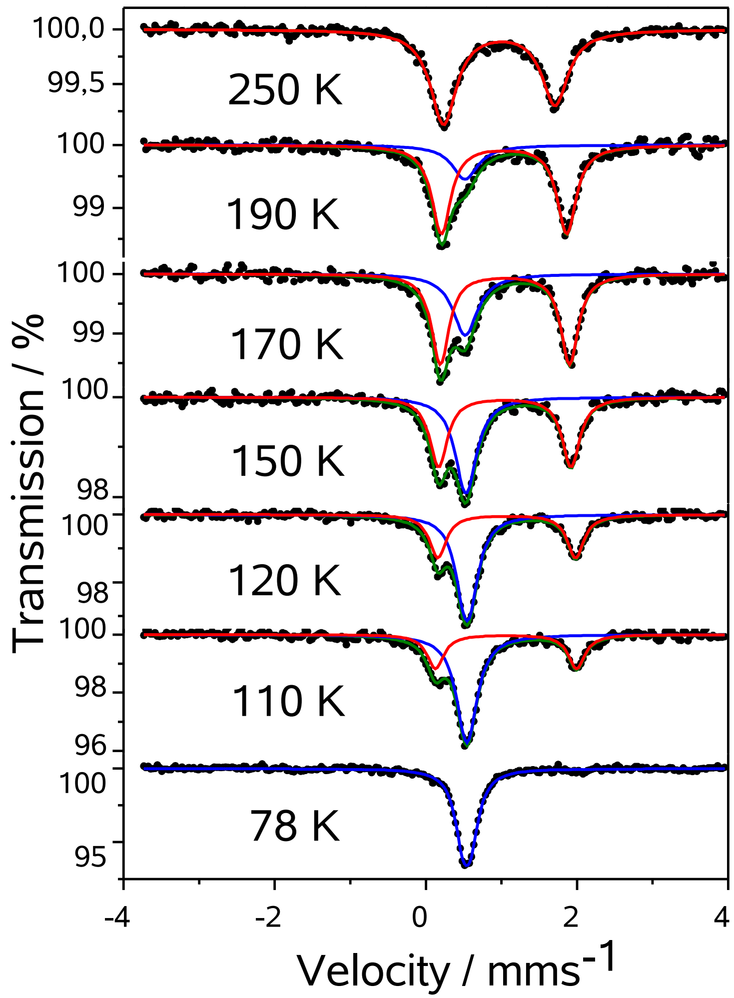


Les spectres Mössbauer ne mettent pas en évidence la présence d un plateau HS-LS vers 110-150 K

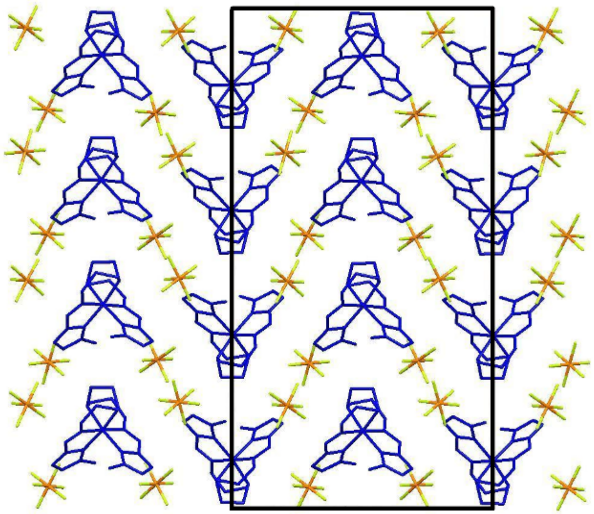
BS (100%, 78 K):
δ = 0.543(3) mm s^{-1} ,
ΔEQ = 0.11(2) mm s^{-1}

HS (100%, 250K):
δ = 0.971(6) mm s^{-1} ,
ΔEQ = 1.48(1) mm s^{-1}

TS en deux étapes:
HS ⇄ (½HS+½LS) ⇄ LS

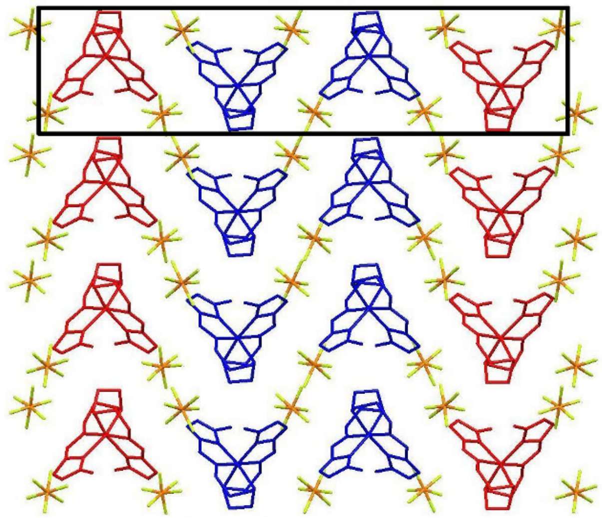


Etude cristallographique de (**4**)



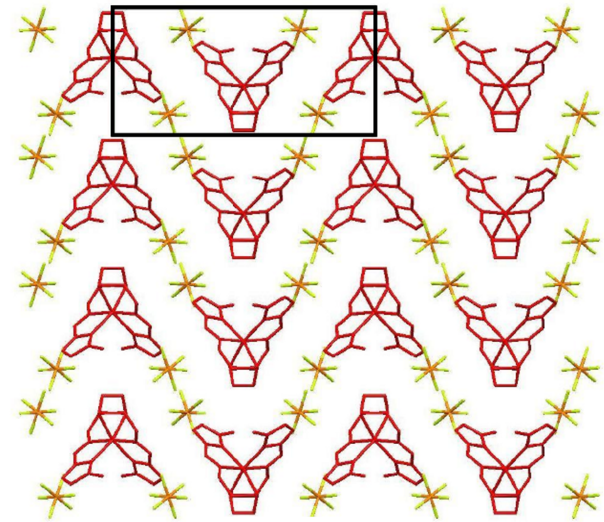
80 K BS

Orthorhombique,
P22$_1$2$_1$
a = 32.532(3), *b* = 9.424(1),
c = 17.054(1) Å



110 K HS/BS

Monoclinique,
P2$_1$
a = 8.185(1), *b* = 9.390(8),
c = 35.543(2) Å, β = 90.011(7)°

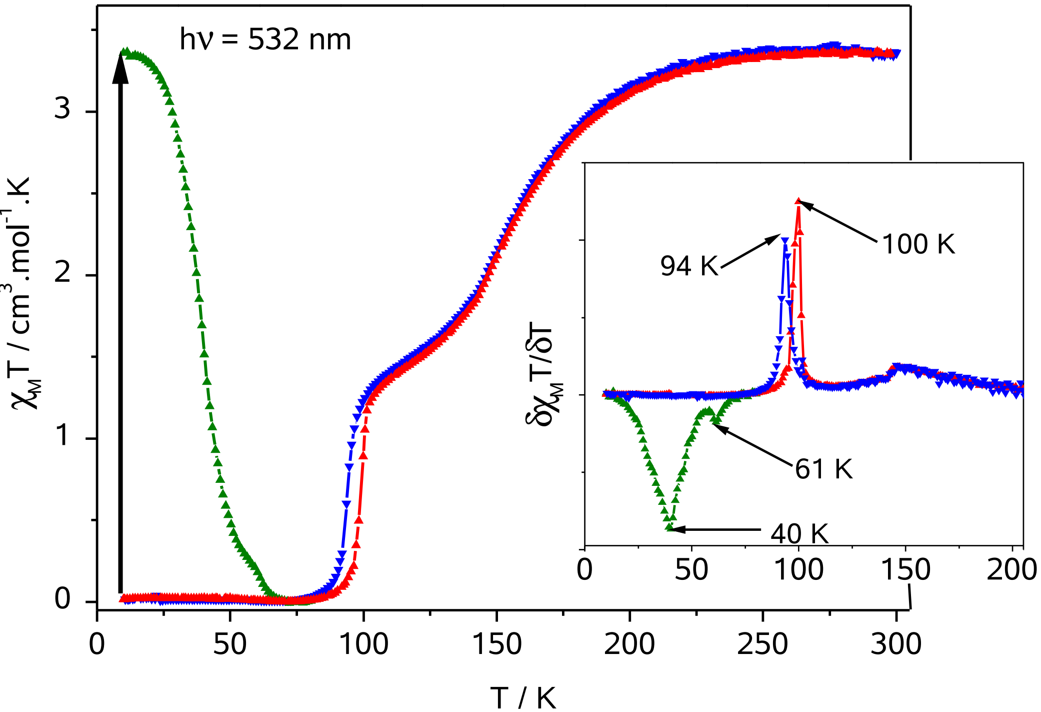


250 K HS

Orthorhombique,
P2$_1$2$_1$2$_1$
a = 8.405(1), *b* = 9.469(2),
c = 17.399(3) Å

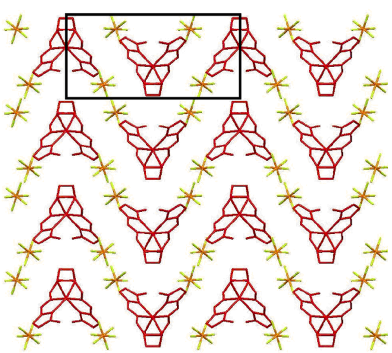
Structure	**250 K HS**	**110 K site 1**	**110 K site 2**	**80 K BS site 1**	**80 K BS site 2**
<Fe-N> (Å)	2.190(2)	2.13(1)	2.05(1)	2.012(3)	2.012(3)

Effet LIESST pour $Fe[H_2L^{2Me}](PF_6)_2$ (**4**)



- Relaxation de l'état HS PI vers l'état BS en deux étapes (40K et 61K)
- Etat HS photoinduit distinct de l'état HS "thermique"

Structure	250 K HS	HS PI site 1	HS PI site 2
<Fe-N> (Å)	2.190(2)	2.17(1)	2.18(1)

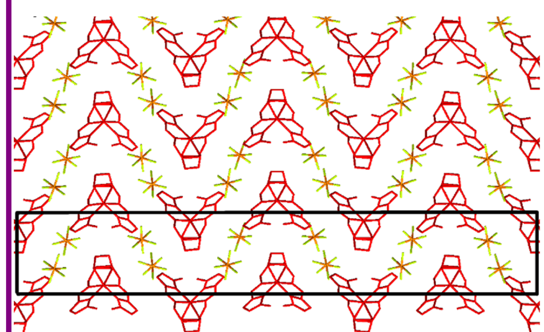


Orthorhombique, $P2_12_12_1$

a = 8.405(1) Å,
b = 9.469(2) Å,
c = 17.399(3) Å

HS (250 K)

≠

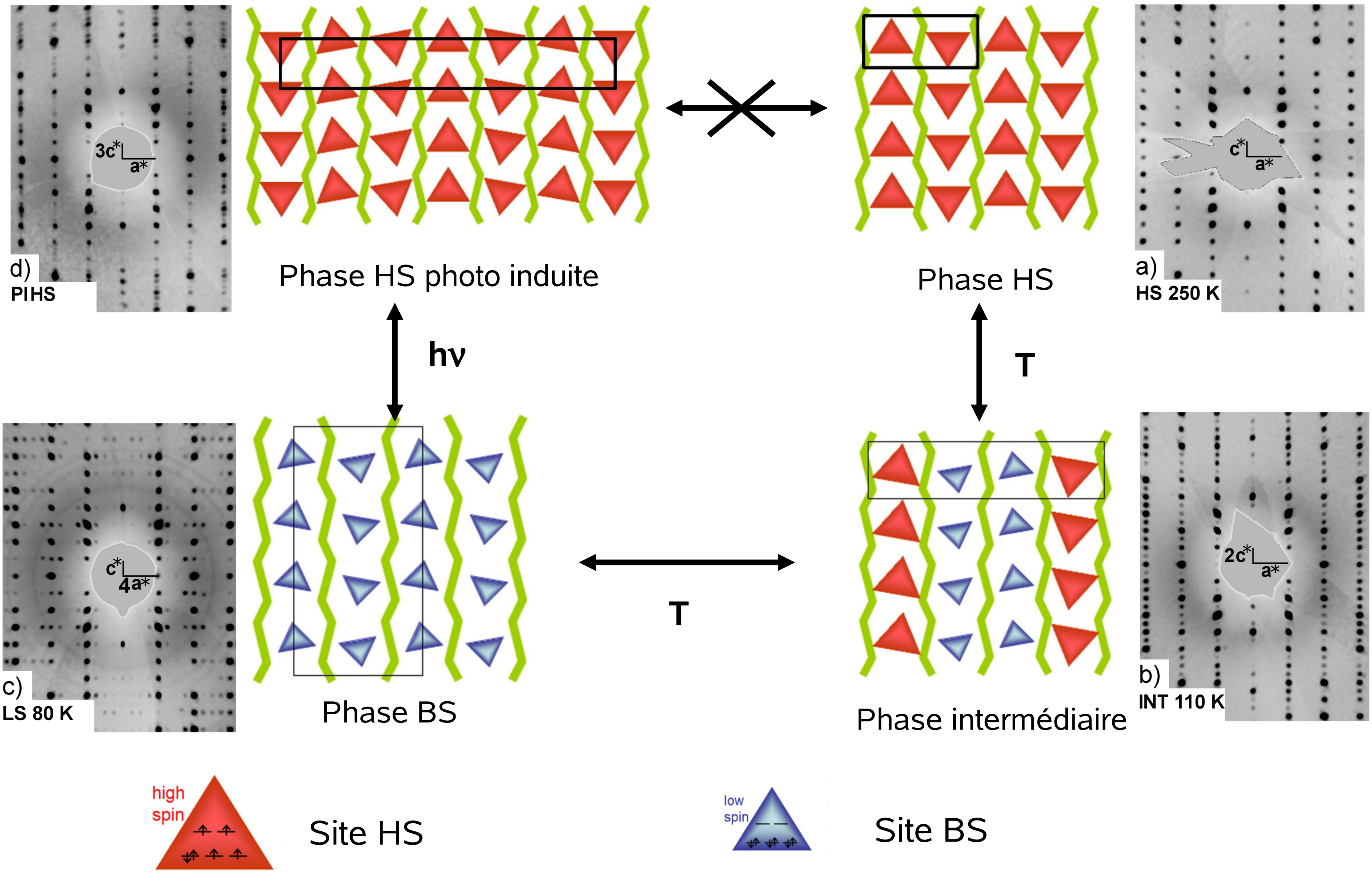


Orthorhombique, $P22_12_1$

a = 8.226(2) Å,
b = 9.330(1) Å,
c = 52.20(1) Å

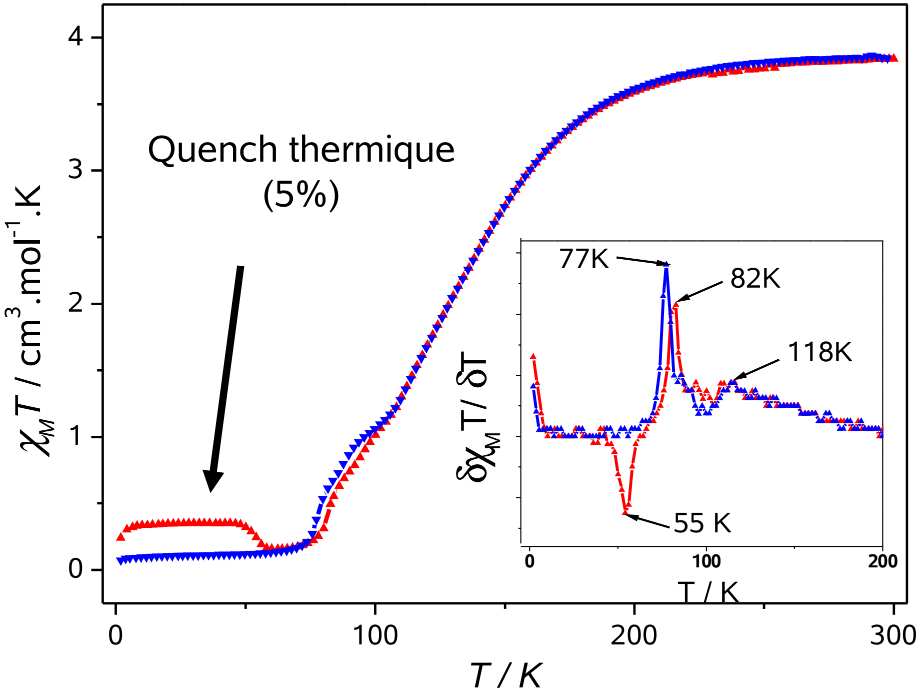
HS PI (10 K)

En résumé…

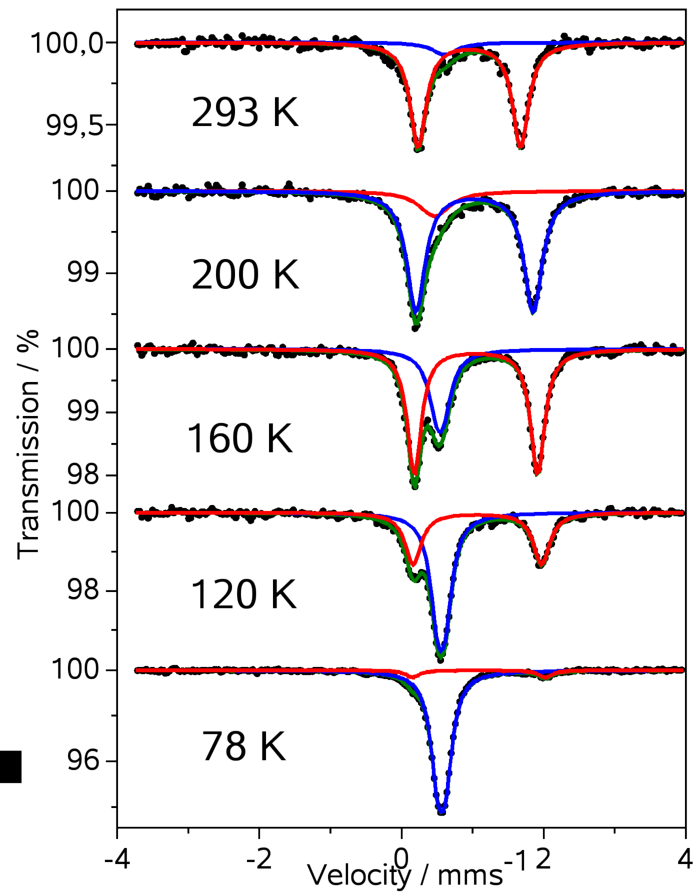


N. Bréfuel et al., accepté *Angew.Chem.Int.Ed.* **2009**

*Etudes magnétiques et Mössbauer de FeH_2L^{2Me} $(AsF_6^-)_2$ (**5**)*



TS graduelle et complète, en deux étapes (1/3, 2/3 ?) avec hystérésis



BS (93%, 78 K):

δ = 0.561(2) mm s^{-1} ,

ΔEQ = 0.112(5) mm s^{-1}

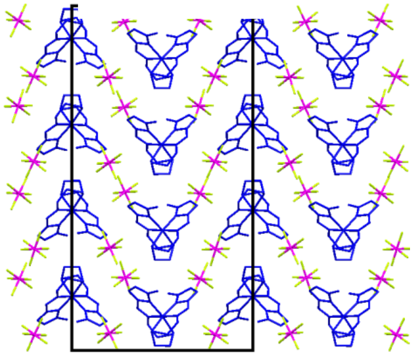
HS (7%, 78K):

δ = 1.08(7) mm s^{-1} ,

ΔEQ = 1.87(1) mm s^{-1}

Etude cristallographique de (*7*)

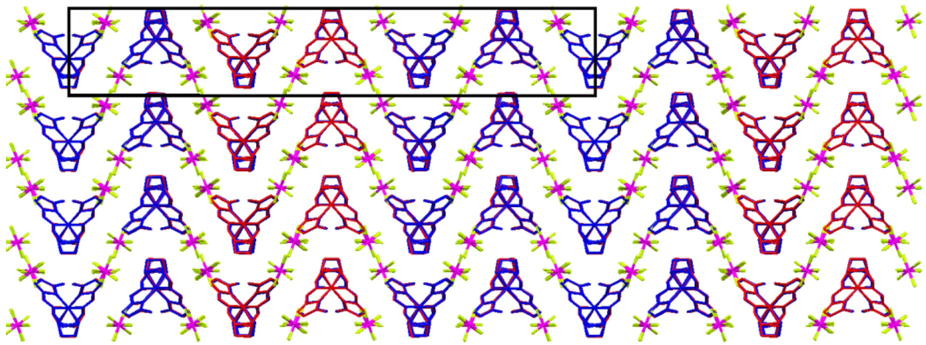
15 K BS



Orthorhombique,
$P22_12_1$

a = 32.746(3), b = 9.454(1),
c = 17.2850(1) Å

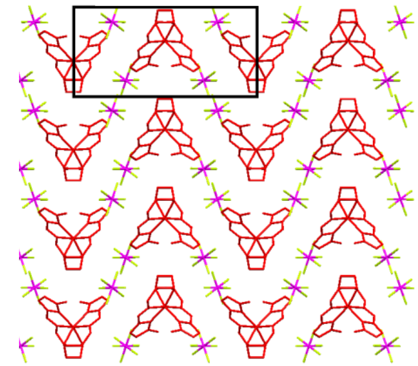
105 K HS/BS



Orthorhombique,
$P22_12_1$

a = 8.2451(7), b = 47.197(4),
c = 52.289(4) Å

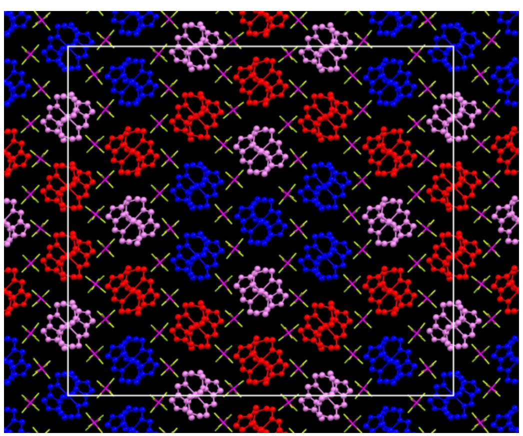
250 K HS



Orthorhombique,
$P2_12_12_1$

a = 8.4897(10), b = 9.505(4),
c = 17.2850(10) Å

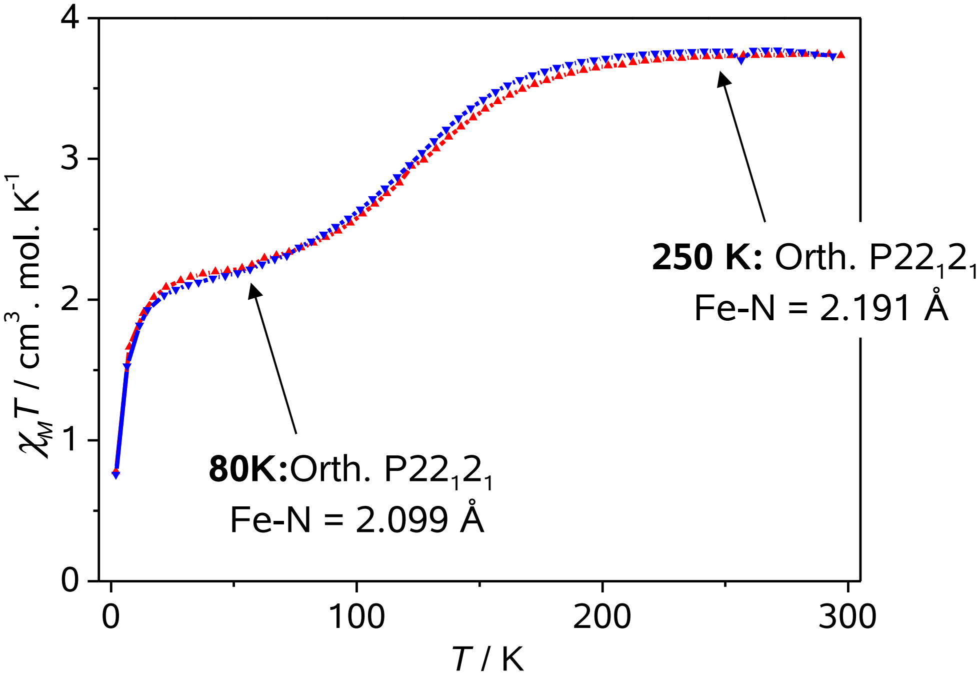
Structure	**250 K HS**	**105 K site 1**	**105 K site 2**	**105 K site 3**	**80 K BS site 1**	**80 K BS site 2**
<Fe-N> (Å)	2.187(2)	2.103(1)	2.056(7)	2.004(1)	2.025(3)	2.021(3)

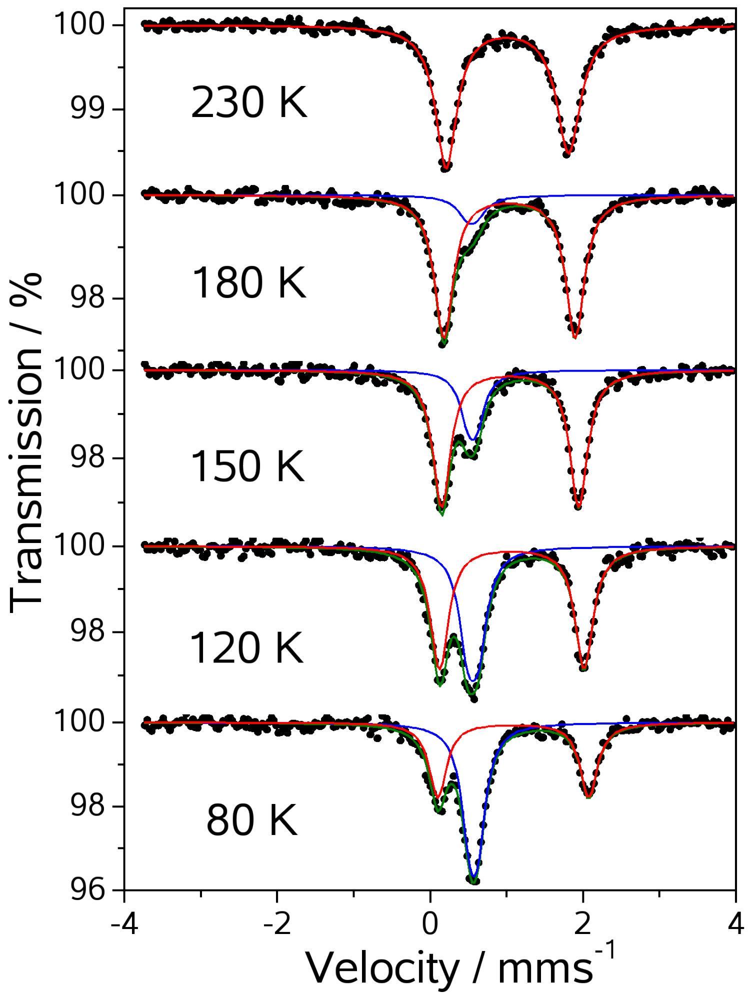


A 105 K: 30 molécules/maille
- 10 molécules **BS** (Fe-N = 2.004 Å)
- 8 molécules majoritairement **BS** (Fe-N = 2.056 Å)
- 12 molécules **HS** (Fe-N = 2.103 Å)

- Bon accord entre les propriétés magnétiques et structurales
- Mise en ordre en « losange »

Etudes magnétiques et Mössbauer de $FeH_2L^{2Me}(SbF_6^-)_2$ (**6**)





TS graduelle et incomplète (50%):

HS ⇄ (½ HS + ½ BS)

BS (53%, 80 K):

δ = 0.567(5) mm s^{-1},

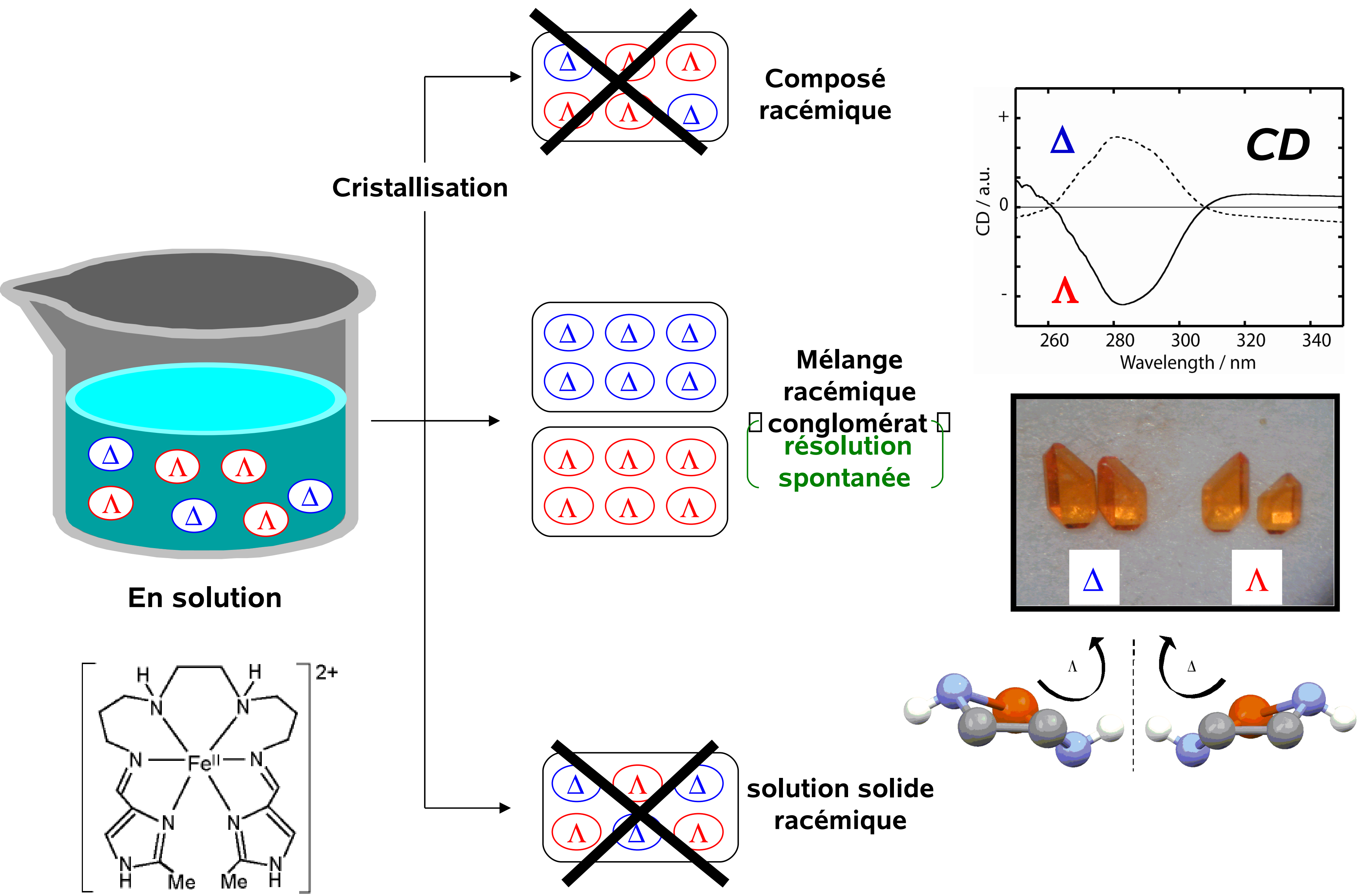
ΔEQ = 0.11(3) mm s^{-1}

HS (47%, 80K):

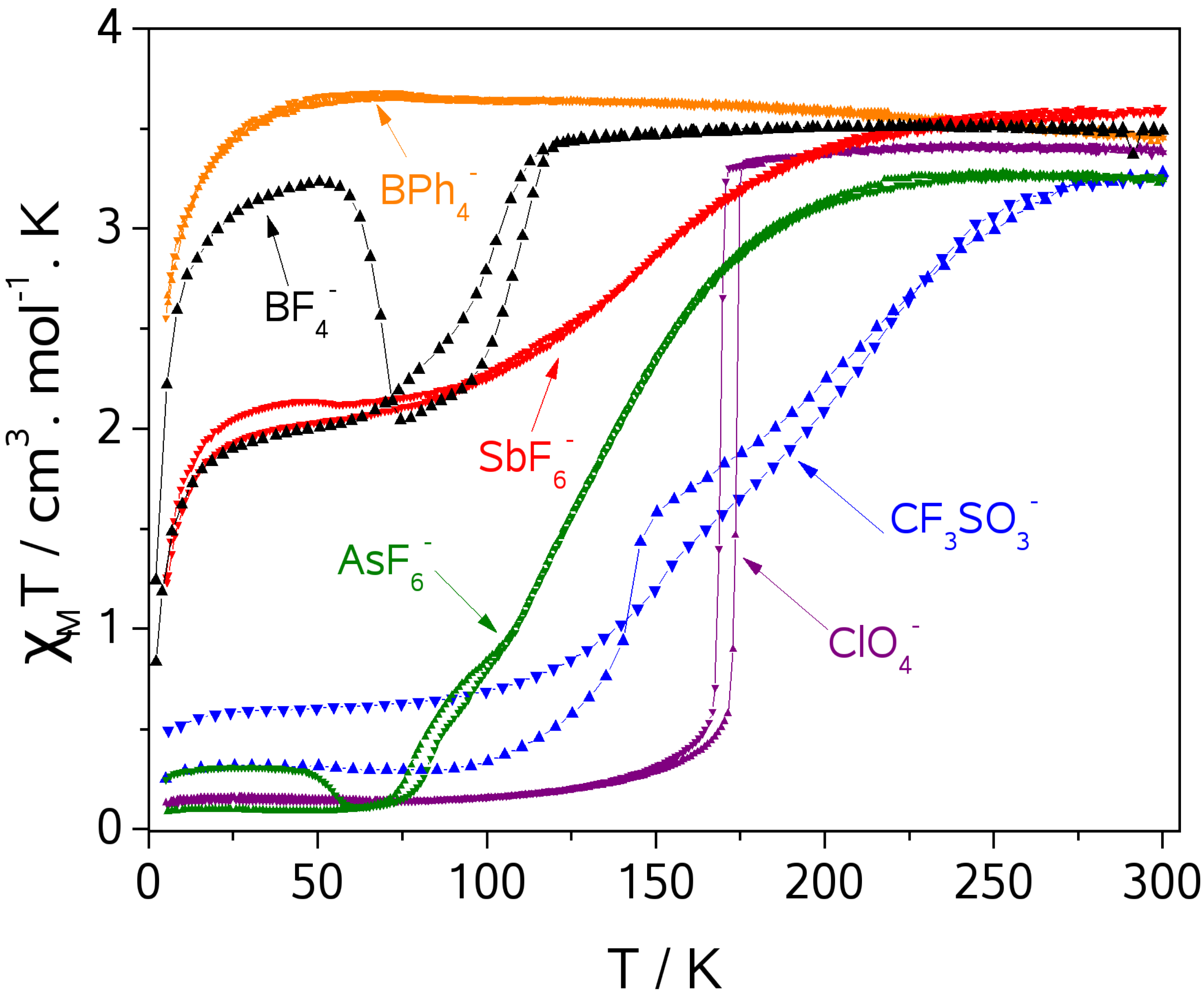
δ = 1.084(8) mm s^{-1},

ΔEQ = 1.98(2) mm s^{-1}

Résolution Spontanée et chiralité

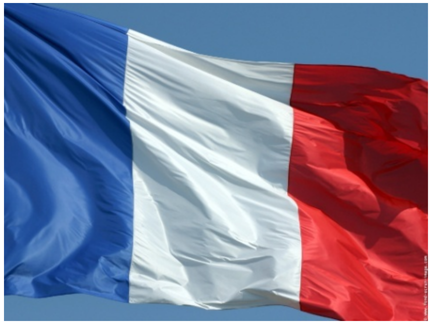


La famille $[FeH_2L^{2Me}]X_2$



La TS peut être modulée par la nature du contre-anion

Remerciements



Prof. J.-P. Tuchagues, Dr. A Bousseksou, Dr. G. Molnar, Dr. S Cobo, J. Come
LCC, Toulouse

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A. Eguchi, Dr. H. Watanabe, Prof. K. Tanaka,
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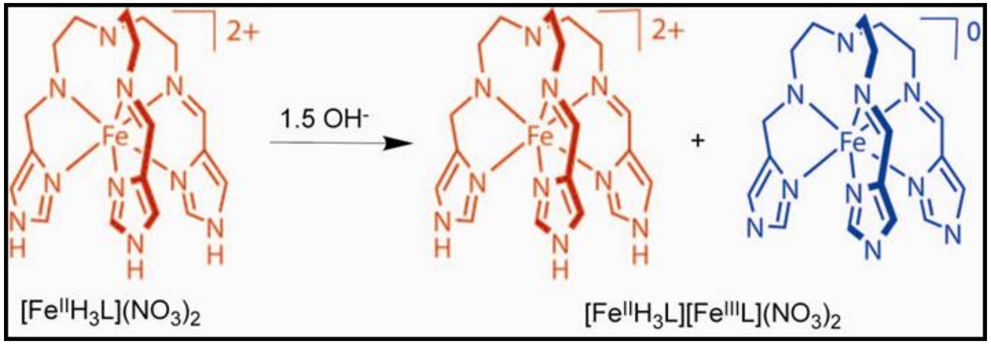
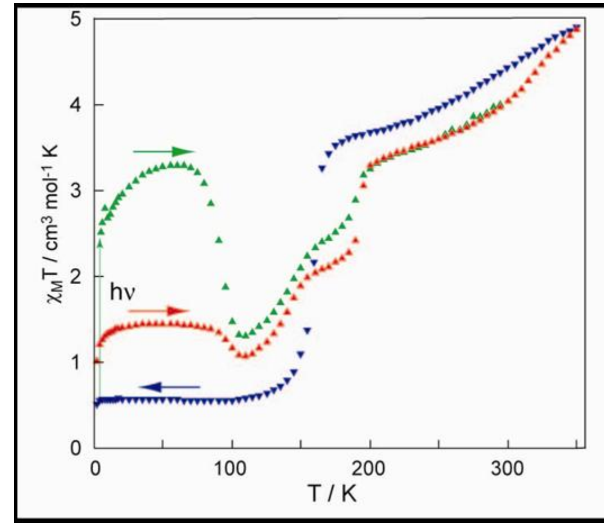
Department of Chemistry, Okayama University

Merci pour votre attention !!

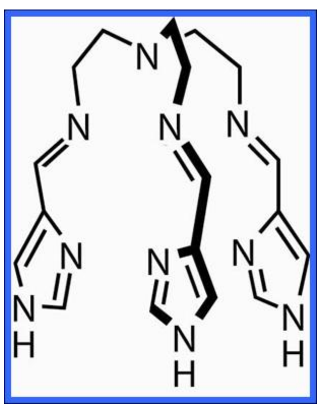
Y. Sunatsuki, N. Matsumoto et al., *Angew. Chem.Int. Ed.* **2003**

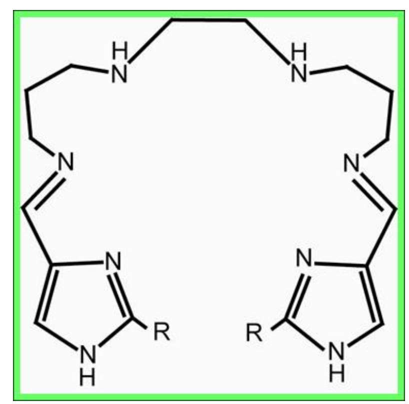




Complexe homochiral à transition de spin et valence mixte (Fe^{II}/Fe^{III})

H_3L^{2H}



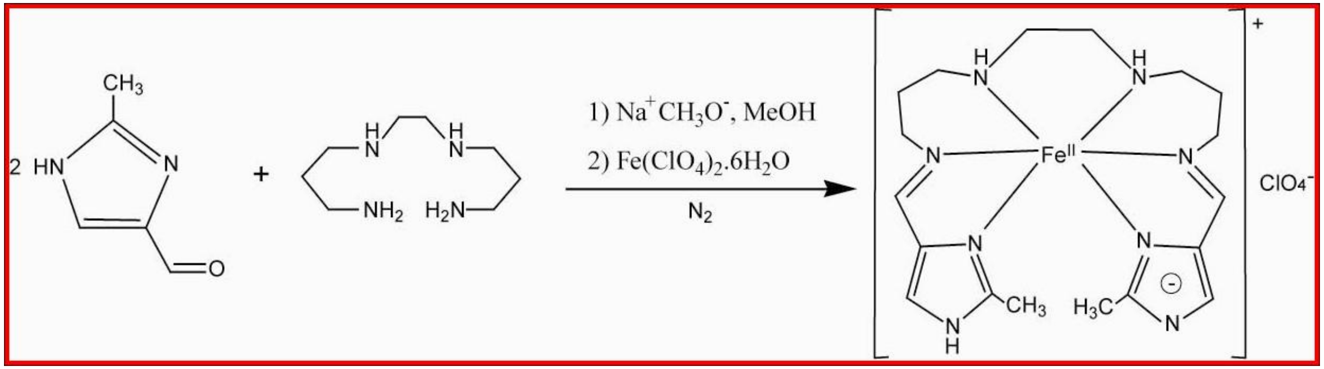


??

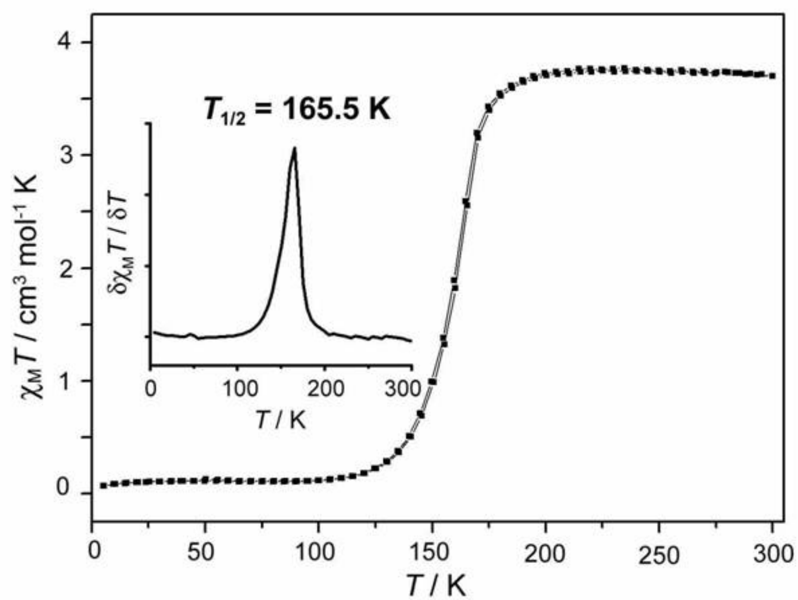
H_2L^{2Me}

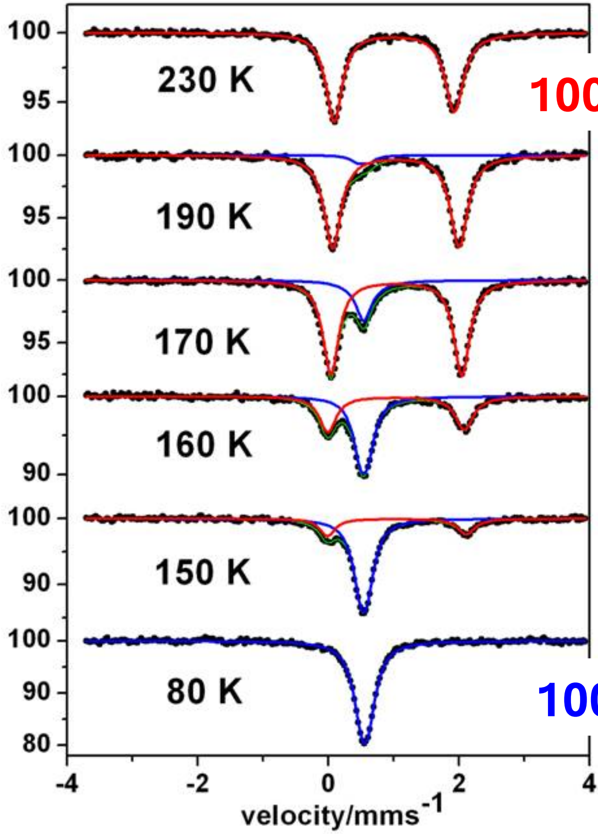
Le cas de $[FeHL^{2Me}]ClO_4$ (**4**)

Synthèse



FeN_6





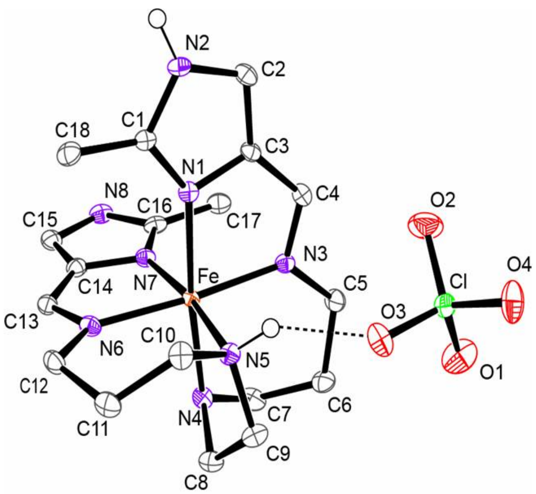
100 % HS

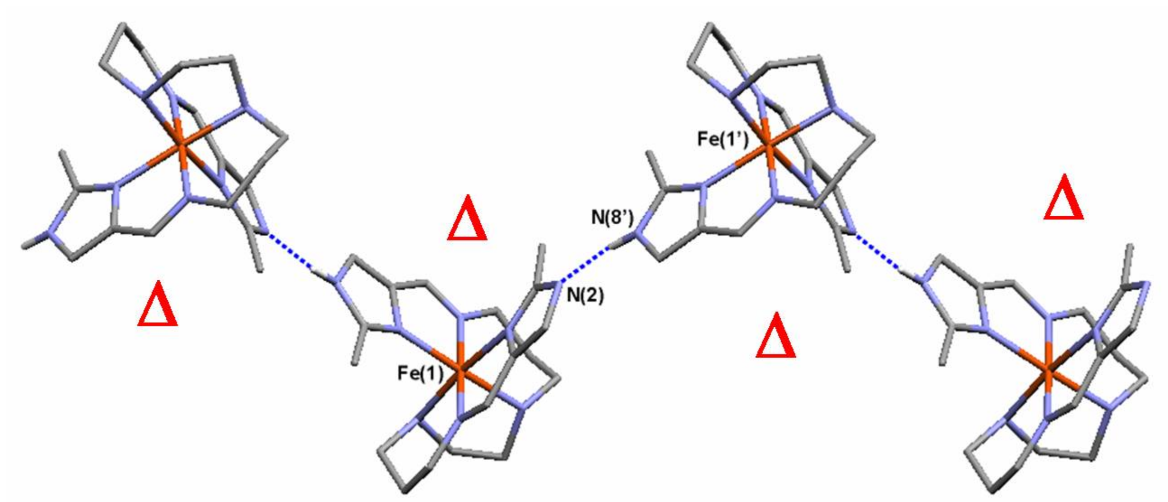
100 % BS

TS graduelle

N. Bréfuel et al., *Chem. Lett.* **2005**

Structure Cristallographique de [FeHL^{2Me}]ClO_4 (**4**)





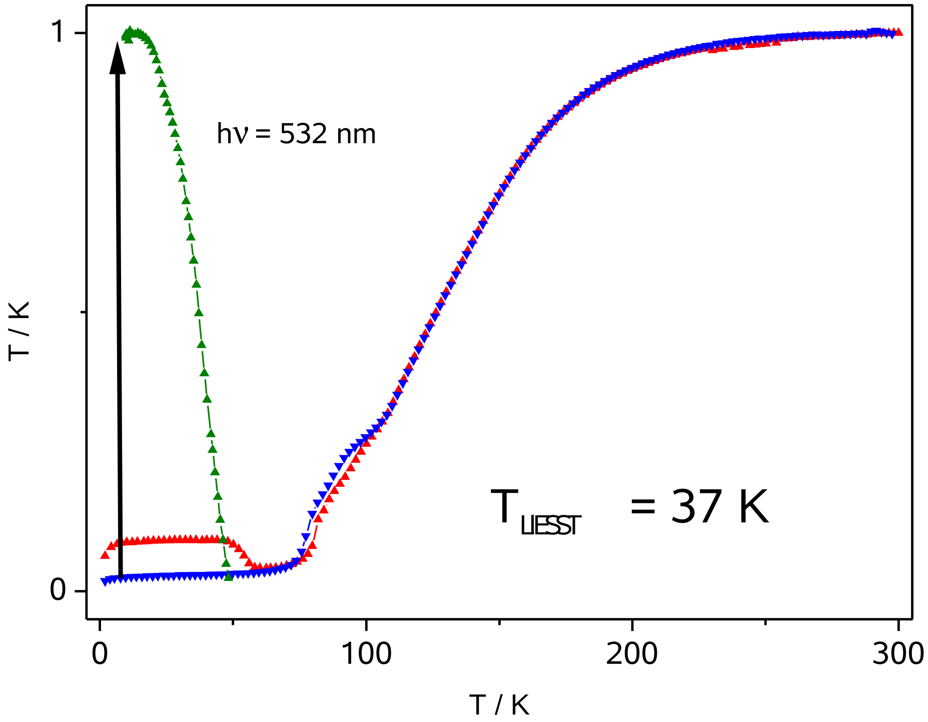
$FeC_{18}H_{30}N_8ClO_4$	
M = 512.79 gmol^{-1}	
Orthorhombique (Z = 8)	
Pbca	
T = 100 K	**T = 180 K**
a = 12.734(3)Å	13.306(3)Å
b = 15.289(3)Å	15.655(3)Å
c = 21.844(4)Å	21.288(4)Å

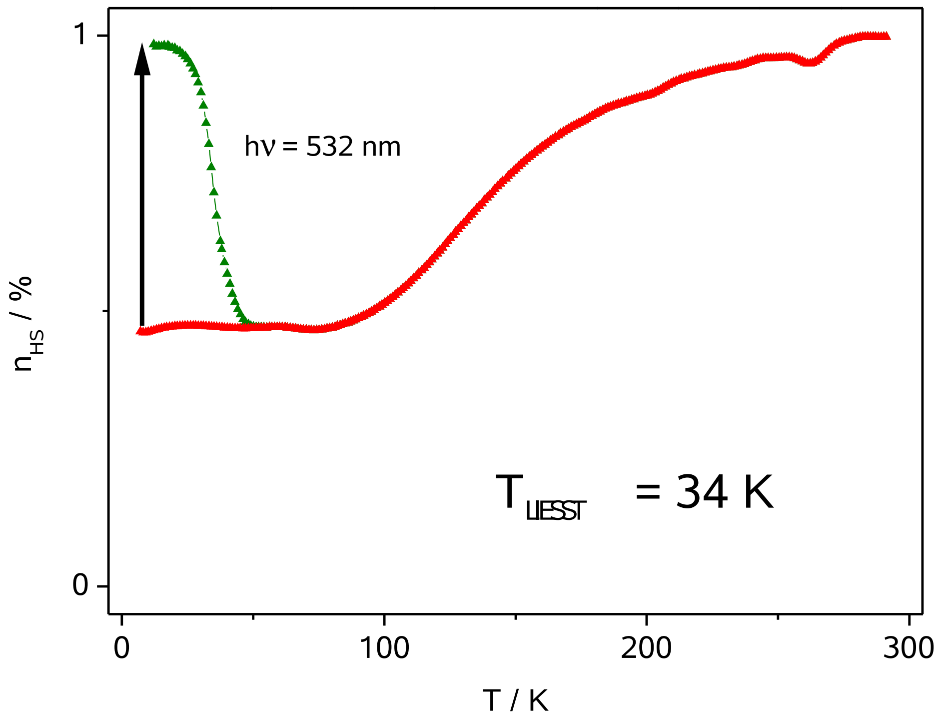
★ Molécules Adjacentes connectées par liaisons hydrogène (imidazole-imidazolate)

➡ Chaînes en zig-zag homochirales

★ Alternance de chaînes de chiralité opposée dans le crystal: <u>materiau achiral</u>

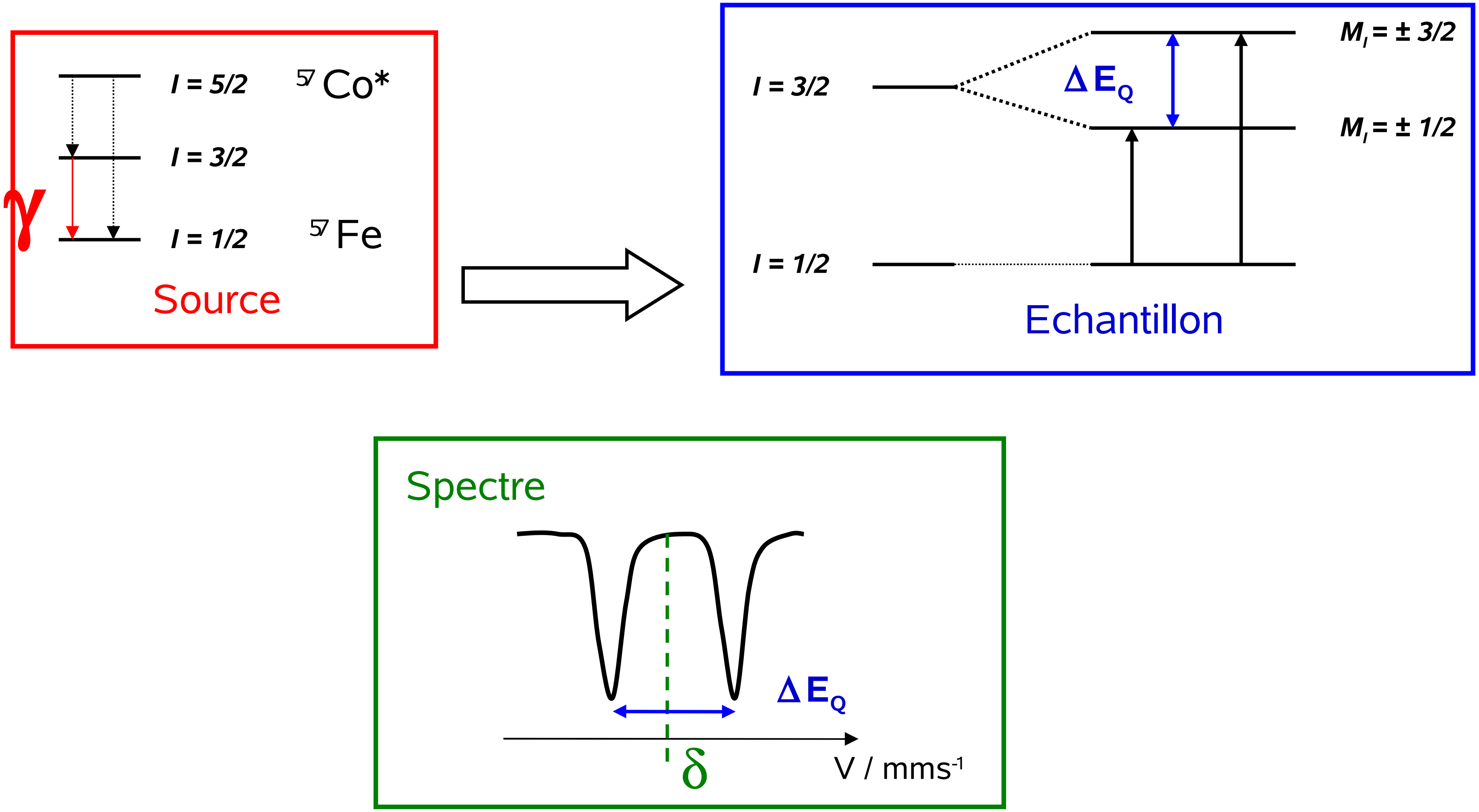
*Effet LIESST de (7) et (**8**)*





Effet LIESST quantitatif

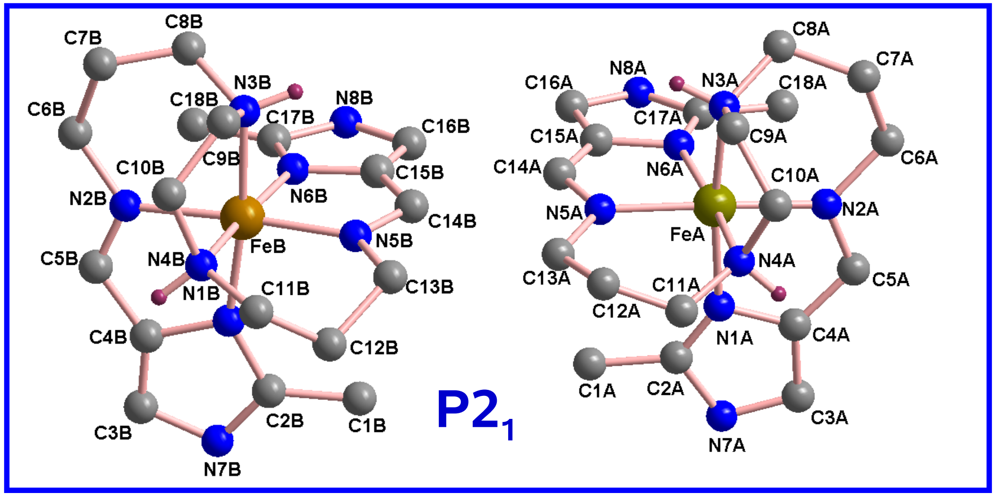
La spectroscopie Mössbauer ^{57} Fe

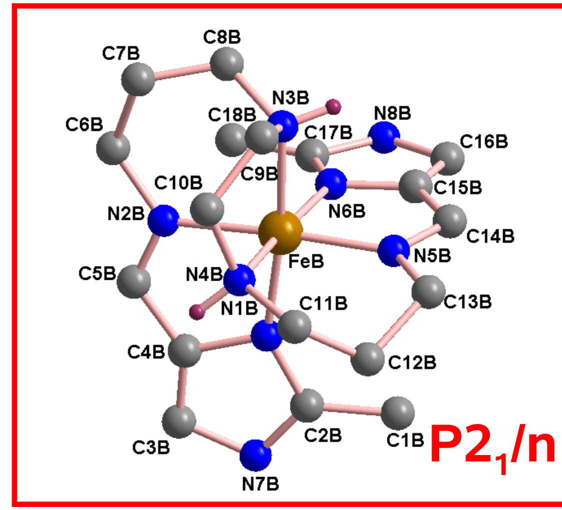


ΔE_Q = éclatement quadrupolaire
δ = déplacement isomérique

Détermination de l'environnement chimique et de la structure électronique

Structure Moléculaire de $[FeH_2L^{2Me}](ClO_4)_2$

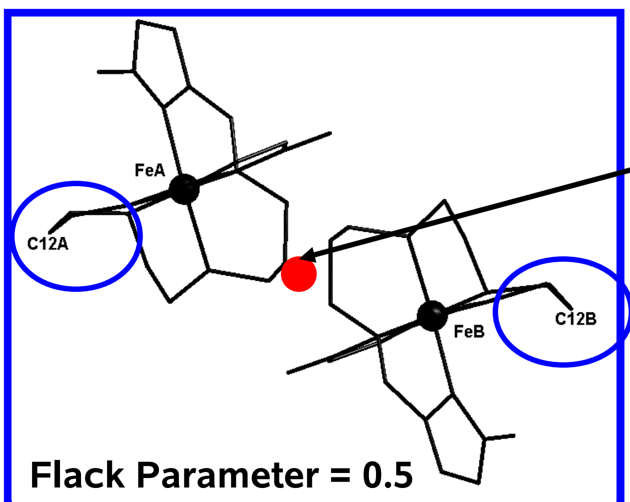




Δ "racemic twin" Λ

Δ / Λ

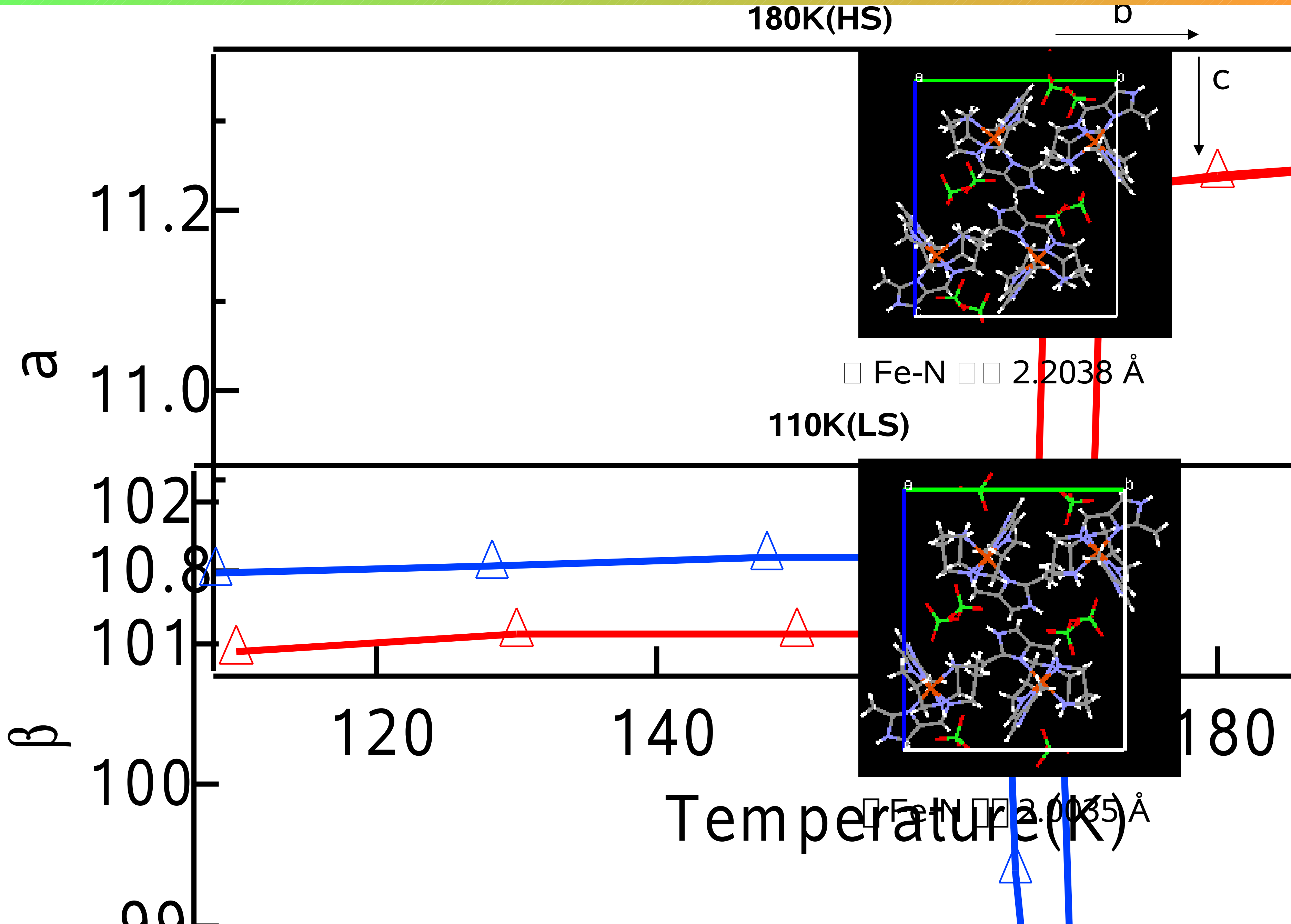
BAS-SPIN ⇄ **HAUT-SPIN**



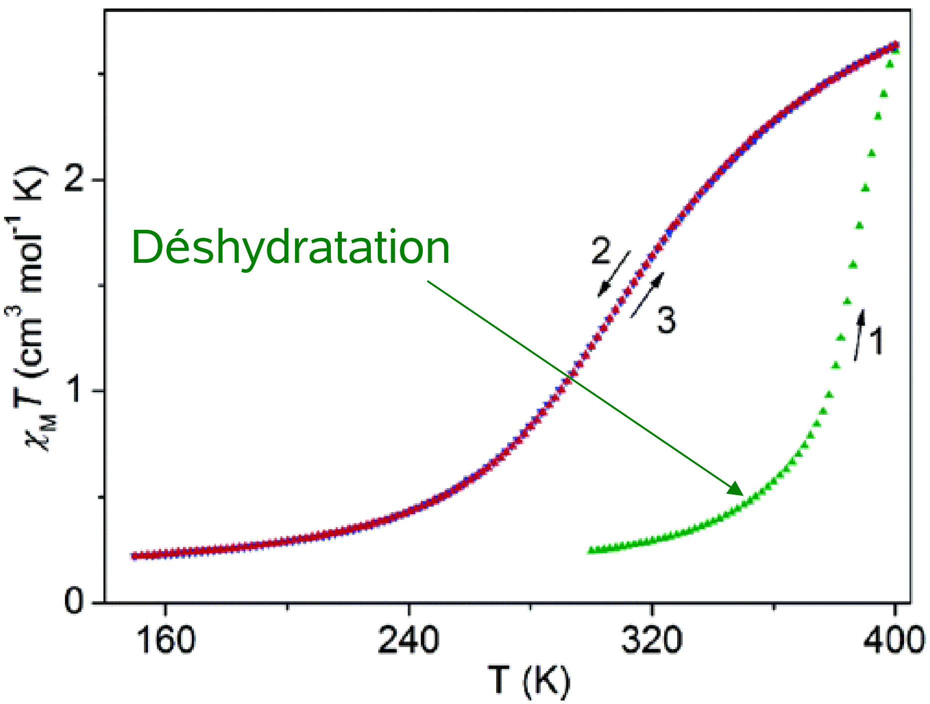
Centre de pseudo-inversion

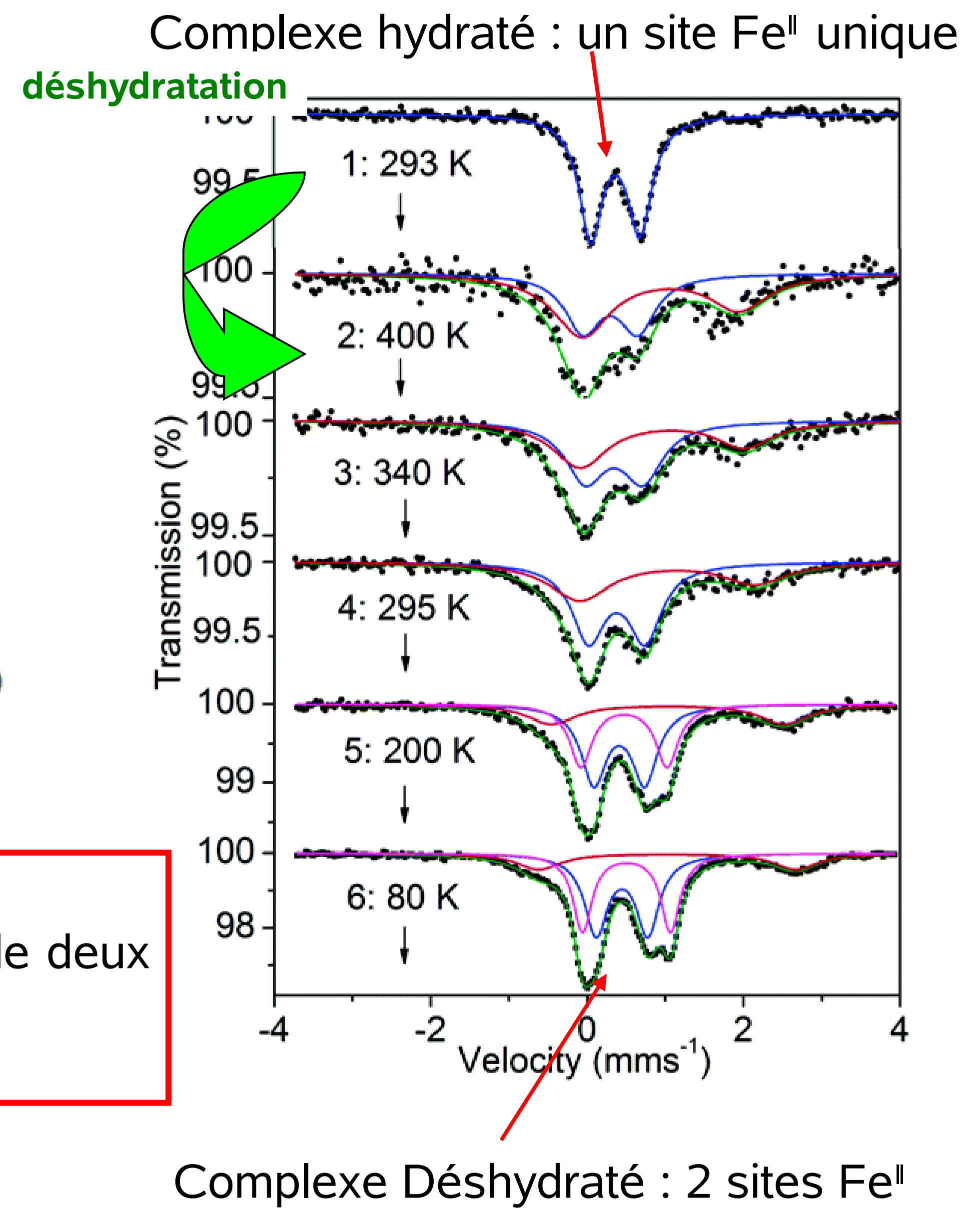
orientation non-opposée des atomes C12B et C12A
Perte de centre de symmétrie
→ Groupe d'espace $P2_1$

*Variation des paramètres de maille de [FeH$_2$L^{2Me}](ClO$_4$)$_2$ (**5**)*



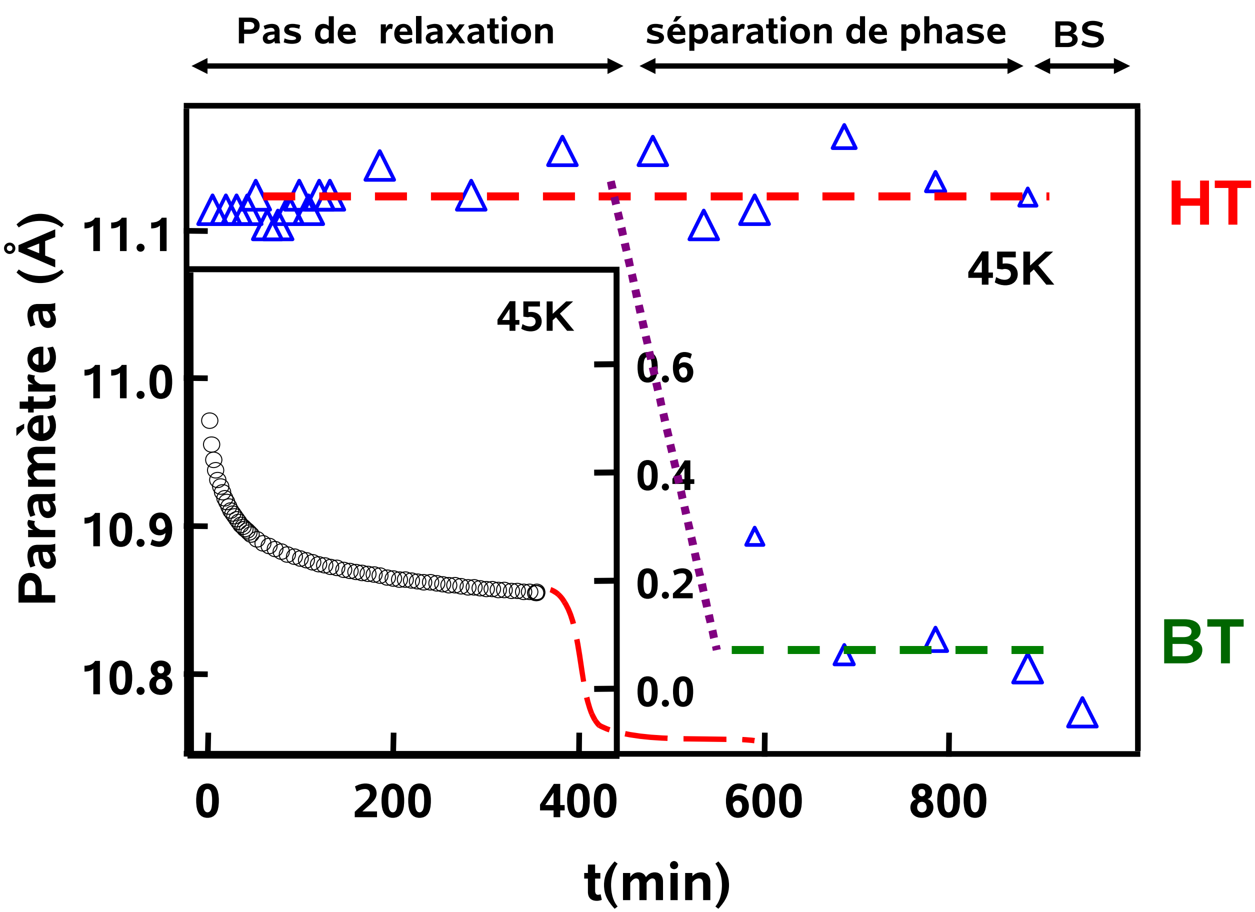
*Propriétés Magnétiques de [FeL²² (NCSe)$_2$].H$_2$O (**2**)*

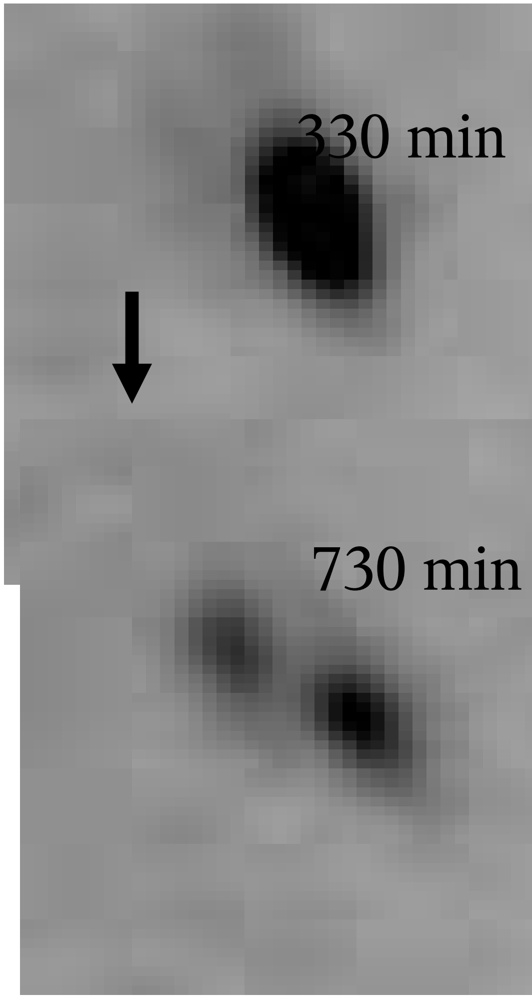




- **TS Graduelle** et **incomplete**
- **Une seule étape** malgré la présence de deux sites Fe^{II} distincts
  → effet de masse S/Se

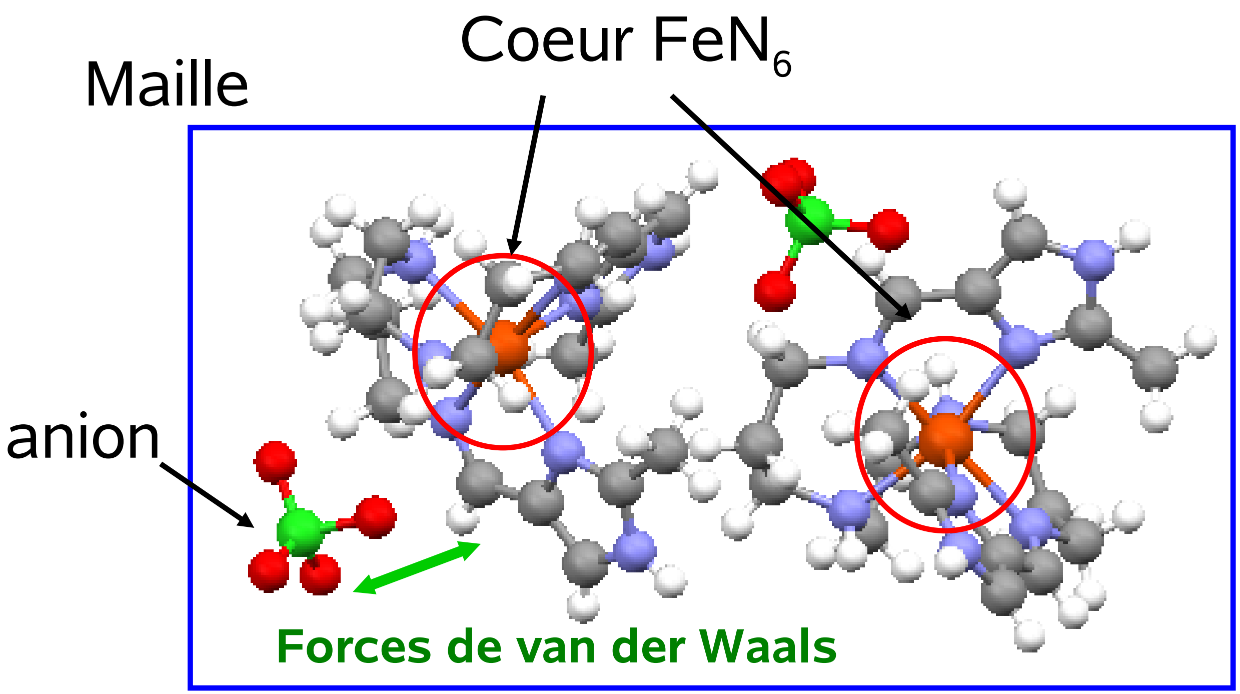
Evolution du paramètre a en f(t) à 45K

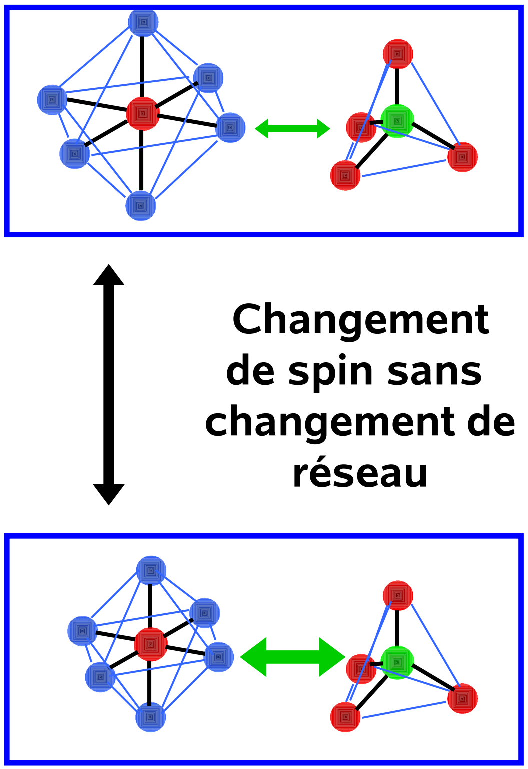




- Séparation de phase entre les états HT et BT
- Décalage entre la relaxation du réseau et de spin: temps d'incubation

Origine de la différence des relaxations de spin et de réseau ?





Changement de spin sans changement de réseau

Maille “élastique” ?