Experiment and Modelling in Structural NMR

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NMR Crystallography

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NMR Crystallography

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NMR Winterschool - INSTN - Nov. 2011

Crystallography

Crystallography is the scientific study of crystals, the branch of science concerned with the structure and properties of crystals

Crystallography

Schönflies

Wyckoff

Fedorov

P. Curie
1859-1906

Lorsque certaines causes produisent certains effets, les éléments de symétrie des causes doivent se retrouver dans les effets produits.

Lorsque certains effets révèlent une certaine dissymétrie, cette dissymétrie doit se retrouver dans les causes qui leur ont donnée naissance.

La réciproque de ces deux propositions n'est pas vraie, au moins pratiquement, c'est-à-dire que les effets produits peuvent être plus symétriques que les causes.

→ The Symmetry of the Crystal reflects the Symmetry of the Property

Bravais Lattices and Crystal Systems

Crystal System	# of Point Groups	# of Bravais Lattices	# of Space Groups
Triclinic	2	1	2
Monoclinic	3	2	13
Orthorombic	3	4	59
Tetragonal	7	2	68
Rhombohedral	5	1	25
Hexagonal	7	1	27
Cubic	5	2	36
Total	32	14	230

Limited Number of Symmetry
'Ideal' Crystal: repetition of Unit cell

Crystallography

Unit Cell: Metrics & Nature of the Atoms

Crystallography by X-ray Diffraction

MAX VON LAUE

Concerning the detection of X-ray interferences

Nobel Lecture, November 12, 1915

Fig. 1.

Fig. 2.

Fig. 3.

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4

Single-Crystal Diffraction

L. B. McCusker, ETH Zurich

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<http://www.crystal.mat.ethz.ch>

5

Powder Diffraction

L. B. McCusker, ETH Zurich

Powder Diffraction

L. B. McCusker, ETH Zurich

Powder: Millions of randomly oriented crystallites

L. B. McCusker, ETH Zurich

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8

Diffraction of an 'ideal' powder

L. B. McCusker, ETH Zurich

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<http://www.crystal.mat.ethz.ch>

9

The Overlap Problem

L. B. McCusker, ETH Zurich

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<http://www.crystal.mat.ethz.ch>

10

Strategies: Diffraction Crystallography

Indexing
Line Extinction

Patterson
Direct Methods
Direct Space Methods

Diffraction Problems:

- Overlap problem, Intensity measurement
- Detection of extinctions, Space Group selection
- Electron density contrast
- Non periodicity, Dynamics

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11

Strategies: NMR Crystallography

Indexing
Line Extinction

Patterson
Direct Methods
Direct Space Methods

Crystallochemical Formula
Distance Measurements

NMR connectivity

Rules to describe periodic and non-periodic sub-networks

→ **Generalized Crystallography** (Mackay, *J. Mol. Struct.* 1995, *Struct. Chem.* 1995...)

Strategies: NMR Crystallography

Rules to describe periodic and non-periodic sub-networks

→ **Generalized Crystallography** (Mackay, *J. Mol. Struct.* 1995, *Struct. Chem.* 1995...)

Space Group Selection

Martineau et al. Inorg Chem. 50 (2011) 2644

TEM (CEMHTI – Orléans)

X-Ray
Synchrotron source (11BM – USA)

Observed reflections condition $hkl = 2n$

→ / lattice with 8 possible space groups:

$I4$, $I-4$, $I4/m$, $I422$, $I4mm$, $I4/mmm$, $I-4m2$, $I-42m$

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13

Space Group Selection

International Tables of Crystallography – Vol. A

Generators selected (1); $i(1,0,0)$; $i(0,1,0)$; $i(0,0,1)$; $i(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5)							
Positions		Coordinates					
Multiplicity,	Wyckoff letter,	$(0,0,0) + (\frac{1}{2},\frac{1}{2},\frac{1}{2}) +$					
Site symmetry							
16	i	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	
			(5) $x,\bar{y},\bar{z}$	(6) $x,y,\bar{z}$	(7) $y,\bar{x},\bar{z}$	(8) $\bar{y},x,\bar{z}$	
8	h	m	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	
8	g	2	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	
8	f	$\bar{1}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	
4	e	4	$0,0,z$	$0,0,\bar{z}$			
4	d	$\bar{4}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			
4	c	$2/m$	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			
2	b	$4/m$	$0,0,\frac{1}{2}$				
2	a	$4/m$	$0,0,0$				

- Possible Multiplicities of a SG (1,2,3,4,6,8,12,16,24,48)

- Wyckoff Spectrum: Number of Sites for each multiplicity
e.g. (0,2,0,3,0,3,0,1,0,0) for $I4/m$

- Crystallochemical Formula (Shubnikov, 1922): splits each atom type into its inequivalent crystallographic sites and associates the multiplicity

Possible SG if the crystallochemical formula can be embedded in the Wyckoff Spectrum

F. Taulelle, Solid State Sci., 6 (2004) 1053

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14

Crystallochemical Formula

Crystallochemical formula
 $\text{Ba}_{20}(\text{Al}_4\text{Al}_8)(\text{F}_2\text{F}_2\text{F}_8\text{F}_8\text{F}_8\text{F}_{16}\text{F}_{16}\text{F}_{16})$

- 2 Al lines of relative ratio 1:2

Space Group Selection

Crystallochemical formula
 $\text{Ba}_{20}(\text{Al}_4\text{Al}_8)(\text{F}_2\text{F}_2\text{F}_8\text{F}_8\text{F}_8\text{F}_{16}\text{F}_{16}\text{F}_{16})$

Required Wyckoff Spectrum (0,2,1,0,4,0,3,0,0)

$I4/m$

Strategies

Rietveld Refinement

Starting model for $\text{Ba}_5\text{Al}_3\text{F}_{19}$
Rietveld Refinement

Validation and optimization of a model: DFT Calculations

Comparison between experimental and calculated NMR parameters

- Determination of the ^{27}Al parameters: δ_{iso} , C_Q , η_Q

δ_{iso} (ppm)	C_Q (MHz)	η_Q
-2.5(0.5)	1.9(1)	0.8(1)
-1.0(0.5)	11.3(1)	0.0(1)

Ba₅Al₃F₁₉: Validation and optimization of the model

DFT calculation of ^{27}Al EFGs : NMR CASTEP (Segall, Pickard et al. , J. Phys.: Condens. Matter, 2001)

Calculated EFGs very sensitive to the precision of the atomic position

➔ Geometry optimization necessary for structure resolved from powder X-ray diffraction data

	Experimental			Calculated SPD structure			Calculated Geometry optimized structure		
	δ_{iso} (ppm)	C_Q (MHz)	η_Q	δ_{iso}^a (ppm)	C_Q^b (MHz)	η_Q	δ_{iso}^a (ppm)	C_Q^b (MHz)	η_Q
Al1	-2.5(0.5)	1.9(1)	0.8(1)	4.6	-7.42	0.44	-1.8	2.30	0.79
Al2	-1.0(0.5)	11.3(1)	0.0(1)	-0.5	11.21	0	-2.4	10.69	0

- Deviation from the experimental values for Al1

Ba₅Al₃F₁₉: Validation and optimization of the model

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Al2	-1.0(0.5)	11.3(1)	0.0(1)	-0.5	11.21	0	-2.4	10.69	0

Closer after G. O. → more accurate location of the F atoms around Al1

Ba₅Al₃F₁₉: Validation and optimization of the model

DFT calculation of ¹⁹F δ_{iso} : NMR CASTEP

Zheng et al., J. Phys. Chem. C 113 (2009) 15018

$$\delta_{iso,exp} = -0.83 \delta_{iso,cal} - 17.6, \text{ with } R^2 = 0.999$$

→ Incorrect sorting of the F atoms

Ba₅Al₃F₁₉: Validation and optimization of the model

DFT calculation of ¹⁹F δ_{iso}: NMR CASTEP

Zheng et al., J. Phys. Chem. C 113 (2009) 15018

$$\delta_{\text{iso,exp}} = -0.83 \delta_{\text{iso,cal}} - 17.6, \text{ with } R^2 = 0.999$$

→ corrected after structure optimization

- Validation of the structure
- Full assignment of the ¹⁹F NMR Spectrum

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22

Strategies

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Ba₅Al₃F₁₉: Anionic Dynamics

- Broadening and Coalescence of some F lines

→ Rigid Framework + Dynamic Sub-network

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Ba₅Al₃F₁₉: Anionic Dynamics

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Ba₅Al₃F₁₉: Exchange Spectroscopy

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26

Ba₅Al₃F₁₉: Dipolar DQ-SQ

Mobile Fluorine atoms are filtered out by the Dipolar Filter

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27

Conclusions

Determination of the
Structural Model

Validation of the Model

Optimization of the
Atomic Positions

NMR Crystallography

TEM, XRD, NMR, DFT calculations...

Life of the Fluorine sub-networks:

- Reorientation and Chemical Exchange

'Diffraction' resolution vs 'NMR' resolution

Layered Aluminophosphate

Bouchevreau, Martineau, Taulelle et al. submitted

Synchrotron Diffraction Crystallography: 1 Building Unit

NMR Crystallography: 3 Building Units

- X-ray diffraction and ^{31}P MAS NMR spectrum $\rightarrow$ 'Average' Structural Model
- Higher-resolution of the ^{31}P MAS NMR spectrum under multiple-resonance decoupling $\rightarrow$ higher-resolution structural description

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