

---

# EDSC summer school

## SOLID STATE CHEMISTRY in BORDEAUX

**June 25 – 28, 2018**

Amphitheatre PABA, Building B5 – Campus Talence



---

**Monday Morning, June 25**

**8:30 - 11:00 am**

---

### **Brief overall presentation of the doctoral school**

**Alain Demourgues**, *Research Director in ICMCB-CNRS (30')*

### **Synthesis in solid state chemistry** ,

**Nicolas Penin**, *Research Engineer in University of Bordeaux. (2h)*

The synthesis is a crucial concern when playing with the tool-box of the “solid state chemist”, that is to say the Periodic Table... The “solid state chemist” keeping in mind the following equation:

Properties =  $\Sigma$  (Nature of the atoms [Chemical composition] + Stacking of the atoms [Structure] + Atom interactions [Chemical bonding] + Synthesis Routes (P, T, Atmosphere))

The most common method used in solid state chemistry is the so-called “conventional ceramic method” which involves synthesis at elevated temperatures and leads to thermodynamically stable phase. This method encounters a serious limitation as many inorganic solids of current interest (having interesting properties) are rather metastable and consequently their preparation requires low temperature (so called “Chimie Douce” synthesis routes).

The goal of this lecture is (i) to acquire the theoretical knowledges and practical know-hows for the synthesis of inorganic compounds as powder state, (ii) to apprehend the various routes to synthesize a compound with a target structure / chemical composition / morphology and finally (iii) to investigate the various routes in term of cost efficiency, large scale transfer possibilities, environmental impact...

### **References**

- J.P. Jolivet, De la solution à l'oxyde, CNRS Editions, 1994
- Anthony R. West, Solid State Chemistry and its Applications, Wiley International, 1984 - ISBN 0-471-90377-9
- Anthony R. West, Basic Solid State Chemistry, Wiley International, 1988 - ISBN-13 978-0471987567 - ISBN-10 0471987565

---

Tuesday Morning, June 26

8:30 - 12:30 am

---

### **How the solid state chemist can tailor the properties of inorganic compounds**

Alain Demourgues, *Research Director in ICMCB-CNRS* & Laurence Croguennec, *Research Director in ICMCB-CNRS*  
(2h)

We will illustrate how tailoring (i) the composition through the anionic and cationic substitution, (ii) the stoichiometry and (iii) the nature of the chemical bond, we can modify the atomic and electronic structure of inorganic compounds to control their electrical, magnetic, optical and electrochemical properties. We will focus the discussion on rock-salt, spinel, layered and perovskite-type structures to show how “subtle” changes in the composition, structure and transport properties of a given compound can make its derivatives interesting for a large panel of applications: for instance, from electrochromic devices to batteries (alkaline, Li-ion, Na-ion ...) and hybrid supercapacitors for the cubic face centered - derived compounds, and from sensors to fuel cells for perovskite-type compounds.

#### ***References***

- (1) A. F. Wells. Structural Inorganic Chemistry, Fifth edition. Oxford Science Publications
- (2) Shriver & Atkins. Inorganic Chemistry. Fourth edition, Oxford University Press

### **Scattering Tools for Solid-State Structural Analyses: X-Ray powder diffraction and beyond**

Matthieu Suchomel, *Researcher in ICMCB-CNRS* (2h)

Scattering tools frequently used in solid state chemistry to probe the atomic structure of materials will be introduced. X-ray powder diffraction will be the primary focus, but other related x-ray and neutron scattering probes will be briefly discussed (PDF total scattering analysis, EXAFS, SAXS, etc). Relevant aspects of basic diffraction and scattering theory will be briefly reviewed. Practical experimental aspects of data collection will be presented; from routine lab-based diffractometers to state-of-the-art measurements at large synchrotron and neutron large user facilities. Select analysis software packages will also be surveyed. Throughout the discussion, appropriate examples from the broad family of solid-state materials will be used to demonstrate both how these experimental with these tools can be performed, and to show what structural information can be determined.

#### ***References***

- Pecharsky, V.; Zavalij, P. Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005 (1st edition) or 2009 (2nd edition) ISBN: 978-0-387-09578-3
- Structure From Diffraction Methods; Bruce, D. W., OHare, D., R. I. Walton, Editors.; Wiley, 2014. ISBN: 978-1-11-995322-7

---

Tuesday afternoon, June 26

2:00 pm - 4:00 pm

---

**Characterization of Solids – ESR, NMR & Mössbauer spectroscopies**

**Mathieu Duttine**, *Engineer in ICMCB-CNRS (2h)*

Among all the characterization techniques commonly used in Solid-State Chemistry, the Nuclear Gamma Resonance (also known as the Mössbauer effect)[1], Nuclear Magnetic Resonance (NMR)[2] and Electron Spin Resonance (ESR)[3] spectroscopies can provide various kinds of valuable information about the physicochemical and structural properties of inorganic materials. Even if the targeted local probes are different (nucleus, nuclear spin or unpaired electron spin), the basic principles are all governed by quantum mechanical rules and described by a similar mathematical formalism (Hilbert space, wave functions, rays, density operators, Hamiltonian, ..).

Besides some theoretical and practical key aspects, a clear focus will be placed on some case studies of simple inorganic materials that are representative of the possible applications of ESR, NMR and Mössbauer spectroscopies to Solid-State Chemistry.

***References***

- [1] B. Fultz, “Mössbauer Spectrometry”, in Characterization of Materials. Elton Kaufmann (Editor), John Wiley, New York, 2011
- [2] J.V. Hanna & M.E. Smith, “Recent technique developments and applications of solid state NMR in characterizing inorganic materials”, Solid State Nuclear Magnetic Resonance 38 (2010) 1-18
- [3] J.A. Weil & J.R. Bolton, “Electron Paramagnetic Resonance”. Wiley-Interscience, Hoboken, NJ, 2007

---

Wednesday Morning, June 27

8:30 - 12:30 am

---

### **Space groups for Solid State Scientists: reading the International Tables for crystallography**

Philippe Guineau, *Professor in ICMCB UB-CNRS (2h)*

Symmetry is a crucial concern when dealing with the physical properties of solids. At any scale, from the coordination polyhedron to the crystal-packing, the nature and degrees of the symmetries existing in the solid play a paramount role in the way the material behaves. Consequently, an accurate description of the whole topology is a major goal in the investigation and design of solids. The international tables for crystallography (vol. A, ITA) provide an exhaustive list of the possible encountered situations as well as a complete and precise vocabulary to describe them. Despite being a remarkable support for solid state chemists, the ITA are quite hermetic at first sight. The goal is here to lift initial locks and to open the students of the course to an efficient and comprehensive use of ITA. To this aim, basic notions such as symmetry operations, asymmetric unit, crystal systems, Bravais lattices, points groups and Space groups will be first recalled. Then, students will be trained to interpret the information contained in ITA on the basis of examples taken directly from their pages and preferentially explained in a practical way.

#### **References**

- [1] International Tables for crystallography, vol A, (2005), Heidelberg: Springer.
- [2] Giacovazzo, C., *Fundamental of Crystallography*, (2002), Oxford University Press
- [3] Müller, U, *Symmetry relationships between crystal structures*, (2013), Oxford University Press

### **Relationships between composition – structure and dielectric and magnetic properties**

Michaël Josse, *Associate Professor in ICMCB UB-CNRS (2h)*

Once equipped with a theoretical and practical framework for the description of crystal structures, crystal chemists can investigate the influence of

- Chemical modifications on the structural features of a given material
- Chemical modifications on the physical properties of a given material
- Structural modifications on the physical properties of a given material

Such studies are performed by discreetly or continuously substituting one element for another in the selected material and surveying the subsequent evolution of structural and physical properties. As stated in its title, the present lecture will focus on functional properties, like magnetic properties and more specifically dielectric properties. Examples will be given of

- subtle structural modifications that question the chemical bonding
- intimate relationships between crystal and magnetic structures that reveal unexpected magnetic interactions
- Hints about the relationship between symmetry and magnetism
- Strong relationship between polarisabilities of chemical elements and permittivities of their combinations
- Inconsistencies in the previous relationship that unveil a specific class of dielectric oxides, and the dependence of their properties on symmetry
- Finally how the symmetry constraints related to some specific magnetic and dielectric properties shape the field in which new multiferroic materials must be researched.

From these examples, it is expected that the students will be in better position to investigate composition-structure-properties relationships.

---

Wednesday afternoon, June 27

2:00 – 4:00 pm

---

**Group Theory - Molecular Symmetry - Illustrated Applications**

Vincent Rodriguez, *Professor in ISM UB-CNRS* (2h)

The systematic discussion of symmetry is called Group Theory. Much of group theory is a summary of common sense about the symmetries of objects. Symmetry can be seen as the most basic and important concept in physics. More generally, every process in physics is governed by selection rules that are the consequences of symmetry requirements. Because group theory is systematic, its rules can be applied in a straightforward mechanical way. In most cases the theory gives a simple, direct method for arriving at useful conclusions with a minimum of calculation.

We will see how to classify any molecule according to its symmetry, and to use this classification to discuss molecular properties without the need for detailed calculation. After describing the symmetry properties of molecules themselves, we will bring the application of group theory to the treatment of electronic states and vibrational modes of molecules. Symmetry properties of tensors will be also discussed.

(Non exhaustive) **References:** from basic textbooks to even complex books

1. “Physical Chemistry”, 9th Edition, P.W. Atkins, J. de Paula, Oxford University Press, Oxford, 2010.
2. “Condensed Matter Optical Spectroscopy”, I. Ionita, CRC Press, Boca Raton, 2015.
3. “Group Theory: Application to the Physics of Condensed Matter”, M. S. Dresselhaus, G. Dresselhaus, A. Jorio, Springer-Verlag Berlin Heidelberg, 2008.

---

Thursday Morning, June 28

8:30 - 12:30 am

---

### **Characterization of Solids – Luminescence spectroscopy applied of doped inorganic materials**

Véronique Jubera, *Associate Professor in ICMCB UB-CNRS (2h)*

Luminescence is a simple technique reflecting light matter interaction [1]. The field of this spectroscopy is as diverse as it is beautiful. Phosphors are part of many devices such as medical equipments, imaging systems, telecommunication fibers, lighting devices [2]...Their radiative transitions are associated not only to their nature but also to the local environment of the doping element which is introduced in low proportions within the host lattice. Syntheses routes, composition, chemical bonding and local symmetry impact the response of the optical active cation.

The luminescence of specific ions will be described to illustrate how the chemist can play with the crystal field to understand the structure/property relations and then to tune the optical response of materials. The lecture will be focused on inorganic materials and their extrinsic luminescence after doping.

#### **References**

[1] Luminescent materials, G. Blasse et B.C. Grabmaier, Springer-Verlag Berlin Heidelberg (1994).

[2] Luminescence, from theory to applications, Cees Ronda, Wiley-VCH Verlag GmbH & Co. KGaA (2004).

### **Characterization of Solids – Magnetic Materials & Properties**

Olivier Toulemonde, *Associate Professor in ICMCB UB-CNRS (2h)*

Magnetic materials are subjects of numerous applications when permanent magnet, magnetic random-access memory and/or spin electronics are considered. However, the field of magnetic materials is not limited to technological application and magnetic properties characterization can be of fundamental interest for Solid State Chemistry. Especially, at the heart of the solid state chemistry is the chemical bond nature in solids allowing to discriminate the localized or delocalized nature of the magnetic properties as summary in the table extracted from [1].

Localized magnetism	Delocalized magnetism
Integral number of 3d or 4f electrons	Nonintegral number of unpaired spins on the ion core
Integral number of unpaired spins per atom	
Discrete energy levels	Spin polarized energy bands with strong correlations
$\text{Ni}^{2+} 3d^8 \quad m = 2 \mu_B$	$\text{Ni} 3d^{9.4} 4s^{0.6} \quad m = 0.6 \mu_B$
$\Psi \approx \exp(-r/a_0)$	$\Psi \approx \exp(-ik \cdot r)$
Boltzmann statistics	Fermi-Dirac statistics
4f metals and compounds; some 3d compounds	3d metals; some 3d compounds

Starting from examples given in the previous lectures or extracted from literatures, students will be encouraged to acquire a solid State chemist approach on the basis of the structure/physical property relations and to step back and propose complementary analyses to character solids.

[1] "Magnetism and Magnetic Materials" J. M. D. Coey CAMBRIDGE UNIVERSITY PRESS (2009)

---

Thursday afternoon, June 28

2:00 – 4:00 pm

---

### **Electronic structure of crystalline solids: physical quantities and material properties**

Antoine Villesuzanne, *Researcher in ICMCB-CNRS* (2h)

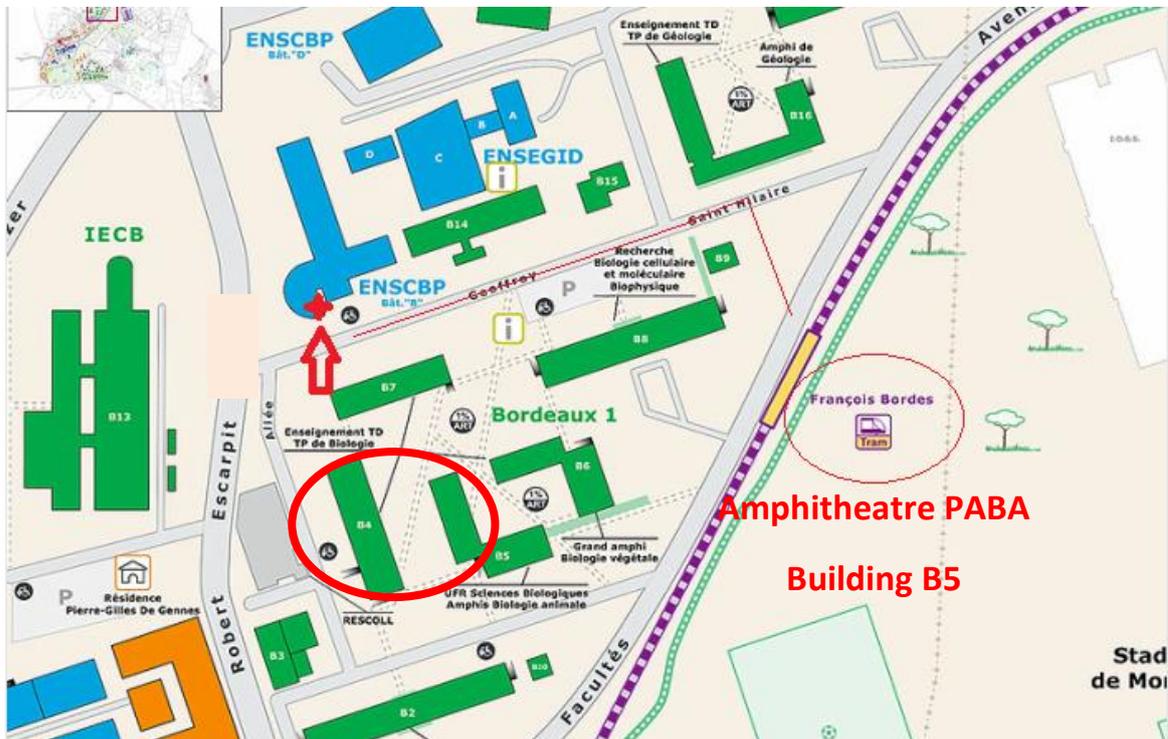
The electronic structure of a periodic solid has many features in common with that of atoms and molecules: energy levels, wave functions (orbitals), quantum numbers ... Translation symmetry and periodic boundary conditions allow treating the “infinite” solid via the sole knowledge of the unit cell (non-equivalent atoms plus lattice parameters). A supplementary quantum number, or wave vector  $k$ , appears then, which belongs to the unit cell of the reciprocal lattice (first Brillouin zone).

Energy levels spread into bands; departures from the ideal infinite crystal (defects, interfaces) will lead to specific energy levels or bands. Electron wave functions are described in the unit cell, and propagated throughout the crystal according to their wave vector  $k$ . Naturally, the electron (or spin) density has the same periodicity than the crystal. For open-shell systems, the electronic structure of majority and minority spin channels are distinct.

Then, the properties of the solid can be discussed on the basis of chemical bonding, crystal structure, density of states, energy gaps, Fermi surface, electron or spin density, dispersion curves (i.e. energy vs.  $k$ ), overlap populations, and many more physical quantities from the electronic structure, or derived from it. For example, instabilities such as electronic or structural phase transitions can be interpreted or predicted. We will discuss the potentialities and limits of band theory for interpreting transport properties (metal vs. insulator, effective mass of carriers, localization phenomena, ionic conductors).

#### ***References***

- Conceptual aspects of structure-property correlations and electronic instabilities  
E. Canadell and M.-H. Whangbo, *Chem. Rev.*, 1991, 91 (5), pp 965–1034
- Solids and Surfaces: A Chemist’s View of Bonding in Extended Structures  
R. Hoffmann, Wiley-VCH (1989)
- The Electronic Structure and Chemistry of Solids  
P. A. Cox, Oxford Science Publications (1987)
- Instabilités électroniques et structurales: quelques propositions  
A. Villesuzanne, Mémoire d’Habilitation à diriger des recherches (2007)



**Contacts :**

Manuel Gaudon, [manuel.gaudon@u-bordeaux.fr](mailto:manuel.gaudon@u-bordeaux.fr), 05 40 00 66 85

Alain Demourgues, [alain.demourgues@icmcb.cnrs.fr](mailto:alain.demourgues@icmcb.cnrs.fr)

Thierry Toupance, [thierry.toupance@u-bordeaux.fr](mailto:thierry.toupance@u-bordeaux.fr)