



1 - STRUCTURES AND PHASE TRANSITIONS

The study of both crystallographic and magnetic structural phase transitions is an important part in the activity of Léon Brillouin Laboratory. Besides macroscopic techniques, such as electrical resistivity, specific heat and magnetic measurements, such studies need microscopic techniques, and among them neutron diffraction and inelastic scattering play an essential role, in order to look simultaneously at light and heavy elements in the crystal structure, at crystal and magnetic structures and/or excitations.

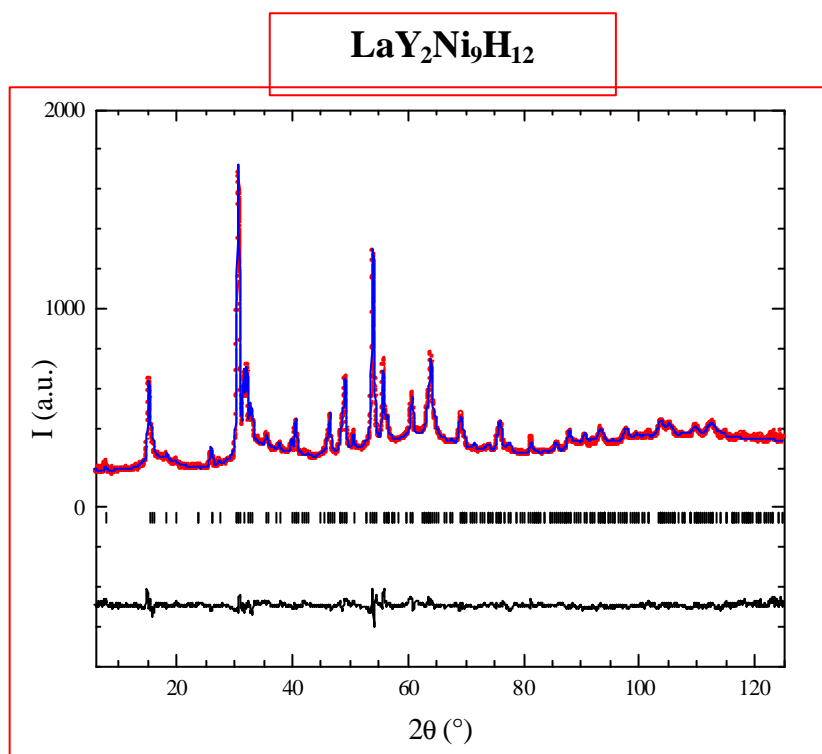
Neutron studies, either diffraction or inelastic scattering, are performed as a function of external parameters, namely temperature and pressure. Many different physical problems, both fundamental and applied, are in connection with phase transitions and the present summary intends to show the main results of the research in the field in 2001 and 2002, from perovskites to molecular crystals, from hydride systems to quantum tunnelling, from commensurate to incommensurate materials...

HYDRIDES: STRUCTURAL STUDIES

Most of the intermetallic alloys of general formula AB_n ($A = \text{Mg, Ti, Zr, Y}$ or $R = \text{rare earth}$; $B = \text{Mn, Fe, Co, Ni...}$; $n = 1, 2, 3, 5...$) are able to store large amounts of hydrogen to create metallic hydrides. The absorption/desorption reaction is reversible in a large domain of temperature and pressure. Therefore these compounds have been developed for energy storage applications. Among the hydride forming compounds, LaNi_5 is able to store more than 6H/formula unit at room temperature.

Neutron diffraction is crucial for the determination of the structural properties of these phases: symmetry, nature of occupied insertion sites and occupation factor. Moreover, due to the neutron penetration depth, structural studies can be performed in closed cell under hydrogen pressure up to 100 bar allowing accurate control of the hydrogen composition. The accurate description of crystal structures of AB_5 host matrices and their hydrides remains our most important contribution in the hydride field, including superstoichiometric AB_{5+x} intermetallic alloys.

New materials are also investigated, such as RY_2Ni_9 ($R = \text{La, Ce}$) compounds, structurally described as an ordered intergrowth of $(\text{R,Y})\text{Ni}_5$ and $(\text{R,Y})\text{Ni}_2$ structure-types. In a more fundamental point of view, the magnetic structures of Laves phases have been studied in connection with their absorption properties, thus allowing a careful description of their phase diagrams and the relationships existing between inserted hydrogen (deuterium) structural order and magnetic order. [Collaboration: Laboratoire de Chimie Métallurgique des Terres Rares-CNRS, Thiais]





MOLECULAR CRYSTALS: QUANTUM EFFECTS AND BIOMOLECULAR SYSTEMS

Quantum entanglement in hydrogenated molecule vs “classic” deuterated analogue

Differences between quantum mechanics and classical physics are specially underlined in KHCO_3 . Quantum entanglement observed in the KHCO_3 crystal then further demonstrates the validity of quantum mechanics at the macroscopic level (see subsequent “ KHCO_3 ” **Highlight**).

Lithium acetate ($\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$) is another prototype system to investigate the interplay of crystal structure and rotational dynamics of nearly free quantum methyl rotors. For the methyl-deuterated salt we [Collaboration: LADIR, Thiais, F. Fillaux; LLB: B. Nicolai (PostDoc), A. Cousson] have observed a phase transition at (17.5 ± 0.5) K that does not occur for the hydrogenated derivative. The disordered CD_3 groups in the high temperature phase become ordered at low temperature, whereas all other atomic positions remain virtually unchanged. The transition is due to quantum effects arising from the increased mass of the methyl groups upon deuteration. It can be said that CD_3 rotors are “more” classical than CH_3 groups. The probability density maps in the rotational plane of the methyl groups combined with the tunnelling spectra of various partially deuterated samples shed a new light onto the quantum rotational dynamics.

Thus we demonstrate that complementary neutron diffraction and inelastic neutron scattering techniques may reveal the otherwise hidden interplay of crystal structures and quantum rotational dynamics, at levels of accuracy and physical understanding far beyond what can be obtained with the most advanced computational methods of quantum chemistry [B. Nicolai, A. Cousson and F. Fillaux *Chem. Phys.* **290** (2003) 101-120].

Localisation of water molecules

Determination of the crystal structure of molecular crystals is most easily accessed via single crystal neutron diffraction. The localisation of water molecules and hence the characteristics of hydrogen bonds, respectively in $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$ and 1-hydroxy-1-phosphono-pentyl-phosphonic acid dimethylammonium salt was studied in connection with biology [Collaboration: Laboratoire de Chimie et Spectroscopie Biomoléculaire, Université Paris XIII, A. Navaza; LLB, G. Chevrier]. $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$ has also been investigated in the 77K-300K temperature range via X-ray powder diffraction (XRD), differential thermal analysis (DTA) and infrared spectroscopy (IRS). The crystal structure of 1-hydroxy-1-phosphono-pentyl-phosphonic acid dimethylammonium salt at room temperature (triclinic, space group P-1) has evidenced a hydrogen bond network formed by the dimethylammonium cation linking hydroxybisphosphonate groups in columns parallel to the $[0\ 1\ 0]$ direction. Results have shown that acids of the hydroxybisphosphonic family can protonate volatile alkaline species like dimethylamine to get particularly stable crystals.

Radioprotective systems

As for the study of medical preparates, 2-thione and 2-cyanoiminepyrimidine compounds were synthesized for applications in the medical treatment of radiation damages on human organisms [Petersburg Nuclear Physics Institute, Moscow State University and Moscow State Academy of Fine Chemical Technology, Russia]. By combining NMR-, IR-spectroscopy, single crystal X-ray diffraction and neutron powder diffraction, more than ten (10) crystal structures were solved, in order to correlate the molecular structures of these compounds and their radioprotective properties.

PHASE TRANSITIONS: LATTICE DYNAMICS UNDER PRESSURE

The study of phonons is one of the main domains accessible to Inelastic Neutron Scattering. A common program [Collaboration: Physique des Milieux Condensés, Université P&M Curie, S. Klotz & al.] on the study of **phonon dispersion curves at very high pressures** continues to be pretty efficient and very successful. As an example, a highly anomalous pressure dependence of acoustic phonons in the chalcopyrite AgGaSe_2 up to 4.5 GPa across a subtle structural phase transition has been discovered (see **Highlight**). Very recently, record pressures of 20 GPa (200 kbars) have been reached using this technique in measurements of the pressure-induced mode softening in SrTiO_3 .

The LLB is the only neutron facility in the world that is able to carry out such studies, and at the same time offers such techniques fully to the user community. Using more standard high pressure methods, soft modes have also been studied in ice Ih (normal ice) up to 0.5 GPa, which revealed for the first time the origin of its negative thermal expansion coefficient.

APERIODIC MATERIALS

An important domain of research at LLB concerns aperiodic materials both in their structural and dynamical aspects. In addition to quasi-crystals systems, aperiodicity is observed into two different classes of materials, incommensurate systems and composite systems with two chemical species or with non-stoichiometric



chemical composition. In contrast to the former case, one cannot define a mean structure in the latter case. Instead, two different sublattices coexist with incommensurate periodicities. The main question in the field concerns the nature and magnitude of interactions between the two sub-systems in order to understand the peculiar electronic or magnetic properties of these composites.

Incommensurate Composite systems

Incommensurate composites are constructed from at least two interpenetrating subsystems with different periodicities in at least one crystallographic direction. The structural properties using the superspace formalism begin now to be well understood, but the lattice dynamics via the phonon modes needs to be elucidated. Following the different coupling mechanisms (nuclear and/or electronic ones), one expects to interpret the acoustic branches and the sliding mode response, which reflects a relative displacement of the subsystems along the incommensurate direction.

The most studied incommensurate crystals are the Bi-based high-Tc superconductors $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_{2n}\text{O}_{2n+4+\delta}$ ($n = 1, 2$). In a composite description, these compounds are assumed to be formed by a rigid perovskite block ($\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_{2n}\text{O}_{2n+2}$) strongly coupled to the $\text{Bi}_2\text{O}_{2+\delta}$ slabs. Recent single crystal neutron diffraction data about Bi-2212 ($n = 2$) have been used to obtain Fourier maps within the superspace formalism, which show discontinuous modulation functions for the oxygen atoms in the BiO layers. The competition between the couplings to the perovskite neighbouring slabs is directly related to the oxygen content δ . The low frequency dynamics ($n = 1, 2$), investigated by inelastic neutron scattering, has given different behaviours for the acoustic and sliding mode branches emerging from main Bragg reflections of each subsystem. Comparison with other oxide materials (spin-chain ladder systems, $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41+\delta}$) is made in order to progress in the understanding of the charge ordering effects in the physical properties.

[Collaboration: J. Etrillard (Université de Rennes), P. Bourges (LLB), B. Keimer (MPI, Stuttgart), J.M. Perez-Mato (Universidad del Pais Vasco, Bilbao), M. Braden (University, Köln), A. Revcolevschi (Université Paris-Sud)].

Another approach to the study of incommensurate composite systems is obtained by applying an external pressure on the crystal and measuring the strain induced on each sublattice via neutron diffraction. This was done in the **Alcane-Urea** system and the original results are described in a subsequent **Highlight** [L. Bourgeois, B. Toudic, C. Ecolivet, GPMC, Université de Rennes].

An incommensurate system, BCCD

Solids with an incommensurate structural thermal instability can exhibit complex phase sequence as a function of temperature with several intermediate commensurate phases where the structural modulation locks into different multiple periodicities of the underlying basic lattice.

Betaine Calcium Chloride Dihydrate (**BCCD**) is the most conspicuous experimental case with more than fifteen intermediate phases. Three axis elastic neutron scattering results demonstrate that the five-fold modulated phase exhibits under electric field a phase transition without change of the superlattice periodicity. The transition is caused by the flip of the average polarization of one of the interface layers. This type of polarization-flip phase transition had been detected and characterized in one-dimensional theoretical models as generalized Frenkel-Kontorova models or spins chains with elastic couplings. We have demonstrated, using a general phenomenological displacive model, the occurrence of this peculiar transition in systems like BCCD. Spin-flip phase transitions yield very peculiar phase diagrams with a checkerboard topological structure and self-similar features. In particular, they may present special critical points as so-called epsilon points. BCCD may be then the first experimental system where they could be observed.

[Collaboration: M. Quilichini (LLB), O. Hernandez (Université de Rennes), J.M. Perez-Mato (Universidad del Pais Vasco, Bilbao), G. Schaak (Würzburg University) and L. Vieira (Minho University, Braga)].

Modulated structure of photo refractive compounds

To make a smooth transition to the next paragraph dealing with ferroelectric systems used in industry, let us also mention the **highlight** on the modulated structure of $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$ from a Swiss neutron team. [PhD, D Schaniel, ETH 2003]

FERROELECTRICS MATERIALS

Giant piezo-electricity in lead-based ferroelectrics relaxors.

Correlation between device-based properties of relaxor compound and their microstructures is a problem extensively studied at LLB by the Laboratoire “Structures, Propriétés et Modélisation des Solides” of Ecole



STRUCTURES AND PHASE TRANSITIONS

Centrale de Paris [UMR-CNRS 8580; J.M. Kiat, C. Malibert, B. Dkhil, ECP]. In these compounds, such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3/\text{PbTiO}_3$ (PMN/PT), giant piezoelectric and electrostrictive properties, high dielectric permittivity etc... are evidenced in a large region of temperatures but in a narrow range of concentrations, called **morphotropic compositions**. These materials are largely used for industrial applications such as high capacity condensators, transducers and actuators, DRAM memories.... Up to now, coexistence of several ferroelectrics phases was assumed to explain the outstanding properties of these mixed compounds. Combination of neutron and X ray diffraction has allowed to evidence new monoclinic phases [PRB 65 (2001) 024104; PRB 65 (2002) 064106] which bridge the ferroelectric phases of the end members of PZN/PT, PMN/PT, PSN/PT systems, allowing a quasi-continuous rotation of the polarization between the well-known antagonist tetragonal and rhombohedral phases. The existence of these low symmetry phases allows understanding why these systems are very «soft» from the standpoint of polar properties and manifesting high technological properties.

Order and disorder in lead-free ferroelectric BST ($\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$)

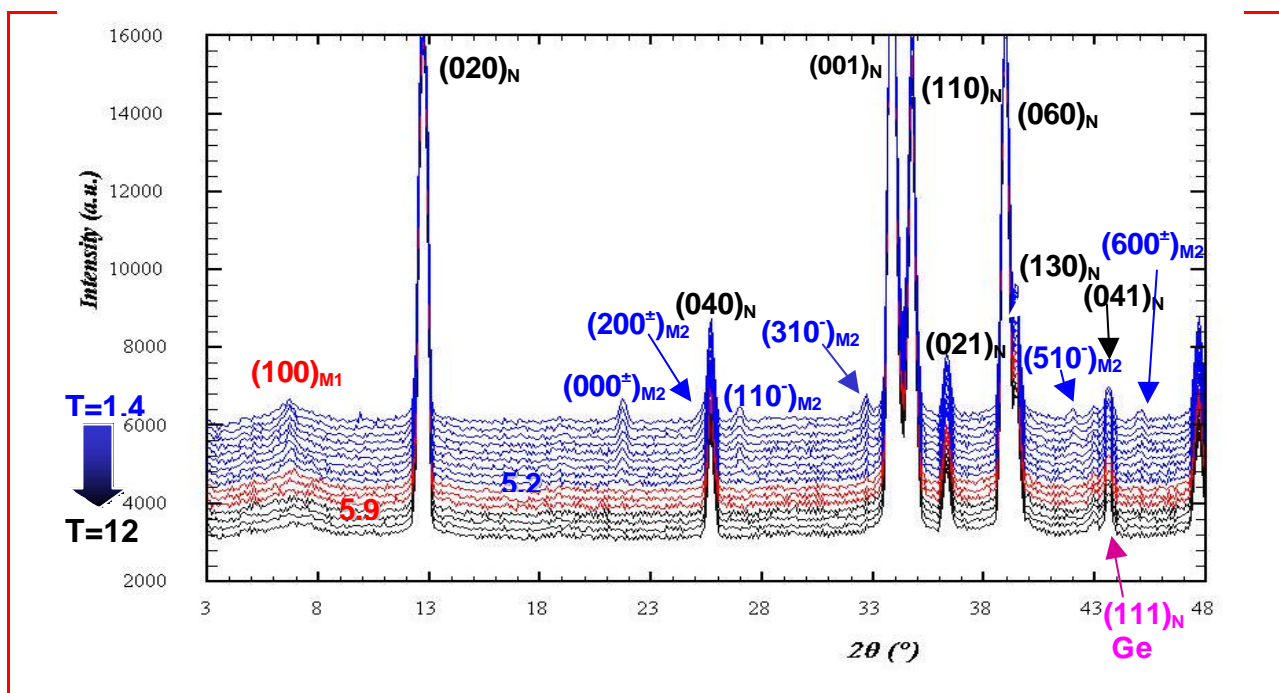
Thin films of ferroelectric materials are more and more studied for their integration in silicium-based devices. BST is of peculiar interest because it is the lead-free system with the highest performances when downsizing from bulk systems toward thin films. Studies at LLB and UMR 8580 have allowed understanding the competition between short and long-range polar orders that results in high dielectric performances. [Thèse C. Menoret [ECP], 18 Décembre 2002, ECP] [PRB 65 (2002) 224104].

MAGNETIC STRUCTURES IN INTERMETALLIC COMPOUNDS

Rare-earth (R) based intermetallics are generally associated to localized R^{3+} magnetism, as R belongs to the second series of the rare-earth elements. At LLB, we were more interested in Cerium and Uranium compounds where Magnetism is partly “delocalised” (see also next section).

Cerium intermetallics

A systematic study of magnetic properties was investigated in the ternary Ce-Ni-Ge system, for which more than 20 stoichiometric compounds were known to exist, in order to connect chemical composition and magnetic properties [Collaboration: ICMCB, Bordeaux; LLB / PhD, L. Durivault, November 2002, Université de Bordeaux]. Both macroscopic (magnetic susceptibility, electrical resistivity, specific heat measurements) and microscopic techniques (X-ray and neutron diffraction, XANES) were used in order to characterise the magnetic state of the systems. See the results in a subsequent **Highlight**.



Neutron thermodiffractogram of CeNiGe_3 between 1.4 K and 12 K showing the \mathbf{k}_1 (100) commensurate magnetic order in red and the \mathbf{k}_2 (0 0.4 0.5) incommensurate magnetic order in blue obtained on G4.1.



Uranium intermetallics

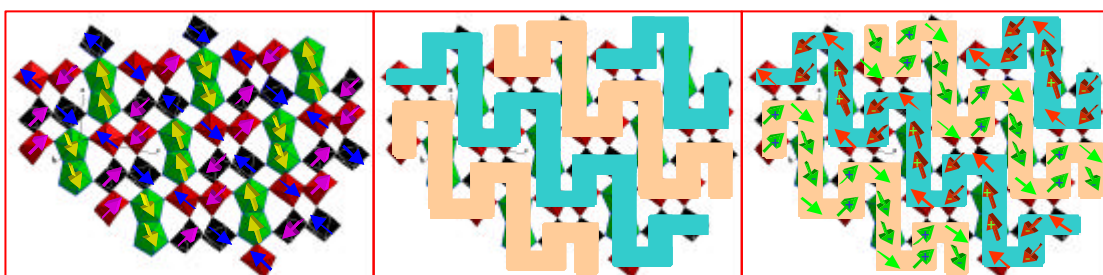
Crystal structures in binary U-Sn intermetallic system have only been recently obtained [1995]: USn_3 , U_3Sn_7 , USn_2 , USn and U_5Sn_4 are known to exist. Depending of the stoichiometry, different types of magnetic behaviours are observed, from ferromagnetic U_5Sn_4 and USn to antiferromagnetic USn_2 and U_3Sn_7 and non-magnetically long range ordered USn_3 . In order to establish a relationship between the crystal and magnetic structures in the series, USn_2 and U_3Sn_7 have been investigated via neutron powder diffraction [Collaboration: LCSIM, Rennes; LLB]. Below $T_N=75\text{K}$, the USn_2 magnetic structure is associated to $\mathbf{k} = (0\ 0\ \frac{1}{2})$ propagation vector (Cmmm space-group) and alternating “+ - + -” ferromagnetic $(0\ 0\ 1)$ planes with magnetic moments along \mathbf{c} ($T=1.4\text{K}$, $M=1.55\mu_B$). As for U_3Sn_7 magnetic structure ($T_N=50\text{K}$, from magnetic measurements), the main result we got from neutron powder diffraction is an upper limit for the uranium magnetic moment, namely $0.3\ \mu_B$ [JAC 329 (2001) 47-49].

MAGNETIC STRUCTURES IN IONIC COMPOUNDS

Among ionic compounds, transition metal oxides attract a lot of interest from the solid-state chemist community, due to “remarkable” properties of some of these materials, such as manganese perovskites and ferroelectrics. Magnetic properties of some of these oxides are also very interesting, showing either reduced dimensionality effects (CuGeO_3 , Y_2BaNiO_5), or frustration (pyrochlore-type oxides with antiferromagnetic interactions...). Magnetic structure determination in insulating compounds was recently renewed by ab-initio methods able to predict the fundamental states from the super-exchange ($\text{M-O-M}'$) and/or super-super-exchange $\text{M-O-O-M}'$ interactions. Computing programs for analysing the topology of exchange interactions [SIMBO] and the classical magnetic energy [ENERMAG] have then been developed (see corresponding **Highlight**, in the “Modelling” section of this report). Two “real” systems are described below, which are controlled by super-exchange ($\text{M-O-M}'$) and super-super-exchange ($\text{M-O-O-M}'$) magnetic interactions.

Terbium ionic compounds

Fluoroterbates magnetic structures, obtained via neutron powder diffraction, are analysed (see subsequent **Highlight**) in order to correlate crystal structures and magnetic properties [Collaboration: Laboratoire des Matériaux Inorganiques (LMI), Université Blaise Pascal, Aubière, France ; LLB ; High Magnetic Field Laboratory (HMFL), Grenoble]. Let us note that the magnetic transition temperature in all of the already studied compounds is less than 4.2K , resulting both from super-exchange ($\text{R-F-R}'$) and/or super-super-exchange $\text{R-F-F-R}'$ magnetic interactions (R and R' stand for either Tb^{3+} or Tb^{4+} ions) and dipolar interactions.



KTbF_5 magnetic structure (left and right parts of the figure); edge-sharing $[\text{TbF}_8]^{4-}$ polyhedral chains (middle and right parts of the figure).

Magnetic phosphates

Magnetic structures of MFePO_5 (with M a divalent transition element, $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) and $\text{CuFe}_2(\text{P}_2\text{O}_7)_2$ phosphates have been obtained and “theoretically” analysed [Collaboration: LLB ; Département de Physique, Faculté des Sciences, Rabat, Maroc; Laboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Rabat, Maroc] / N. El Khayati, PhD, Décembre 2001, Université de Rabat, Maroc]. MFePO_5 oxyphosphates are all isomorphic, with orthorhombic Pnma space-group, M^{2+} and Fe^{3+} metallic ions being located on distinct crystallographic sites. The M^{2+}O_6 and Fe^{3+}O_6 topological arrangement leads to the existence of a complex map for super-exchange interactions (J_1 , J_2 , J_3 et J_4), which allowed to explain the observed antiferromagnetic structures, which are collinear, with magnetic moment along \mathbf{b} -axis, except for $\text{M} = \text{Co}$



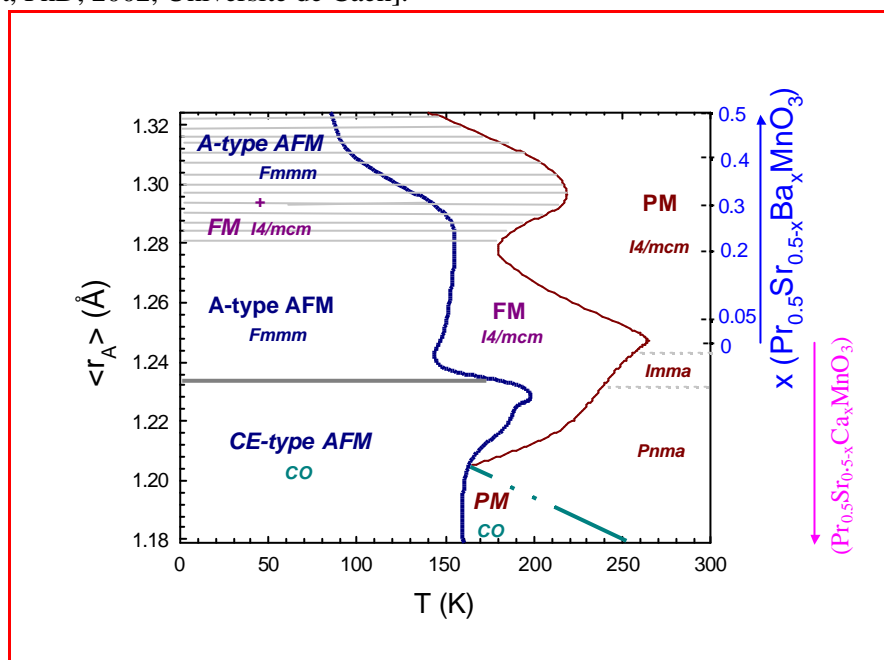
[European Journal of Physics B : Condensed Matter Physics 22 (2001) 429-442]. Let us note that Goodenough-Kanamori-Anderson rules give positive J_1 and J_2 exchange parameters.

The crystal structure of $\text{CuFe}_2(\text{P}_2\text{O}_7)_2$ pyrophosphate [monoclinic, $\text{P2}_1/\text{n}$ space-group] has centrosymmetric $\text{Fe}^{3+}\text{-Cu}^{2+}\text{-Fe}^{3+}$ trimers, with square-planed coordinated Cu^{2+} [CuO_4], and 6- coordinated Fe^{3+} [FeO_6 octahedra]. Within this topological arrangement, both Cu-O-Fe super-exchange (inside the same $\text{Fe}^{3+}\text{-Cu}^{2+}\text{-Fe}^{3+}$ trimer), and Cu-O-O-Fe and Fe-O-O-Fe super-super-exchange interactions (between metallic ions in neighbouring trimers) are present. Magnetic structure below $T_N=15.5\text{K}$ is described with a $(\frac{1}{2} 0 \frac{1}{2})$ propagation vector, the magnetic moments of the metallic ions within a trimer being parallel to each other (ferromagnetic trimer) and to **b**-axis. The observed magnetic structure was then analysed via SIMBO and ENERMAG, with seven (J_{1-7}) exchange constants [Solid State Science 4 (2002) 1273-1283].

CMR MANGANITES AND PEROVSKITES

As for manganese perovskites with Colossal MagnetoResistance (CMR) behaviour, an essential problem is the existence, or non-existence, of Mn^{3+} and Mn^{4+} charge ordering at low temperature, according to the nature of the cations and the stoichiometry of the structure. This problem has been "revisited" by a careful analysis of the crystal structure of a half-doped manganite (single crystal X-ray and neutron diffraction) [M. Daoud-Aladine, PhD, 2001, Université Paris VI; J. Rodriguez-Carvajal, LLB; in collaboration with L. Pinsard-Gaudart, A. Revcolevschi, Laboratoire de Physico-Chimie des Solides, Université Paris-Sud; M.T. Fernandez-Diaz, ILL] and new insights obtained in a polaronic approach of the Mn-Mn couplings. These results are described in one of the following **Highlights**.

Seeking for new oxides materials (cuprates, manganites...) with defined properties, either superconductive and/or magnetoresistive, is an essential task for the « New Materials » scientific team in CRISMAT, Caen. A collaboration does exist between CRISMAT and LLB, in order to get via neutron diffraction a precise description of the crystal and magnetic structures of the synthesized compounds. Half-doped manganites $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ba}_x\text{MnO}_3$ have been considered and their crystal and magnetic phase diagrams carefully established as a function of temperature and $\langle r_A \rangle$ and σ_A , the mean values characteristic of the cation atomic radius [C. Autret, PhD, 2002, Université de Caen].



Structural and magnetic phase diagram ($\langle r_A \rangle$ vs T) for half-doped manganites: $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ba}_x\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ (from neutron powder diffraction results). AFM, FM and PM stand for AntiFerromagnetism (A-type and CE-type), Ferromagnetism and ParaMagnetism, CO for Charge Order. The crystallographic structures are described by the Fmmm, I4/mcm, Imma and Pnma space groups.

In the same work, and in order to connect crystal and magnetic properties, the $n=1$ Ruddlesden-Popper “bidimensional” components $\text{Pr}_{2-x}\text{Ca}_x\text{MnO}_4$ were characterized ($1.5 \leq x \leq 1.75$). Let us note that the crystal structure of these compounds (K_2NiF_4 -type) is derived from the perovskite crystal structure, alternating perovskite and NaCl type-layers and that electron microscopy and neutron diffraction revealed the existence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering ($x=1.5$).



Another goal of this CRISMAT team is to study the effect of substitution on the Mn site of the perovskite. In fact, an efficient way to destabilize the charge ordering is to substitute Mn with other elements, in accordance with the formula $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ and $\text{M} = \text{Cr}, \text{Ru}, \text{Al} \dots$. Depending on the x values and the substituting cations, different behaviours are observed, leading, more often, to interesting properties due to the existence of a phase-separated system at low temperature. Within this framework, two compounds were first studied by neutron diffraction: $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Cr}_{0.05}\text{O}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Al}_{0.05}\text{O}_3$ and it was thus shown that 5% Cr induces long-range ferromagnetism (FM) while 5% Al only weakens the charge ordering (CO) and the associated CE-type antiferromagnetism (AFM). Nevertheless, due to the FM-AFM competition, CMR is evidenced in both cases. For the phase separation scenario, the second type of compounds exhibits, of course, more interest. It is why the study of other Mn-site doped $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ samples is always a subject of research and recently, a puzzling effect was reported in the low level substituted $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ compounds ($x < 0.10$). Actually, their field dependent magnetization curves, collected at low temperature, exhibit abrupt steps, that are attributed to transformations of AFM regions into FM ones. The occurrence of steps in the magnetization is a general feature of these doped manganites, but particularly large jumps are obtained for the Ga substituted compounds, and a careful structural study is now in progress on the 3%Ga compound, by combining neutron diffraction (3T2, G41 and PAXY) and electron microscopy (CRISMAT) in connection with transport and magnetic measurements (resistivity, susceptibility, magnetization and specific heat). See also the 1c paragraph and the **highlight** manganites in the next section “Magnetism and superconductivity”.

In 2001-2002, our Russian collaborators on G4.2 performed neutron diffraction experiments on “magnetoresistive” manganites. Crystal and magnetic structures of $^{154}\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ were obtained, also derived from resistivity, magnetic susceptibility and second harmonic magnetic measurements [Petersburg Nuclear Physics Institute, Moscow State University, Russia]. The influence of Fe doping was characterized in a second series $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$: transformation from a weakly frustrated FM (ferromagnetic) phase in the 0-0.05 x -range to a strongly frustrated, mixed FM and glassy phase in the 0.07-0.09 x -range [Petersburg Nuclear Physics Institute, Russia and Wihuri Laboratory, University of Turku, Finland]. The magnetic properties of lightly doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites, with both Nd and Mn magnetic sublattices, have also been considered [Petersburg Nuclear Physics Institute, Russia and Low Temperature Physics and Engineering Institute, Kharkov, Ukraine].

GEOMETRICALLY FRUSTRATED MAGNETIC SYSTEMS

Study of geometrical frustration and magnetic instability is a long-term activity in LLB. In geometrically frustrated systems, the lattice geometry of chemically ordered compounds does not allow all magnetic interactions to be minimised at the same time. In this respect, they differ from classical spin glasses, which combine frustration and chemical disorder. A well-known case of geometrical frustration is obtained by antiferromagnetic first neighbour interactions in a triangle. The 2D Kagomé and 3D pyrochlore lattices are other extensively studied systems. Especially when combined with magnetic instability (transition from localized to itinerant magnetism), geometrical frustration leads to numerous and spectacular effects in the field of phase transitions. Some recent results are given below, on

- (i) Laves phases RMn_2 and their hydrides RMn_2H_x [I. Goncharenko, I. Mirebeau, P. Cadavez-Peres, O. Makarova, F. Bourée, R. Kahn, I. Golosovsky (PNPI, Gatchina, Russia), A. Irodova (Kurchatov Institute, Moscow), A. Markosyan (Moscow University)] and
- (ii) $\text{Tb}_2\text{Ti}_2\text{O}_7$ [I. Mirebeau, I. Goncharenko, P. Cadavez-Peres, G. Dhalenne and A. Revcolevschi (Université Paris-Sud), S. Bramwell (UK), M. Gingras and J. Gardner (Canada)].

Let us mention also the neutron single crystal diffraction study of the magnetic structure of paramélaconite Cu_4O_3 , a system with a spin $S = 1/2$ pyrochlore lattice [J. Rodríguez-Carvajal, A. Gukasov (LLB) — L. Pinsard-Gaudart (LPCES, Univ. Paris-Sud) — Ph. Monod (LPS, ESPCI Paris)].

Laves phases RMn_2 and their hydrides

In the RMn_2 compounds, the Mn atoms are also situated in a pyrochlore lattice, and they exhibit magnetic instability, depending on the Mn-Mn first neighbour distance. The study of GdMn_2 and $\text{Ho}(\text{Mn}_{0.9}\text{Al}_{0.1})_2$ under high pressure revealed several phases transitions: starting from complex short range ordered phases at ambient pressure, new ferromagnetic phases are induced under high pressure, (6-8GPa), with a stabilization of ferrimagnetic phases (either canted or collinear) at intermediate pressures. The experiment allowed separating the different contributions to the magnetic energy (from dominant AF Mn-Mn interactions at $P=0$,



to dominant R-R ferromagnetic interactions at high pressure). The influence of Al substitution which combines two opposite effects, a negative chemical pressure and a magnetic dilution of the frustrated Mn lattice, was also studied in a wide range of concentration in RMn_2 compounds with $\text{R}=\text{Ho}, \text{Dy}, \text{Er}$.

In the Laves hydrides RMn_2H_x , the H lattice strongly interacts with the frustrated Mn lattice. The cubic Laves hydrides $\text{R} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ (PhD, P. Cadavez-Peres, Décembre 2002) show number of magnetic transitions controlled by existence of R magnetism, the substitution in the Mn lattice and the chemical ordering of the H sublattice. Hydrogen disorder may induce new short range ordered magnetic phases with unusually high freezing temperatures. The magnetic structure and spin excitations in these phases have been studied by powder neutron diffraction and inelastic neutron scattering. Experiments under applied pressure helped to discover other unusual phase transitions in these compounds: chemical segregation in the hydrogen sublattice and transitions from short-range to long range ordered magnetic structures.

Oscillating chemical and magnetic order of hexagonal hydrides

Study of the hexagonal hydrides $\text{R}=\text{Er}, \text{Tm}, \text{Lu}$ (PhD, O. Makarova, 2002) revealed a very surprising feature: an oscillating dependence between the chemical and magnetic orders. Whereas the H sublattice progressively orders with increasing H content denoted x , inducing ordered superstructures at high concentrations, the correlation length in the magnetic sublattice oscillates between long range (LRO) and short range (SRO) ordered structures: SRO for $x=2 \rightarrow$ LRO for $x=3$, propagation vector $\mathbf{k}=1/2\ 0\ 0 \rightarrow$ SRO for $x=4.2 \rightarrow$ LRO for $x=4.6$, $\mathbf{k}=1/3\ 1/3\ 0$. For the first time, a long-range magnetic order was induced by short-range order in the chemical lattice (transition $x=4.2 \rightarrow x=3$). This surprising effect is still unexplained.

Crystallisation of a spin liquid under pressure

$\text{Tb}_2\text{Ti}_2\text{O}_7$ is an ideal spin liquid where magnetic moments still fluctuate down to very low temperatures (10 mK), well below the Curie-Weiss temperature (-19K) which characterizes the strength of the magnetic interactions. Under high pressure (up to 8 GPa), we observed by powder neutron diffraction the onset of long-range antiferromagnetic order, coexisting with the spin liquid state below 2.1K (see the **highlight**).

New pressure experiments on oriented single crystals, with different types of pressure (hydrostatic, quasi-hydrostatic, and uniaxial) are now in process to investigate the origin of this effect, and follow it down to very low temperatures (0.1K). The future prospects concern the characterization of the new observed phases and the understanding of their stability. The pyrochlore lattice with $S=1/2$ is an excellent candidate to test the validity of recent theories about quantum fluctuations in these frustrated systems and their predictions: existence of a quantum spin liquid state, analogous to the Resonant Valence Bond (RVB) one, nature of the spin excitations. In rare earth pyrochlores, where the spin values are high, the mechanisms that govern the onset of magnetic phases are still rather poorly understood. High-pressure neutron diffraction (a unique feature available in LLB) is a very powerful tool to study the stability of such phases. Pressure could also induce new magnetic phase transitions like those quoted above, or the transition from metallic ferromagnet to insulating spin glass in $\text{R}_2\text{Mo}_2\text{O}_7$ pyrochlores, whose study is foreseen.

CONCLUSION

If we had to have a short summary of the above results, the first characteristics to be pointed out would be the wide diversity of the subjects needing neutron scattering, in both fundamental and applied research. Another character is the high number of collaborations existing between physicists or chemists in LLB and out LLB, either in France or Europe. As for experimental conditions, non "ambient" temperatures and samples under controlled atmospheres are easily available with neutron scattering. A "new" parameter is also more and more used in neutron experiments: "high pressure". And, in the recent years, neutron diffraction experiments under very high hydrostatic or quasi-hydrostatic pressures became available at the LLB. At the present moment, the LLB disposes of higher pressures (up to 500 kbars) than any other neutron source in the world. The development is based on a combination of high-intensity neutron diffraction and compact pressure cells with sapphire (pressures up to 100 kbars) or diamond (pressures up to 500 kbars) anvils. New high-pressure version of the G6.1 diffractometer ("MICRO"), equipped by a special focusing system, allows studying samples as small as $0.1\text{-}0.001\text{ mm}^3$ in the wide range of pressures and temperatures.