

# 1 - STRUCTURES AND PHASE TRANSITIONS

Studies on both crystallographic and magnetic structural phase transitions are an important part of Laboratoire Léon Brillouin's scientific activity. Neutron studies, either diffraction and/or inelastic scattering, are performed as a function of external parameters, namely temperature and pressure. Many different physical problems, either fundamental and/or applied, are in connection with structural phase transitions and the present summary intends to show the main results of the research in the field in 2003 and 2004.

## HYDRIDES: STRUCTURAL STUDIES

Metallic hydrides absorb reversibly hydrogen near ambient pressure and room temperature. These remarkable properties lead to both fundamental research and application development in the frame of energy storage. To localize hydrogen atoms within the metallic matrix, to study magnetic structures of the resulting hydrides, neutron diffraction is a crucial technique. The first **Highlight** below is partly dedicated to the (Zr,Ti)Ni system, a potential compound for hydrogen storage, partly to the  $\text{YFe}_2(\text{H}_y\text{D}_{1-y})_4$  system. By using different elaboration techniques, two different crystallographic forms of the same solid solution  $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$  are available at room temperature, which exhibit different hydrogenation properties. An accurate description of the  $\alpha$  (cubic),  $\beta$  and  $\gamma$  (orthorhombic)  $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$  hydrides has been obtained through the determination of hydrogen Wyckoff positions in the crystal structure(s). In a more fundamental point of view, the magnetic properties of the Laves phases  $\text{YFe}_2(\text{H}_y\text{D}_{1-y})_{4.2}$  have been carefully studied, as a function of temperature but also depending of the nature of the hydrogen atoms (H or D), showing unexpected isotopic effects on the magnetic behaviour.

[Collaborations: Laboratoire de Chimie Métallurgique des Terres Rares - CNRS, Thiais]

## BIOMATERIALS: STRUCTURAL STUDIES

Synthetic hydroxyapatite (HA) is one of the most important bioceramics used in dentistry and orthopaedic surgery. In order to explain the higher bioactivity of the silicon-substituted hydroxyapatite (SiHA), synthetic HA and SiHA have been structurally studied by neutron scattering. The Rietveld refinements have shown that the final compounds are oxy-hydroxyapatites, when obtained by solid-state synthesis under air atmosphere. By using neutron diffraction, the substitution of P by Si into the apatite structure has been corroborated in these compounds. Moreover these studies also allowed to understand the better bioactive behaviour of SiHA in terms of higher thermal displacement parameters of the H located at the (4e) site (see **Highlight**).

## FERROELECTRICS MATERIALS

### Morphotropic phases in giant piezoelectric/dielectric lead-based compounds in bulk and thin films: correlation between chemical disorder and polar ordering

Insulating perovskite solid solutions are of tremendous technological importance due to their exceptional piezoelectric and dielectric properties. Up to date, the largest electromechanical and dielectric responses have been found in  $\text{PbTiO}_3$ -based alloys -- PZT [ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ], PMN-PT [ $\text{Pb}(\text{Mg},\text{Nb},\text{Ti})\text{O}_3$ ], PZN-PT [ $\text{Pb}(\text{Zn},\text{Nb},\text{Ti})\text{O}_3$ ] -- in a large temperature range but in a narrow composition range, known as the morphotropic phase boundary (MPB). In this context PSN-PT [ $\text{Pb}(\text{Sc},\text{Nb},\text{Ti})\text{O}_3$ ] is of peculiar importance due to the fact that this alloy exhibits the highest piezoelectric constant ever reported and chemical ordering of Sc / Nb / Ti cations via long time annealing is known to have strong consequences on the piezoelectric properties. When decreasing the Ti composition across the MPB, the overall sequence of crystal structures deduced from the analysis of both neutron and high resolution X-ray diffraction data on PSN-PT is: "Tetragonal - Monoclinic C - Monoclinic B - Rhombohedral". From theoretical calculations this rather unusual scheme (Monoclinic C and Monoclinic B phases observed, instead of Monoclinic A) has been shown to exist only if the samples "deviate" from the perfectly homogeneous and disordered situation, in the form of chemically-ordered regions.

In the case of films with MPB compositions the structural evolutions show a competition between bulk monoclinic symmetries and substrate-induced tetragonal distortion which can result, depending on the composition of the substrate (STO or MgO) and the thickness of the films (between 50nm and 500nm), in the disappearance of phases or large shifts for the critical temperature value, with strong consequences on the piezo/dielectric properties.

[Collaboration : SPMS - Ecole Centrale, Paris ; L. Bellaïche, Arkansas University, USA; Y. Uesu, Waseda University, Tokyo, Japan]

[R. Haumont et al, PRB 68 (2003) 014114; PRB (2005)]

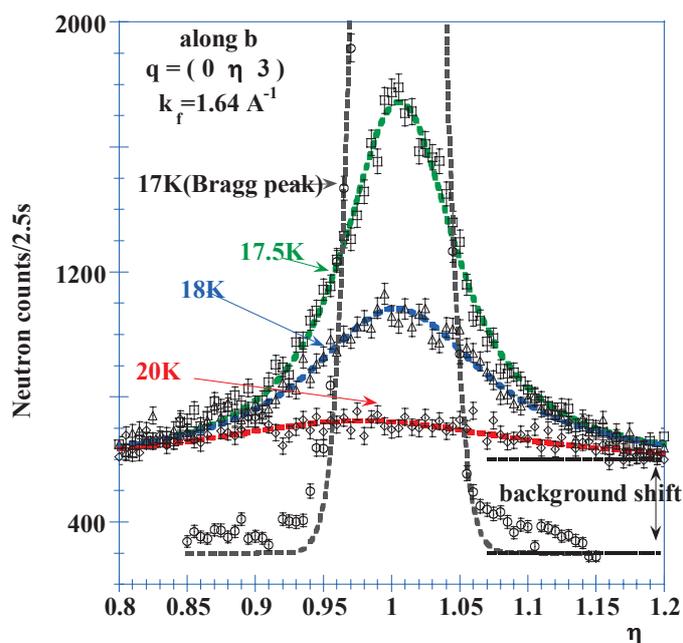
### MOLECULAR CRYSTALS: CH<sub>3</sub> AND H DYNAMICS

Investigating the interplay of crystal structure and rotational dynamics of methyl groups is of crucial importance to understand the phase transitions that undergo methylated compounds in the solid state. Such a study is presented (see **Highlight**) in the case of the 4-methyl N-oxy pyridine, **C<sub>5</sub>H<sub>4</sub>NO[CH<sub>3</sub>]**, which exhibits two structural phase transitions below room temperature (RT).

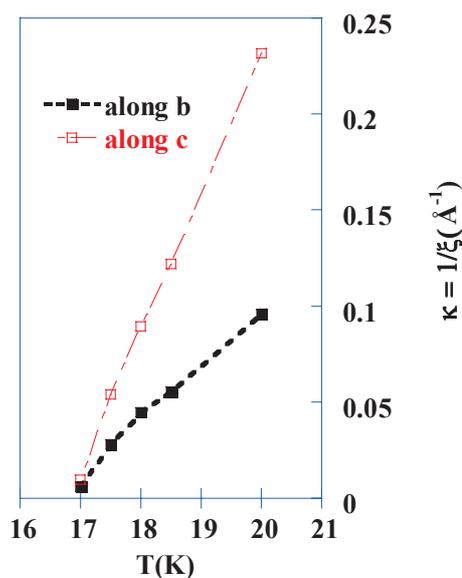
**Lithium acetate (LiCH<sub>3</sub>COO,2H<sub>2</sub>O)** is another prototype system to investigate this interplay. The roles of H and/or D on methyl rotation was evidenced in lithium acetate comparing the neutron diffraction data obtained with either fully hydrogenated, either fully deuterated, either "mixed" (CH<sub>3-x</sub>D<sub>x</sub>) systems. Whatever the temperature, the crystal structure of LiCH<sub>3</sub>COO,2H<sub>2</sub>O is orthorhombic, with *Cmmm* symmetry, and free rotation observed for methyl groups. Neutron diffraction applied to the partially deuterated analogues, LiCD<sub>3</sub>COO,2D<sub>2</sub>O has evidenced a crystal phase transition from *Cmmm* to *Pman*, with CD<sub>3</sub> groups ordered at low temperature. The *Cmmm* to *Pman* transition is observed at T<sub>C</sub>= 17K (x = 3), T<sub>C</sub>= 14K (x = 2) and T<sub>C</sub> = 6K (x = 1). According to symmetry analysis the structural transition is predicted to occur at the Y *Cmmm* space group zone boundary point. This has been effectively observed in LiCD<sub>3</sub>COO,2D<sub>2</sub>O, with pre-transitional anisotropic diffuse neutron scattering measured above T<sub>C</sub>, condensing into the (013) Bragg peak at T<sub>C</sub> and (013) quasielastic scattering also measured above T<sub>C</sub>, associated to a life-time of correlated domains (≈10<sup>-6</sup>s) which in turn diverges at T<sub>C</sub>. Another feature observed at the transition, is a strong reduction of the incoherent elastic background. Finally, anomalies in the energy-scan of a phonon measured at the zone boundary and at T<sub>C</sub> can be understood in the frame of an order-disorder-displacive mechanism.

[Collaboration: LADIR, Thiais, F. Fillaux; LLB: A Cousson, M. Quilichini, P. Teles, PhD]

[B. Nicolai, A. Cousson and F. Fillaux Chem. Phys. **290** (2003) 101-120].



Pre-transitional neutron diffuse scattering observed in fully deuterated lithium acetate, at the expected transition location in reciprocal space, for temperatures just above T<sub>C</sub> = 17K, along the **b** direction.



Anisotropic thermal variation of the Half Width at Half Maximum (HWHM- $\kappa$ ), measured along the two high-symmetry directions (**b**, **c**)

### Crystal structures and proton dynamics in potassium and cesium hydrogen bistrifluoroacetate salts with strong symmetric hydrogen bonds

The crystal structures of potassium and cesium bistrifluoroacetates,  $MH(CF_3COO)_2$  with  $M=K$  or  $Cs$ , were determined at room temperature and at 20K and 14K, respectively, with the single crystal neutron diffraction technique, utilising the four circle diffractometer 5C2 at LLB. There is no visible phase transition. For both crystals, the trifluoroacetate entities form dimers linked by very short hydrogen bonds lying across a centre of inversion (Figure 1). Any proton disorder or double minimum potential can be rejected. The inelastic neutron scattering spectral profiles in the OH stretching region between 500 and 1000  $cm^{-1}$  previously published [F. Fillaux *et al*, Chem. Phys. 158(1991)113] were reanalyzed. The best fitting potential has the major characteristics already reported for potassium hydrogen maleate [F. Fillaux *et al*, Chem. Phys. 244(1999)387], composed of a narrow well containing the ground state and a shallow upper part corresponding to dissociation of the hydrogen bond upon excitation of the OH stretching mode. [Collaboration: F. Fillaux, LADIR, Thiais; A Cousson, LLB; J.F.R. Archilla, Sevilla, Spain; J. Tomkinson, RAL, UK]

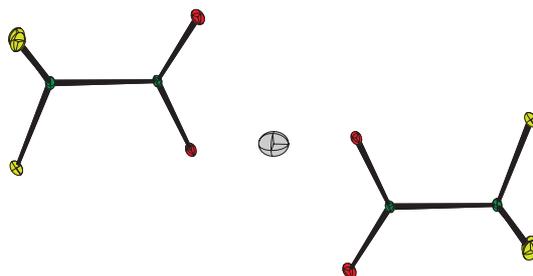


Figure 1. Schematic representation of the centrosymmetric dimers in the  $KH(CF_3COO)_2$  crystal at 14K

### MAGNETIC STRUCTURES IN INTERMETALLIC COMPOUNDS

#### $LaFe_{11.4}Si_{1.6}$

Crystallographic and magnetic structures of giant magnetocaloric intermetallic compound  $LaFe_{11.4}Si_{1.6}$  have been studied by means of neutron powder diffraction. Rietveld analysis indicates that Si atoms substitute for Fe atoms randomly on the two different Fe sites of the cubic  $NaZn_{13}$ -type structure. All spins in the unit cell are aligned ferromagnetically with the  $Fe^I$  (8b) moment smaller than the  $Fe^{II}$  (96i) one. The long-range FM (FM = FerroMagnetic) ordering induces a drastic expansion of the lattice and the coexistence of large and small volume phases near the Curie temperature  $T_C$ . Even in the FM state, the lattice expansion still correlates strongly with the spontaneous magnetic moment, marked by a large positive magneto-volume coupling constant [ $1.14 \cdot 10^{-8} cm^6 emu^{-2}$ ]. From the temperature dependence of Fe-Fe bond lengths, it was suggested that the magnetic exchange interaction between the clusters (each formed by a central  $Fe^I$  atom and 12 surrounding  $Fe^{II}$  atoms) plays an important role in the magnetic properties of  $La(Fe_{1-x}Al/Si_x)_{13}$ .

F. Wang, G-J. Wang, F-X. Hu, A. Kurbakov, B-G. Shen, Z-H. Cheng - Strong interplay between structure and magnetism in the giant magnetocaloric intermetallic compound  $LaFe_{11.4}Si_{1.6}$ : a neutron diffraction study - *J.Phys.: Condens.Matter* 15 (2003) 5269-5278 .

#### $U(Pd_{1-x}M_x)_2Ge_2$

The crystal and magnetic structures of  $U(Pd_{1-x}M_x)_2Ge_2$  compounds with  $M = Fe, Co, Ru$  has been studied by neutron powder diffraction [G4.2 and G6.1 LLB-diffractometers] and  $\mu SR$ . The effects of M doping and external applied pressure on the crystal and magnetic structures were compared. It was found that even at small M-doping level the magnetic structure drastically changes, while the values of the lattice parameters and interatomic distances change only slightly. In contrast, high external pressure modifies the crystal structure more significantly, while the magnetic structure remains the same. The drastic changes of magnetic structure of  $U(Pd_{1-x}M_x)_2Ge_2$  compounds with increased M doping could then result from modifications of the RKKY indirect exchange interactions due to variation of conduction-electron number per U atom, rather than from lattice contraction.

V.V. Sikolenko, E.V. Pomjakushina, V.Yu. Pomjakushin, A.V. Gribanov, U. Zimmermann, A.I. Kurbakov, D.P. Kozlenko, I.N. Goncharenko, A.M. Balagurov - Modulated spin-density waves in uranium intermetallic compounds with  $ThCr_2Si_2$  structure - *Physica B: Condensed Matter* 350 (2004) 163-166.

## HoFe<sub>4</sub>Ge<sub>2</sub>

The re-entrant magneto-elastic transition of the AFM (AFM = AntiFerroMagnetic) HoFe<sub>4</sub>Ge<sub>2</sub> compound has been studied by neutron powder diffraction at D1B, D2B, G4.1 and G4.2 2-axis diffractometers as a function of temperature. The magnetic phase diagram is complex, including three wave vectors ( $\mathbf{q}_{10}$ ;  $\mathbf{q}_{20}$ ;  $\mathbf{q}_{1t}$ ) and three magnetic transitions, two of them occurring simultaneously with a structural change at  $T_C = T_N = 52\text{K}$  and  $T_C = T_{ic1} = 15\text{K}$  respectively, the third being purely magnetic at  $T_{ic2} = 40\text{K}$ . From high [HT] to low [LT], via intermediate [IT] temperatures, the sequence of phases is:  $P4_2/mnm$  (HT)  $\setminus T_C = T_N = 52\text{K} \setminus Cmmm$  (IT) ;  $\mathbf{q}_{10} = (0, \frac{1}{2}, 0) \setminus T_{ic2} = 40\text{K} \Rightarrow \mathbf{q}_{20} = (0, q_y, 0) \setminus T_C = T_{ic1} = 15\text{K} \setminus P4_2/mnm$  (LT);  $\mathbf{q}_{1t} = (0, \frac{1}{2}, 0)$ . The first transition is of second order while the latter two of first order. The magnetic structures described by the wave vectors ( $\mathbf{q}_{10}$ ;  $\mathbf{q}_{20}$  and  $\mathbf{q}_{1t}$ ), where the components are referred to the reciprocal basis of the conventional Cmmm cell, correspond to canted multi-axial arrangements. Solving the magnetic structures of all the phases appearing in this complex situation, arising from competing ordering mechanisms and anisotropies of the underlying sublattices, has been only possible via high-resolution neutron powder diffraction data and simulated annealing data treatment.

P. Schobinger-Papamantellos, J. Rodríguez-Carvajal, G. André, C. Ritter and K. H. J. Buschow - Re-entrant magneto-elastic transition in HoFe<sub>4</sub>Ge<sub>2</sub> a neutron diffraction study - *JMMM* 280 (2004) 119-142

## 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 “other” oxides are also very interesting, showing for instance frustration effects (pyrochlore-type oxides with antiferromagnetic interactions...). Among them, the geometrically frustrated pyrochlore system, **Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>**, offers the very intriguing case of a spin liquid state for large classical spins, persisting down to very low temperatures ( $\leq 70\text{mK}$ ), well below the energy scale of antiferromagnetic interactions given by the Curie-Weiss constant (-19K). In the liquid state, Tb<sup>3+</sup> magnetic moments fluctuate down to  $T \approx 0\text{K}$ , being strongly correlated in a large T range [0-100K], yielding a liquid-type peak in the neutron diffraction patterns, the position of which corresponds to first neighbours distances. In bulk samples (powders), we previously observed the “crystallization” of the spin liquid under high pressure, namely the onset of long range antiferromagnetic order below  $T_N = 2.1\text{K}$  (Nature 2002). We have now performed neutron diffraction experiments on oriented **Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>** single crystals (PRL 2004, in press), combining extreme conditions: high pressures (2.8GPa), anisotropic stress (0.3GPa), low temperature (0.1K) and magnetic field (7T). These new measurements allow to clarify the role of pressure. The isotropic pressure component enhances the exchange interactions between the fluctuating spins in the spin liquid state above  $T_N$ . Applying additional uniaxial stress induces magnetic order, and one can tune both  $T_N$  and the ordered terbium magnetic moment by varying the orientation of the stress relative to the crystal structure. The stress is then more efficient along the [110] direction, suggesting that it relieves the frustration by creating uncompensated bonds of near neighbour Tb<sup>3+</sup> spins. Under magnetic field, the pressure induced AF structure transforms into a non collinear ferromagnetic structure at 0.6T and the non-collinearity persists up to 7T. We performed a quantitative structure analysis, showing that a small field reorients tetrahedra of strongly coupled Tb<sup>3+</sup> spins, whereas much higher fields are needed to align spins in a tetrahedron. These measurements provide a key to understand and control the mechanisms which govern the stability of anomalous magnetic phases in highly frustrated magnets.

[Collaboration: I. Mirebeau, I. Goncharenko, A. Gukasov, A. Cousson, LLB; G. Dhalle, A. Revcolevschi, Orsay University]

**Hydroxysulfates** of 3d-elements have been carefully studied by mineralogists, where the principal interests were the identification of the crystal phases and the mechanism(s) of their formation with respect to their geographical location. Only the crystal structures of the most abundant forms have been characterized, and there are more phases that are not characterized due to the lack of single crystals in the natural sources of sufficient purity and quality. With the advances in hydrothermal synthesis, some of these missing links could be realized in the laboratory and on a shorter time scale. Furthermore, compounds prepared by hydrothermal method in the laboratory allow one to study the properties of pure samples, whereas samples from the mineral source are usually quite complex due to the presence of mixtures or traces of several cations and anions. In the case of transition metal hydroxysulfates, studies of their magnetic properties are sparse due to the low purity of samples from the mineral source. In the case of copper hydroxysulfates, hydrothermal synthesis gave two compounds that are isostructural with the corresponding minerals, **antlerite**

**Cu<sub>3</sub>(OH)<sub>4</sub>SO<sub>4</sub>** and **brochantite Cu<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>**. No other phase was obtained under all the experimental conditions attempted. For **M = Mn, Co** and **Ni**, numerous new compounds have been obtained and the isostructural **M<sub>3</sub>(OD)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(D<sub>2</sub>O)<sub>2</sub>** family has been investigated by neutron powder diffraction. The magnetic structures of all these ionic compounds have been obtained (see **Highlight**). As magnetic structure determination in insulating compounds was recently renewed by ab-initio methods able to predict the fundamental states from the super-exchange (M-O-M') and/or super-super-exchange M-O-O-M' interactions, the next step in the present work will be to analyse the topology of magnetic exchange interactions and minimize the classical magnetic energy in each of the studied geometries [SIMBO and ENERMAG computing programs].

### **MANGANITES: CHARGE (CO), ORBITAL (OO) AND SPIN ORDERING**

The perovskite manganites Ln<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub> (Ln = La, Y or Rare Earth, A = alkaline earth) became subjects of considerable research effort because of their prospects as materials of colossal magnetoresistance (CMR) or metallic conductors with spin polarized carriers. These materials are interesting also from a fundamental viewpoint: in the manganites the charge, spin, and lattice degrees of freedom are strongly coupled together, leading to a delicate balance of interactions that gives rise to a rich variety of physical phenomena in condensed matter science. Recently, much interest was attracted to unusual phase separation processes: in mixed valent manganese-oxides, within specific electronic doping ranges, the ground state, is intrinsically inhomogeneous, usually composed of ferromagnetic metallic (FM-M) and charge ordered, orbital ordered (CO/OO) antiferromagnetic insulating (AFM-I) domains that co-exist and compete at a nano- and/or sub-micrometer scale.

For several years already, a strong collaboration does exist between CRISMAT [ENSICAEN] and LLB, with both macroscopic [magnetic and transport properties] and microscopic techniques [X-ray, neutron powder diffraction (NPD) and transmission electronic microscopy (TEM)] systematically used on the same samples. C. Autret's PhD [2002, Université de Caen] focused on the "half-doped" manganites, characterized by a Mn<sup>3+</sup>:Mn<sup>4+</sup> = 1:1 ratio, with **Pr<sub>0.5</sub>Sr<sub>0.5-x</sub>Ba<sub>x</sub>MnO<sub>3</sub>** and **Pr<sub>0.5</sub>Sr<sub>0.5-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>** systems carefully investigated (crystal and magnetic phase diagrams) and on **Pr<sub>2-x</sub>Ca<sub>x</sub>MnO<sub>4</sub>** compounds (1.5 ≤ x ≤ 1.75), n = 1 member of the Ruddlesden-Popper family (K<sub>2</sub>NiF<sub>4</sub>-type structure), in order to study the effect of "dimensionality" on the physical properties (magnetism, charge order, CMR). A new common PhD work started in early 2004 [M. Giot], devoted to Bi<sub>1-x</sub>A<sub>x</sub>MnO<sub>3</sub> manganites (A = Ca, Sr) and charge ordering (CO) properties within.

No CO is present in the **Y<sub>2</sub>Ba<sub>2</sub>Mn<sub>4</sub>O<sub>11</sub>** manganite, a "CO/OO" system (only Mn<sup>3+</sup> ions) for which crystal and magnetic structures have been investigated (see **Highlight**).  
[Collaboration: LLB, LPCES, Orsay]

From neutron powder diffraction investigations and electrical resistivity measurements on **<sup>152</sup>Sm<sub>0.55</sub>Sr<sub>0.45</sub>MnO<sub>3</sub>** (SSM) and **(Nd<sub>0.545</sub>Tb<sub>0.455</sub>)<sub>0.55</sub>Sr<sub>0.45</sub>MnO<sub>3</sub>** (NTSM) manganites, replacement of the "rare-earth" cation while leaving <r<sub>A</sub>> unchanged (Nd and Tb contents in the latter composition are such that the average radius of the A cation <r<sub>A</sub>> in the two compounds is the same) was shown to have practically no effect; indeed, both compounds are metals at low temperatures, have the same crystal structure from liquid-helium to room temperature, and exhibit the same pattern of structural distortions at the onset of magnetic ordering. Magnetic moments of Mn ions in both compositions are ferromagnetically ordered at low temperatures, with T<sub>C</sub> = 122 and 90 K for the SSM and NTSM, respectively. Below 80 K, the rare-earth cation moments in NTSM undergo additional ordering.

In contrast to compositions that are close in Sr concentration (x<sub>Sr</sub> = 0.4, 0.5), which feature a phase-separated state with a mixture of the the FM-M [ferromagnetic metallic] and AFM-I [antiferromagnetic insulating] phases in **<sup>152</sup>Sm<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>** manganites, the ground state of both studied compositions with x<sub>Sr</sub> = 0.45 is uniformly ferromagnetic and metallic. However, Oxygen isotope substitution, <sup>16</sup>O → <sup>18</sup>O, was shown to bring about a substantial change in the **<sup>152</sup>Sm<sub>1-x</sub>Sr<sub>x</sub>Mn<sup>16</sup>O<sub>3</sub>** phase diagram in the intermediate region 0.4 < x < 0.6, inducing for instance a phase-separated state in the case of **<sup>152</sup>Sm<sub>0.55</sub>Sr<sub>0.45</sub>Mn<sup>18</sup>O<sub>3</sub>**.

[Collaboration: LLB, A. Kurbakov; Petersburg Nuclear Physics Institute, Moscow State University, Russia]. Interplay between crystal structure(s) and physical properties in transition metal oxide compounds with strong electronic correlations is also evident in **Ca<sub>2-x</sub>Sr<sub>x</sub>RuO<sub>4</sub>**, **La<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3+δ</sub>** and **La<sub>1-x</sub>Sr<sub>1+x</sub>MnO<sub>4</sub>** systems, as studied by M. BRADEN's team at Cologne University.

The phase diagram of the  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  exhibits an astonishing variety of physical phenomena in view of the fact that one changes only the radius of the earth-alkali ion. Through the smaller radius of Ca compared to Sr, structural distortions are induced, which consecutively reduce the electronic band widths. In this sense the electronic correlations get enhanced with increasing Ca content. The structural-electronic coupling in these layered ruthenates may be resumed as following:

1. a first rotational transition is related with a change of the Fermi-surface topology,
2. an additional tilting of the  $\text{RuO}_6$ -octahedra reduces the tendency towards ferromagnetism at intermediate Ca content. Metamagnetism in such compounds is related with a change in orbital occupation as evidenced by changes in the RuO-bond lengths,
3. different tilt and rotation stacking schemes yield different magnetic ground states due to orbital ordering effects,
4. the metal insulator transition finally is associated with a pronounced flattening of the octahedron.

A direct relation between minor structural distortions and the magnetic as well as the electronic properties could also be established for  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ ; in particular it has been shown that pure  $\text{LaTiO}_3$  exhibits orbital ordering and is not a realisation of an orbital liquid model.

Layered manganates,  $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$  were found to exhibit a strong structural variation both with temperature and with doping, which arise from a change in the orbital occupation. When going from the undoped antiferromagnet,  $\text{LaSrMnO}_4$ , to the CE-type ordered material at half doping,  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , the  $e_g$  orbitals appear to flip from the c-axis into the a,b-planes. Similar effects are studied in layered cobaltates.

## PHASE TRANSITIONS WITH ELECTRON LOCALIZATION OR TRANSFER

In organic systems made of stacks of potentially donors and acceptors of electrons, the properties of the electrons, nearly always coupled with the lattice, are at the origin of very rich phase diagrams. Two cases of such transitions are presented in this report.

### Spin-Peierls ground state in $(\text{TMTTF})_2\text{PF}_6$ (Highlight)

A first study of the Spin-Peierls (SP) transition in the  $(\text{TMTTF})_2\text{PF}_6$  organic conductor by elastic neutron scattering has been achieved at LLB. Indeed, at 18K, a Spin-Peierls [SP] transition occurs: two electrons (one per dimer of TMTTF molecules) form a localized pair, leading to a  $S = 0$  state through a tetramerization of the organic stacks. Because of such electron-lattice coupling, this non-magnetic state is detected by a superstructure Bragg peak ( $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ). When compared with other similar organic systems where a SP transition occurs, the intensity of this satellite reflection appears very small, several explanations are proposed to account for the weakness of the 3D-SP amplitude of distortion in the  $(\text{TMTTF})_2\text{PF}_6$  system.

[Collaboration: LPS Orsay; LLB]

### Neutral-to-Ionic phase transition under pressure (Highlight)

The prototype compound TTF-CA exhibits a phase transition from a high temperature Neutral paraelectric phase (N) to a low temperature Ionic and ferroelectric phase (I) where an electron is transferred from a donor to an acceptor molecule. This charge transfer occurs together with a dimerization, so it can be detected by neutron scattering through a structural distortion inducing a change in the symmetry between the (N) and (I) phases. A Bragg peak, forbidden in the (N) phase, is lighted in the (I) phase. The "Pressure, Temperature" phase diagram has been compared to a Gas-Liquid-Solid phase diagram. Recently, a study under pressure on a similar compound, (BEDT-TTF)-(ClMeTCNQ), reveals that the (N)-(I) transition which does not exist at ambient pressure, is induced near  $T = 0$  K, by a moderate pressure: 2Kbar. When compared to TTF-CA, the phase diagram of this new compound shows both similar and different properties, the most interesting feature is that this compound shows an example of transition near 0K, so it appears as a quantum limit case.

[Collaboration: GPMS, Université de Rennes ; LLB ; ILL]

## COMPOSITE SYSTEMS

Phonon studies have always represented an important activity in the laboratory. They often display interesting dynamic signature(s) of the structural transitions. The phonons are also measured in more complex compounds. In the composites, they are the proof that this system has characteristic acoustic modes, and in the superconductors, they underline a strong electron-phonon coupling.

The properties of the incommensurate composites are fascinating. These systems are built from at least two interpenetrating subsystems with incommensurate periodicities in at least one crystallographic direction. The resulting Bragg peaks are then indexed in a super-space: some of them are characteristic of each subsystem, the others, the satellites, are characteristic of the inter-modulation. The lattice dynamics appears also very rich. Two such composites have been investigated at LLB: Alkane-Urea and  $\text{MnSi}_x$ .

### Alkane-Urea (Highlight)

In that case, the host network (hexagonal symmetry) is made of honeycomb-like channels of helical ribbons of urea molecules in which linear guests, alkane molecules, are packed in a 1D arrangement. Under normal pressure, an hexagonal to orthorhombic transition occurs at  $T=150\text{K}$  in the basal plane: a neutron diffraction signature is the (2 2 0) Bragg peak splitting and Brillouin scattering shows a splitting of the longitudinal phonons modes. At 5Kbar, the “same” transition occurs at 225 K, but even if the symmetry at low temperature is orthorhombic, the metric remains hexagonal: no splitting of the Bragg peak, nor of the sound velocity are observed. Alkane-Urea is the first example where ordering in self-organized materials occurs without any significant deformation of the host matrix.

[Collaboration: GPCM, Université de Rennes ;LLB ; Universidad del Pais Basco, Bilbao, Spain]

### $\text{MnSi}_x$

The  $\text{MnSi}_x$  system has the advantage to present much less disorder than alkane-urea. So, neutron inelastic scattering has successfully allowed the determination of the different long-wavelength collective phonons originating from every kind of Bragg peaks: two low frequency optical phonon branches characteristic of both Mn and Si subsystems, and **one acoustic branch characteristic of the composite** (the same one visible by Brillouin scattering but on a much larger q-range). We must underline that it is the first time that an acoustic mode of a composite is measured by neutron scattering. The main argument at the origin of the attribution of the different branches is based on the q-dependence of the intensity of the modes. As q or the energy increases, the scattered neutron intensity is progressively transferred from the acoustic mode to the optic ones.

[Collaboration: L. Bourgeois (LLB), P. Bourges (LLB), R. Currat (ILL), J. Etrillard (Université de Rennes), S.B. Vakhrushev (St. Petersburg), S.V. Ordin (St. Petersburg)].

## SUPERCONDUCTING MATERIALS

### Phonon Anomalies in High $T_C$ Superconductors related to Charge Stripe Order

The Karlsruhe group has continued its long-standing effort to explore the phonon properties of perovskite materials, i.e. primarily cuprates, but also manganites and nickelates. It has been established that the lattice dynamics of the undoped parent compounds is governed by strong Coulomb forces typical of ionic insulators. On doping, however, a particular kind of phonon modes, i.e. the metal-oxygen bond-stretching vibrations, shows strong deviations from the classical behaviour. It has been long conjectured that this anomalous behaviour is related to the various charge ordering phenomena occurring. Recent results on  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$  (see **Highlight**) have provided strong support for this view. When doped with Sr or Ba, the  $\text{La}_2\text{CuO}_4$  system becomes superconductor. But if the hole doping rate is close to 1/8, the holes tend to segregate into stripes that separate antiphase AF domains and the superconductivity is suppressed. Static stripe order has been found in  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$  and  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$ . The new idea was that a tendency to hole segregation into stripes may also exist in the superconductor phase, but instead of being static, these stripes should be dynamic. This was demonstrated in  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$  where the damping of a peculiar bond-stretching phonon has been found to be maximum at the precise q-position of the static stripe. This is the signature of strong electron-phonon coupling. The thermal evolution of the same phonon mode (half bond-stretching) in YBCO seems to confirm a tendency to dynamic stripe order also in this compound.

[Collaboration: Forschungszentrum, Karlsruhe; LLB; Nagoya University, Japan; Tohoku University, JJapan]

### Ab Initio Study of Carbon substitution in the superconductor $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$

The effects of C substitutions in  $\text{MgB}_2$  are studied within the two-band model in the Eliashberg formulation. The B-B stretching mode frequency and the partial densities of states  $N_N^\sigma(E_F)$  and  $N_N^\pi(E_F)$ , calculated at various x values from first-principles density functional methods, are used as input of this model. In particular, the predicted hardening of the stretching mode with increasing x, agrees pretty well with the Raman data. The prefactor in the Coulomb pseudopotential matrix,  $\mu$ , and the interband scattering

parameter,  $\Gamma^{\text{opt}}$ , are taken as the only adjustable parameters. The C content dependence of  $T_C$  and of the gaps  $\Delta_\sigma$  and  $\Delta_\pi$  experimentally measured in single crystals, indicates an almost linear decrease of  $\mu$  on increasing  $x$ , with an increase in interband scattering that makes the gaps merge at  $x=0.132$ . However, further ab-initio studies are required to improve the agreement with experimental data.  
[Hamid Moudden, LLB]

### PHASE TRANSITIONS: LATTICE DYNAMICS UNDER PRESSURE

Among the twelve crystalline phases known presently, **ordinary ice Ih** shows two distinct anomalies which have been extensively studied in the past. Ice Ih has a negative thermal expansion coefficient below 70 K, and under pressure applied at low temperatures (<130 K), ice Ih transforms to high density amorphous ice (HDA). The microscopic origin for these two phenomena has remained unclear, though it was suspected that the key for its understanding lies in a detailed study of the lattice dynamics of ice.

In a recent study (it is the first detailed investigation of the pressure dependence of the phonons in ice), we have investigated the phonon dispersion of ice Ih under purely hydrostatic pressure by coherent inelastic neutron scattering. The experiments were carried out at the 1T1 triple axis spectrometer using the LLB gas cell up to 0.5GPa and fluid nitrogen as pressure transmitting medium.

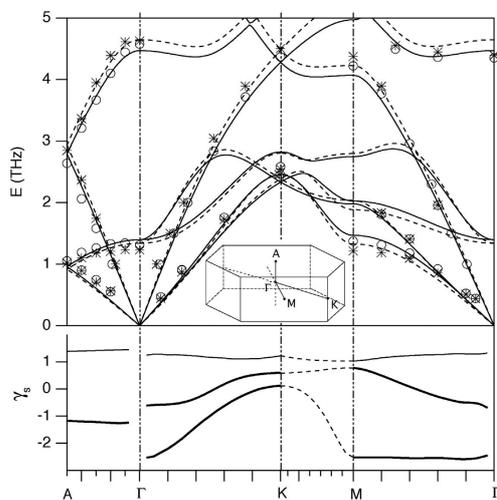


Figure 2a. Upper: Phonon dispersion of low-energy branches of ice Ih ( $T=140$  K) at 0.05GPa (circles) and 0.5GPa (stars). The lines through the data are fits to a Born-von- Kármán model. Lower: mode Grüneisen parameters  $\gamma_s(q)=-\partial \ln E_s(q)/\partial \ln V$  of transverse and longitudinal acoustic branches (thick and thin lines, respectively).

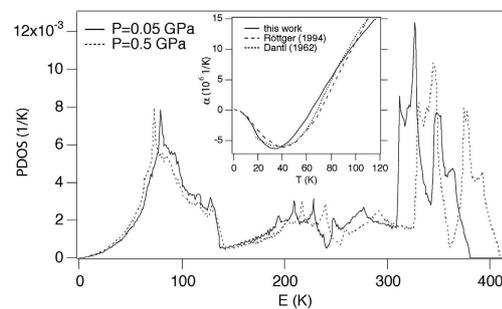


Figure 2b: Phonon density of states (PDOS) of ice ( $T=140$  K) at 0.05GPa and 0.5GPa (main figure) and reconstructed thermal expansion coefficient compared to literature data (inset).

The measurements revealed a pronounced softening of various low-energy phonon branches, in particular the TA modes along [100] ( $\Gamma$ -M) with polarisation in the hexagonal plane (Figure 2a). The data were fitted to a Born-von-Kármán model, which allowed calculating the phonon density of states as well as the thermal expansion coefficient from the measured mode Grüneisen parameters (Figure 2b). The extrapolation of the model parameters to higher pressures indicates a violation of Born's stability criteria at a pressure of  $\sim 2$ GPa which appears to be associated with the observed pressure-induced amorphisation (PIA). PIA seems therefore to be a consequence of a "mechanical melting" of ice under compression.

These investigations revealed hence that the negative thermal expansion coefficient and the PIA of ice Ih have their common origin in an instability of the lattice. Since PIA occurs in various other compounds (some of them of geophysical importance, such as  $\text{SiO}_2$ ), our measurements contribute to a better understanding of this phenomenon in general.

[Collaboration : LLB ; Université P&M Curie, Paris; Université de Cologne, RFA]  
[Th. Strässle, M. Saitta, S. Klotz & M. Braden, Phys. Rev. Lett. 93, 225901 (2004)]

### PHASE TRANSITIONS: NEUTRON DIFFRACTION UNDER VERY HIGH PRESSURE

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, either with powder or single-crystal samples. At the present moment, the LLB disposes of higher pressures (up to 50GPa) than any other neutron source in the world. New “hybride” pressure cells allow us to carry out combined X-ray and neutron studies under pressure on the same sample.

The capabilities of the LLB pressure and neutron techniques have been demonstrated in the recent study of magnetic order in high-pressure **oxygen (Highlight)**.