



STRUCTURE AND PHASE TRANSITIONS

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Introduction

The field of structure and phase transitions grows and evolves. The possibility to synthesize new materials, or to study model systems in a peculiar state, like in confined media or under extreme conditions of pressure, temperature or magnetic field, opens a wide variety of interesting phenomena. It also stimulates new concepts and theoretical approaches.

Neutron is a privileged probe to investigate condensed matter at a microscopic level, thanks to its unique characteristics. Among others, one can mention the simultaneous study of magnetic and crystalline orders, the possibility to play with isotopic contrast (H-D substitution for instance), to vary easily the physical parameters, the non destructive study of “precious compounds”. As a general trend, neutrons are combined with other probes, not only for standard characterization, but in fully common analysis, allowing one to better understand the complex states of matter, their stability and the connection with their physical properties. Synchrotron X ray diffraction is the most prominent example, and common fields of research are expected to grow with the collaboration LLB-Soleil. Local probes are also involved (like EPR, α SR), as well as a large variety of macroscopic probes. We briefly review in the next sections the trends in phase transitions and structure studies which appeared in LLB for the last two years, and introduce some highlights and clips which illustrate them. At the end, we present some emergent fields, which might grow in the next years.

Recent trends in phase transitions

Many studies are devoted to states of matters in which phase transitions have to be described with new concepts, well beyond the classical approaches like Landau's mean field theory. We will successively present four points:

- Materials confined in a restricted geometry, where confinement could either suppress or strongly modify the transitions observed in the bulk material.
- By changing interatomic distances, pressure allows one to tune the energy balance and the physical properties. It induces new phases, changes transition temperatures, or induces $T=0$ transitions. Applied pressure is often compared with chemical substitution, considered as “chemical pressure”. Experiments under pressure are a strong point in LLB, as shown by several examples.
- Geometrical frustration provides nice examples of materials with ground state entropy, like spin liquids or spin ices, without transition down to $T=0$. In such materials, perturbations may induce new transitions, yielding a large variety of magnetic states often sensitive to applied pressure or magnetic field.
- An original study of an electrochemical oxidation allows one to tune oxygen composition and finely investigate the phase diagram.

PHASE TRANSITIONS IN CONFINED MEDIA

The synthesis of materials in mesoporous matrices, like the MCM-matrix with regular system of monodisperse nano-channels and their potential application stimulated works by several groups. A full understanding of the systems requires the knowledge of their atomic and mesoscopic structures together with their dynamics. Therefore studies were done by combining neutron diffraction, small angle neutron scattering, X ray synchrotron diffraction and inelastic neutron scattering.

In a **smectic crystal** confined in one dimensional nanopores of porous silicon films, the smectic transition is completely suppressed, and short range order settles in, while the molecular dynamics slows down. This spectacular effect is attributed to random fields coupling with the smectic order parameter. This is developed in the thesis work of R. Guégan. [*H1*, R. Guégan].

In magnetic and dielectric materials, confinement can lead to a suppression of the phase transitions, a change in the critical exponents, or even to a new reentrant transition. These effects were studied in detail in model antiferromagnets or ferrimagnets such **MnO**, CoO, Fe_2O_3 , Fe_3O_4 , confined in different media (porous glass, nanochannels, twinned channels). These studies were performed through an INTAS project coordinated by the LLB (2003-2006) in which seven West and East European laboratories were involved, which led to more than ten publications [*H2*, I. Golosovsky].

The influence of confinement on the crystallization and vitreous transitions was studied in **liquid Toluene** confined in nanoporous matrix. The studies allowed an Orsay team¹ to follow the structure and dynamics of the confined fluid, as well as its density, which can be controlled by applied pressure. It will be developed in the thesis work of F. Audonnet.

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PRESSURE INDUCED TRANSITIONS

A very nice example of a pressure induced transition in a confined medium is provided by the **Urea-alkane** crystals under pressure. Urea inclusion compounds form solid 1D channels via host urea hydrogen bonds, which can accommodate guest alkane molecules. Pressure induces in the guest system a transition from incommensurate to commensurate structure, opening the possibility of tuning 1D structure of confined materials and therefore to manipulate their tribological properties at a molecular level [C1, B. Toudic].

The manganites LaCaMnO_3 with colossal magnetoresistance show a strong coupling between electric and magnetic properties. In these compounds the insulating metal transition temperature T_{IM} is sensitive to pressure. The study of the magnetic order in $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ under pressure performed at LLB by an Italian team of Rome, showed that the Curie temperature T_{C} and the insulating-metal temperature T_{IM} scale with pressure, yielding a unique transition line from a paramagnetic insulator to a ferromagnetic metal up to 8 GPa [C2, M. Baldini].

The geometrically frustrated $\text{R}_2\text{Mo}_2\text{O}_7$ pyrochlores undergo a threshold transition from an insulating spin glass to a ferromagnetic metal depending on the rare earth ionic radius. The study of the new system $(\text{Tb}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$ where the lattice constant is suitably adjusted, allows one to cross the threshold in both ways, by tuning interatomic distances. So, starting from the spin glass $\text{Tb}_2\text{Mo}_2\text{O}_7$, with only short range magnetic order, the dilution by non magnetic La ion expands the lattice and induces long range magnetic order, which can be destroyed by pressure. By combining neutron techniques, muons and X ray synchrotron at ambient pressure and under pressure, one can follow the evolution of magnetic order and spin fluctuations in the crossover region. It is a part of the thesis work of A. Apetrei [H3, A. Apetrei].

GEOMETRICAL MAGNETIC FRUSTRATION

In some frustrated ferromagnets situated just above a magnetic threshold, the huge sensitivity of itinerant d electrons to pressure combined with the geometrical frustration allows one to tune the magnetic state with pressure and induces order-disorder transitions. Long term studies of GdMn_2 with a threshold from localized to itinerant magnetism², and $\text{Gd}_2\text{Mo}_2\text{O}_7$ with a threshold from ferromagnetic metal to insulating spin glass³, were performed in LLB. They involved extended collaborations with ESRE, ILL and PSI muon source. They revealed non trivial pressure effect in itinerant magnets, which could either suppress the frustration (GdMn_2) or induce it ($\text{Gd}_2\text{Mo}_2\text{O}_7$).

Geometrically frustrated systems can stabilize exotic magnetic states such as spin liquids, spin ices or chemically ordered spin glasses. In $\text{Tb}_2\text{Sn}_2\text{O}_7$, where Tb ions occupy a pyrochlore lattice of corner sharing tetrahedra, a two steps transition towards a new type of order was observed. This magnetic structure was called “**ordered spin ice**” since it possesses a local spin ice order inside a tetrahedron and a long range ferromagnetic order. (C3, I. Mirebeau).

Other unusual phase transitions are observed in frustrated **Laves hydrides** due to the coupling of the magnetic and the hydrogen lattices. Hexagonal hydrides RMn_2H_x (R=rare earth), including new compounds obtained at high pressures, show intricate magneto-structural transitions. In some cases, a transition to a chemically *less* ordered state yields a *more* ordered magnetic sublattice, showing a rare example of an “order by disorder” transition. In such systems, hydrogen insertion can be used as a gentle way to tune the magnetic properties⁴.

Geometrical frustration is also involved in $\text{Sr}_3\text{HoCrO}_6$ where the spin chains are triangularly arranged. The ground state shows partial disorder as expected for 1D frustrated compounds, and an applied field induces puzzling steps in the magnetization [C4, V. Hardy]. Such steps recall the magnetization plateaus observed in other systems with ground state degeneracy, like spin ices, quantum dimer systems, or molecular magnets with quantum tunnelling.

IN SITU SUCCESSION OF PHASE TRANSITIONS IN AN ELECTROCHEMICAL MEDIUM

Electrochemical oxidation of antiferromagnetic $\text{SrCO}_{2.5}$ was studied in situ, combining neutron diffraction and X-ray absorption spectroscopy at the Co absorption edge. It allowed to characterize two intermediate phases and to follow the evolution of the Co valence state during the reaction [C5, R. Le Toquin]. This thesis work received the prize of the Société Française de Neutronique (SFN 2005 prize).

Recent trends in structures

Many efforts are currently devoted to the synthesis of new materials, requiring high accuracy in the structure determination in order to improve their physical properties. On the other hand emerging studies of biomaterials (like kidney stones) or archeomaterials (like Etruscan weapons) find in neutron scattering a unique technique to answer some specific questions. More and more, the analysis yielded the development of sophisticated structural models to account for the experimental data. Finally, several studies were performed under extreme pressure conditions, confirming the LLB leader role in this field. One can mention the determination of the phase diagrams of H_2 and O_2 , the study of FeO and MnO antiferromagnets, and of compounds of geological interest.

NEW MATERIALS

Laves hydrides have been synthesized by two groups under high pressure conditions, leading to new compounds stable at ambient pressure. Magnetic and hydrogen orders were studied by neutron diffraction. RMn_2D_6 ($R=Y, Ho, Dy, Er$) compounds show only short range or partial magnetic orders, attributed to the chemical Mn or R disorder. [C6, V. Paul-Boncour]. The $TbMn_2D_{2.9}$ compound at the verge of a transition from itinerant to localized magnetism, was studied in both hexagonal and cubic crystal structures, leading to different types of magnetic order. This study showed that the Mn-Mn distance is not the only parameter which governs the itinerant-localized transition, but that the lattice topology plays an important role [C7, O. Makarova].

The study of ternary compounds with alkali, tetrahydrofuran and carbon **nanotubes** revealed the very interesting possibility of *tuning the intertube spacing* through the alkali cations, which form a single layer surrounding the nanotubes. This study is a part of the thesis work of J. Cambedouzou [C8, J. Cambedouzou].

The magnetic structure of the **manganese sulfides** or chlorosulfides compounds with 1D or 2D crystalline structuration was solved, showing 3 dimensional magnetic order but with an incommensurate modulation coexisting in some cases with 1D magnetic correlations. This study belongs to the thesis work of C. Doussier-Brochard [C9, C. Doussier-Brochard].

In a series of new hydrothermally synthesized M^{II} -hydroxysulfates, the possibility to choose the 3d element from Mn to Cu allows one to change progressively the magnetic interactions and the geometrical frustration caused by α -3-OH bridges, resulting in various canted antiferromagnetic structures [C10, S. Vilminot].

In the **manganite** field, M. Giot (LLB-CRISMAT thesis), studied in detail the complex charged ordered $Bi_xCa_{1-x}MnO_3$ ($0.5 < x < 0.64$) series, confirming nicely the Zener polaron ordering model. She determined a classical CE-type magnetic structure for $x = 0.5$, evolving towards a ferromagnetic coupling for higher x [C11, M. Giot].

In **life science** a collaboration with D. Bazin (LPS, Orsay) and M. Daudon (Necker Hospital, Paris) has started focusing on the specific structural information available from powder neutron diffraction on biological materials like kidney stones. Such biomaterials can differ from each other in composition, structure and microstructure, revealing a large variety of specific diseases. Thanks to the high penetration depth of the neutron beam, it is possible to study, in a non-destructive way, the whole sample (of a few mm typical size) obtaining a quantitative phase analysis of the kidney stone together with the average crystallites size. This information is complementary with the results obtained by other techniques (synchrotron radiation, α -X-ray fluorescence, X-ray absorption spectroscopy). These data are compared with the macroscopic morphologies of the calculi and their medical classification and pathologies [C12, D. Bazin].

NEW TOOLS FOR STRUCTURE ANALYSIS

The structural models developed to simulate the structure factors of the nanotube bundles, have inspired simulations in the nanoporous channels. The precise description of the bundle geometry allowed one to ascertain the position of the alkali metal with respect to the nanotubes, as well as the ribbon/wire shape of the MnO confined in the nanochannels. [C8, J. Cambedouzou and H2, I. Golosovsky].

The interplay between crystal structure and rotational dynamics of methyl groups which has been nicely established in the 4-methylpyridine-N-oxide molecule. Rotational dynamics cannot be described by the quantum sine-Gordon model in 1D. The obtained structure shows the existence of eight distinct molecular sites suggesting that the four tunnelling transitions observed with inelastic neutron scattering could correspond to different effective potentials for the methyl rotors. [C13, F. Damay].

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MODEL MATERIALS UNDER EXTREME CONDITIONS

A structural transition was observed under pressure in solid D₂, and the structure of the pressure induced quantum phase was solved by combining X ray synchrotron and neutron diffraction on a single crystal. The study, which involved the development of a hybride pressure cell, was performed at the extreme conditions of 38 GPa and 1.5K. An orientational order of the D₂ molecules showing topological frustration was suggested. The result of this study was published in Nature (2005) (*H4*, I. Goncharenko).

FeO and MnO antiferromagnets were studied under high pressure. The neutron study was combined with synchrotron X ray diffraction, ultrasonic interferometry (elastic constants), Mössbauer effect (Fe hyperfine field). It allowed one to determine the pressure dependence of the magnetic and structural transitions. The two transitions do not occur systematically at the same temperature and could be decoupled under pressure [*CI4*, L. Dubrovinsky].

Perspectives

Studies of elementary molecular crystals such as H₂ and O₂ under pressure have shown spectacular effects in the last years and will be continued. In particular, quantum effects on orientational ordering in hydrogen isotopes will be studied. Another objective is to search for weak magnetism in O₈ clusters in the epsilon phase of solid O₂ at pressures above 10 GPa. The recently developed technique combining neutron and synchrotron studies on the same sample brings new possibilities to study crystal and magnetic structures under pressure. Among others things, it opens a route to the exact determination of crystal structures of light hydrides under pressure.

Geometrically frustrated systems keep being a hot topic of solid state physics, attracting an increasing number of scientists, as shown by the recent creation of a European GDR, and the onset of devoted conferences. By yielding complex magnetic structures, geometrical frustration is a tool allowing one to tune specific properties, like the giant abnormal Hall effect in R₂Mo₂O₇ pyrochlores, the magneto-striction in spinels, or the coupling between piezoelectric, ferroelectric and magnetic properties in multiferroic materials. Neutron scattering has a prominent role to play here.

The confinement of materials is an open door to many new behaviours, and studies of materials in confined media (including nanotubes) will certainly develop. These studies are performed through close collaborations of LLB scientists with external groups. Several theses are being starting (at Orsay, Rennes, Montpellier) which will include experiments in LLB.

The synthesis of functional materials with dedicated properties related to energy constitutes a challenge for humanity. The contribution of neutrons should be essential. Among them, let us cite the synthesis and study of new hydrides developed by external groups (Kurchatov, Thiais) in collaboration with LLB. They offer a potential interest for hydrogen storage. On thermoelectricity and magnetic refrigeration, S. Tencé is starting thesis work (LLB/ICMCB-Bordeaux).

Materials combining several functional properties are very attractive, like for example manganites and multiferroics. Their study should develop as well as the investigation of ionic and protonic conductors (collaboration LLB/CIRIMAT-Toulouse).

The high penetration of neutron beam and its non-destructive ability to explore massive or precious samples should trigger specific studies on biological materials and archeological pieces (teams of Florence-Milan).

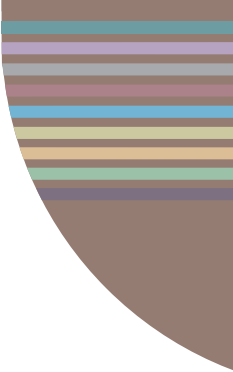
Experimental geosciences and mineral physics now focus on in-situ investigations under high pressures and high temperatures rather than on quenched samples to model real processes inside earth or other planets. Here again, the combination of neutron and synchrotron studies should be very useful. In LLB high pressure studies of geological samples are already developed in collaboration with a geophysical laboratory in Bayreuth.

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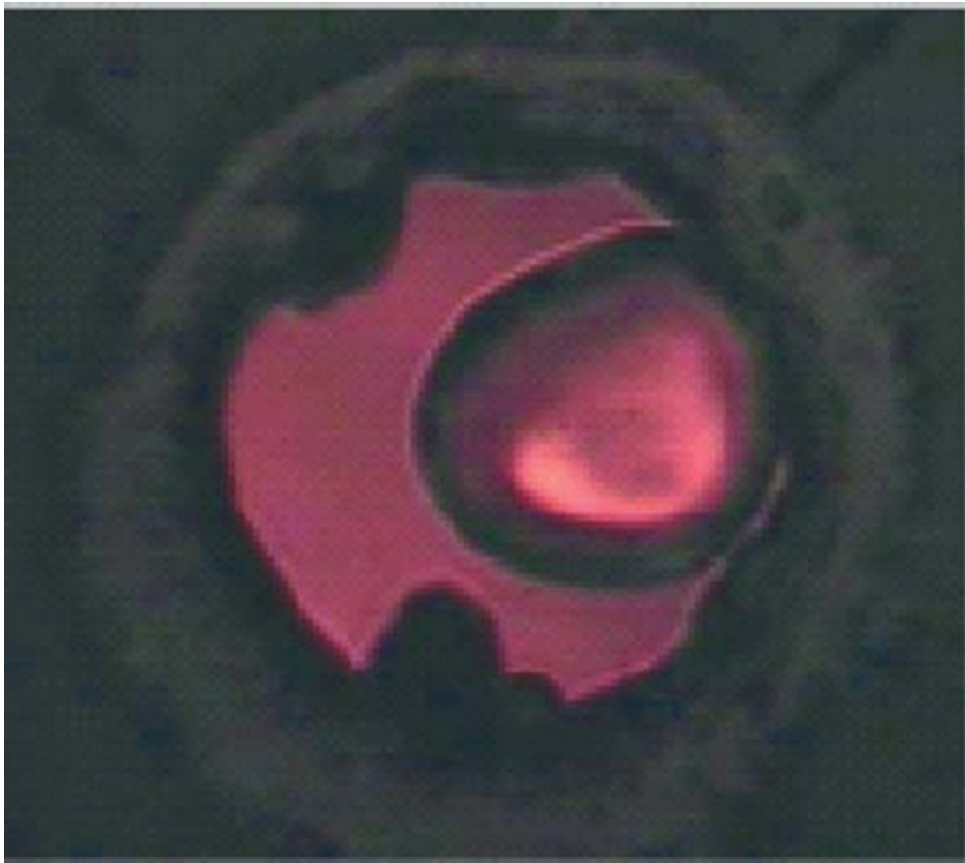
²Pressure induced magnetic transitions in the frustrated laves compound GdMn₂, I. Goncharenko et al. Phys. Rev. B 72, 014420 (2005).

³Ferromagnetic spin glass transition induced by pressure in Gd₂Mo₂O₇, I. Mirebeau et al. condmat 06006420, to appear in Phys. Rev. B (2006).

⁴Oscillating dependence between magnetic and chemical ordering in the frustrated Laves hydrides RMn₂D₂, O. Makarova et al Phys. Rev B 67, 134418, (2003); article in preparation.



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- H1. Anisotropic quenched disorder effects on a liquid crystal confined into nanochannels**
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- [C11. **M. Giot**] Magnetic structure of the charge ordered $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ manganites
- [C12. **D. Bazin**] Structural study of pathological calcification : the case of kidney stones
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H1. ANISOTROPIC QUENCHED DISORDER EFFECTS ON A LIQUID CRYSTAL CONFINED INTO NANOCANNELS

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Intense experimental and theoretical efforts have focused on quenched disorder effects in condensed matter as they bring about some most challenging questions of modern statistical physics. Most universal features of quenched disorder effects can be envisaged in the frame of random field theories.

From this standpoint, liquid-crystals (LC) confined in random porous materials are definitively recognized as paradigm systems, which allows one to address experimentally general questions on phase transitions, critical scaling and non-ergodicity in the presence of quenched random fields [1].

LC present many different phase transitions in bulk conditions, involving a variety of universality classes and the breaking of continuous symmetries. They offer unique opportunities to test some general theoretical predictions. The smectic transition has retained a special interest because it is predicted to be unstable towards the presence of an arbitrarily weak quenched disorder. A positionally disordered but topologically ordered "smectic Bragg glass" (SBG) is even predicted in the case of anisotropic random media [2]. However, this new thermodynamically distinct low-temperature phase remains enigmatic experimentally. LC are elastically soft materials and may directly couple to the surface of the porous matrix, which acts as an external field. Confinement in strongly disordered porous materials can be used as an experimental way to introduce an external random field coupling to the LC order parameters. Primary studies have been carried out with random porous silica (aerogels) and aerosil LC-dispersions [1,3], which lead to an almost spatially homogeneous random pinning of the LC. In the present contribution, we prove that it is possible to introduce anisotropic random fields in one-dimensional (1D) conditions of confinement [4]. These new openings rely on the use of aligned nanochannels formed in porous silicon films (PSi) [5].

Anodization of heavily p+-doped (100) oriented silicon leads to a parallel arrangement of unconnected channels (diameter: ~30 nm, length: 30 μm) running perpendicular to the surface wafer (called columnar form of the PSi). The aspect ratio of each channel exceeds 1000:1 and induces a low dimensionality (quasi 1D) to the system (cf. Fig. 1). The preferential alignment of all the channels perpendicularly to the silicon surface prevents powder average limitations when measuring anisotropic observables of unidimensional nanoconfined systems.

Under these conditions of confinement, anisotropic quenched disorder is introduced by the highly corrugated inner surface of the 1D pores, which has been proved to be strongly irregular at the microscopic length scales i.e., ~1 nm.

Fully hydrogenated octylcyanobiphenyl (8CB) has been chosen as a reference LC. It undergoes with increasing temperature the following sequence of phases: crystal (K), Smectic A (A), Nematic (N) and isotropic (I) with the following transition temperatures: $T_{KA}=294.4$ K, $T_{NA}=305.8$ K and $T_{NI}=313.5$ K.

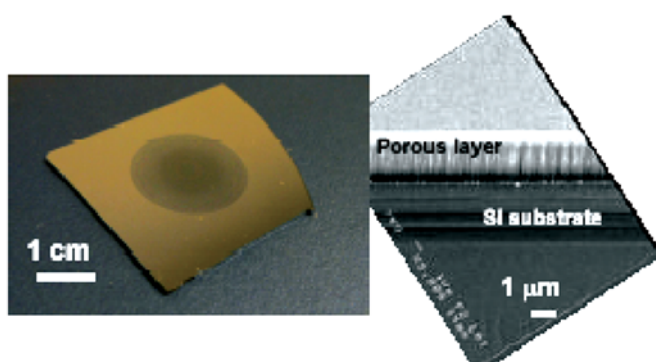


Figure 1. Top view of the porous silicon wafer (left). Side view of the porous layer by scanning electron microscopic (right)

A spontaneous alignment of the mesophases and crystalline phases has been observed in confinement. It corresponds to a preferential orientation of the nematic and smectic orderings along the pore axis, as revealed by spectroscopic ellipsometry, polarized microRaman and small angle neutron scattering (PAXY, LLB) [6]. This direct consequence of confinement has been related to the unidirectional character of the porous geometry. The nature of the surface interaction (anchoring) is not prevailing here, since changing the interaction from hydrophilic to hydrophobic by surface chemical treatment (silanization) does not affect qualitatively the overall structure and phase behaviour of 8CB in PSi [5].

A precise structural description of the confined phases requires an improved q-resolution, which can be achieved with a monochromatic cold-source double-axis neutron diffractometer (G6.1). The macroscopic parallel alignment of the porous nanochannels allows one to investigate the effects of anisotropic quenched disorder on the structure of the mesophases by selecting peculiar incidence angles so that the transfer of momentum q is practically parallel or perpendicular to the pores axis. An extreme alteration of the phase diagram of 8CB in PSi has been observed (cf. Fig. 2). Crystallization is strongly depressed on cooling and leads to two crystalline phases below 250 K, which do not correspond to any stable phase of bulk 8CB.

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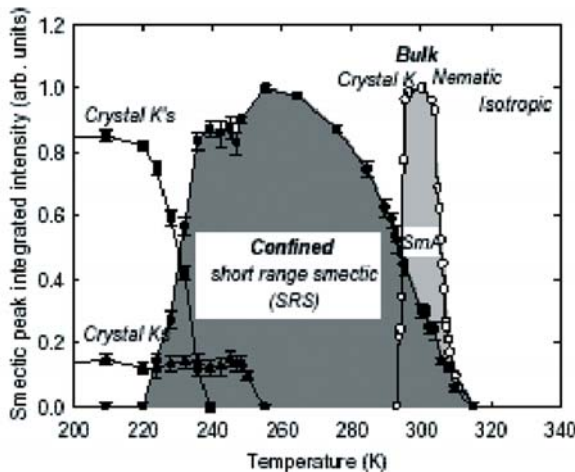


Figure 2. Phase behaviour of bulk and confined 8CB, revealed by the temperature variation of the Bragg peaks characteristic of the different phases.

More remarkable is the absence of a nematic-smectic transition, which is replaced by a reversible and gradual increase of a short-range translational order. This short range ordered smectic phase (SRS) is stable and evolves on an extremely wide temperature range down to 50 K below the bulk crystallization. Its structure factor is characterized by a single broad diffraction peak at $q = 0.2\text{\AA}^{-1}$, which corresponds to the location of the smectic Bragg peak in the bulk. A lineshape analysis of this peak has revealed the existence of two components, which agrees with recent random fields theoretical predictions. The first term (of Lorentzian type) dominates at high temperature and reflects the smectic thermal fluctuations also observed in the bulk. An additional term is required in the presence of quenched disorder and prevails in the SRS phase at low temperature. The fitting of the structure factor with this theoretical expression provides a smectic correlation length, which increases continuously from 3 nm at the bulk nematic-smectic transition temperature up to 12 nm at 250K (cf. Fig. 3). This variation strongly differs from what is expected for more usual nanoconfinement effects in terms of surface interaction and finite size effects. These latter effects are exemplified by the case of 8CB confined in alumina nanochannels of the same size (30 nm), which are known to present a fairly regular wall structure. In this case, the signature of a sharp transition from the nematic to the smectic phase is maintained although it is slightly rounded and depressed (about 2 K). The variation of the smectic fluctuations correlation length follows the critical behavior of the bulk, although the smectic domains are ultimately spatially limited at the transition by finite size effects. An additional independent proof of the primacy of quenched disorder effects for 8CB in PSi is the apparent linear dependence between κ_{SI} and the smectic susceptibility obtained by

integration of the pseudo- Bragg peak intensity. Such a relationship, which has been predicted theoretically, points up the origin of the SRS phase. The gradual increase of short-range correlation length is resulting from the competition between the elasticity of the smectic layers and the strength of disorder introduced by the porous solid.

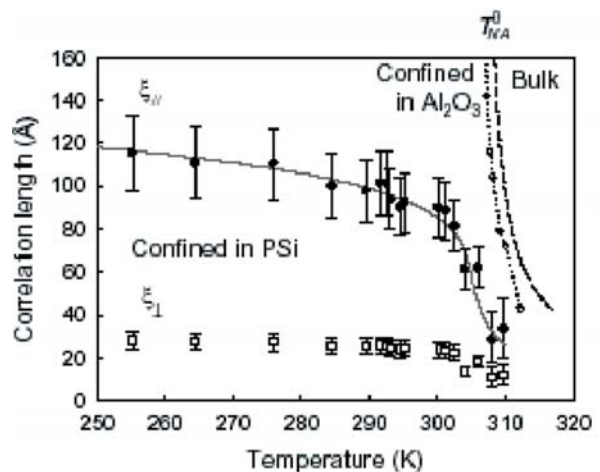


Figure 3. The temperature variation of the smectic correlation length for bulk 8CB (dashed line), for 8CB confined in porous alumina (dotted line) and for 8CB confined in porous silicon (filled circles).

The confinement of LC in PSi has opened new perspectives in the unexplored regime of anisotropic and strong quenched disorder, which may inspire future investigations. Our results already imply that much of the scenario expected for weak disorder is retained in the regime obtainable with PSi. Additional crucial aspects related to the ergodicity of the system and the occurrence of a glassy dynamics resulting from quenched disorder remain to be explored [7,8].

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H2. DIFFRACTION STUDIES OF MnO CONFINED IN NANOCANNELS OF MESOPOROUS MATRICES.

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The properties of magnetics confined in nanometer scale cavities drastically differ from those in the bulk material. The investigation of model materials in the unusual conditions of a so-called “restricted geometry” is of fundamental interest since the confined geometry and the influence of the surface yield unusual properties.

During the past years, we carried out systematic studies of 3d-oxides in confinement, first in MnO confined in a vycor glass matrix with a random network of pores [1] then in MnO confined in MCM-41 or SBA matrix with a regular system of nanochannels [2,3,4] and MnO confined in MCM-48 matrix with a gyroidal channel system [5]. These amorphous silica matrices known as molecular sieves were discovered in 1992 and attracted much attention. They do not produce Bragg reflections and are very suitable to diffraction studies. Oxides within the matrix cavities were synthesized from solutions by the “bath deposition method”. The high specific surface of the matrices and the good wetting of the channel walls by the liquid solution ensure that MnO predominantly occupies the channel voids.

Since the discovery of antiferromagnet order in MnO in 1949, this oxide has been the subject of intense experimental and theoretical interest. In MnO the antiferromagnetic order, which appears at 117 K by a first order phase transition, is accompanied by a rhombohedral contraction of the cubic lattice. In the magnetic structure, which consists of ferromagnetic sheets stacked antiferromagnetically along the (111) axis, the moments in the first coordination sphere are frustrated. Greenwald and Smart in the early 50's suggested that the distortion removes the frustration. So the structural distortion and the magnetic ordering in MnO are mutually dependent.

Shape of the nanoparticles.

Neutron diffraction and x-ray synchrotron experiments showed that, in contrast within the porous glass where MnO forms isotropic aggregates, inside the channel type matrices MnO forms nanowires or nanoribbons. In the latter, the two-dimensional character of the diffracting objects leads to a specific lineshape known as a “saw-tooth” profile and to a specific shift from the Bragg position towards larger diffraction angles. This yields an “effective” lattice parameter which is systematically lower than the corresponding lattice parameter of the three-dimensional lattice.

The profiles measured at the synchrotron source LURE were compared with those calculated numerically for objects of different dimensions using the Debye formula (Figure 1,2). This analysis allowed us to estimate the dimensions of the

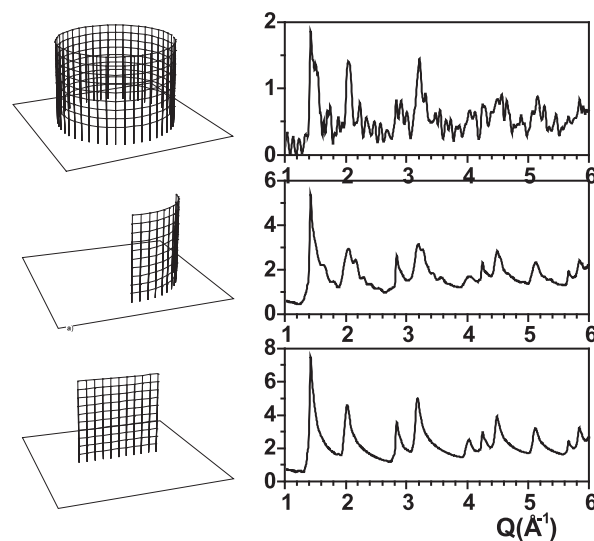


Figure 1. Numerical simulation of diffraction patterns from diffracting objects of different shapes.

nanoparticles, which appear to be thin (~ 10 Å) ribbon or wire-like structures. In all cases, the nanoparticle lengths are in the interval of 180–260 Å, increasing with the channel diameter [2].

Magnetic order and phase transition.

Neutron diffraction studies of confined MnO, performed at the diffractometer G6-1 showed that the magnetic structure is similar to the structure in the bulk.

However, the volume-averaged magnetic moment of confined MnO appears to be noticeably smaller than the moment in the bulk. This is a well known phenomenon in confined magnets, which is explained by the disorder of the magnetic moments at the surface.

In all type of matrices, the magnetic transition in confined MnO becomes continuous with a Néel temperature T_N enhanced with respect to the bulk [1,3]. Such behavior is well known as a finite-size “rounding” of the phase transition and results from the limitation of the correlation length by the nanoparticle size.

The observation of an enhanced Néel temperature is surprising, since a common effect expected in all nanostructured material is the decrease of T_N when the correlation length becomes limited by the nanoparticle size. In the present case, the magnetic disorder and the violation of the translation symmetry at the nanoparticle surface result in a small surface ferromagnetic moment whereas the core remains antiferromagnetically ordered. Taking into account the

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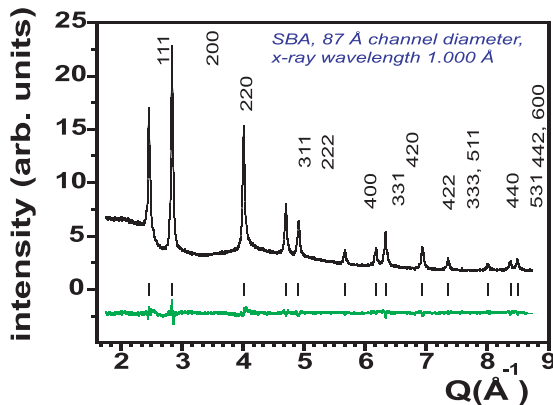


Figure 2. Observed x-ray diffraction pattern of MnO confined in SBA matrix with 87 Å channel diameter; in green, the difference pattern

ternary interaction of the non-critical ferromagnet, a critical antiferromagnetic behavior and the associated structural order parameters, the enhanced T_N can be explained within the framework of the Landau theory [3].

In MnO within channels of MCM-41 matrices, the critical exponent in the temperature dependence of the magnetic moment decreases with decreasing the channel diameter. We attribute the observed change of the magnetic transition to the increasing anisotropy and the change in the dimensionality of the magnetic system to a quasi-one-dimensional case (Figure 3).

Néel temperature (K) Exponent(β)

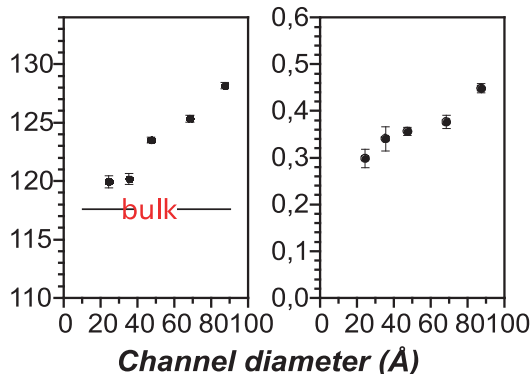


Figure 3. Dependences of the Néel temperature and critical exponent β with the channel diameter, as calculated by fitting the data with a power law.

Structural distortion and magnetic order.

According to conventional theory, antiferromagnetism in MnO is stabilized by the structural distortion. However, in the case of nanoparticles, the high anisotropy and the inner stresses add new terms to the free energy, which could drastically change the energy balance.

Interestingly, low temperature high-resolution x-ray diffraction experiments, performed in ESRF on nanoparticles of MnO confined in MCM-41 matrix with 35 Å channel diameter, showed a new structural transition at about 60 K, well below

the Néel transition which occurs at about 120 K. At this second transition, the structural distortions which appeared below T_N suddenly disappear and the structure becomes cubic as in the paramagnetic region. This "reentrant" transition is accompanied by an increase of the lattice parameter, of the amplitude of atomic motion and the appearance of inner stresses (Figure 4). Surprisingly, there is no change in the temperature dependence of the magnetic moment associated with the low temperature transition. Such behavior drastically differs from the behavior known for the bulk.

Loss of long-range atomic order in MnO confined in MCM-48 matrix with a gyroidal system of channels.

The matrix MCM-48 is marvelous because the channels piercing in its amorphous silica body comply with the symmetry of the cubic space groups. The channel wall surface exactly follows the so-called "periodic minimal surface", forming a gyroidal structure with a three-dimensional network of channels.

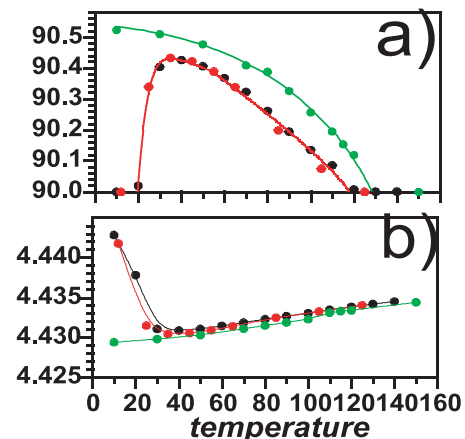


Figure 4. Temperature dependences of the angle of rhombohedral distortion (α) and the unit cell parameter.

Synchrotron X-ray experiments performed at ESRF showed that the nanoparticles of MnO have a ribbon-like shape with a length of about 50 Å and do not show long-range atomic ordering. In spite of the disordered atomic structure, a phase transition from the cubic structure accompanied with a rhombohedral distortion was observed, like in the bulk material. The parameters of the phase transition appear to be similar to the parameters of the transition observed in MnO within the MCM-41 matrix, where atomic ordering extends over much longer length scales [5].

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H3. PRESSURE INDUCED FERROMAGNETIC SPIN GLASS TRANSITION IN THE GEOMETRICALLY FRUSTRATED PYROCHLORE $(\text{Tb}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$

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In the pyrochlore compounds $\text{R}_2\text{Mo}_2\text{O}_7$, both rare earth R^{3+} and M^{4+} transition metal ions form a three-dimensional network of corner sharing tetrahedra. The pyrochlore lattice is geometrically frustrated both for antiferromagnetic (AF) and ferromagnetic (F) nearest-neighbour exchange interactions, leading to intriguing magnetic states such as spin liquids, spin ices or chemically ordered spin glasses. Pyrochlores are extensively studied since their electrical and magnetic properties strongly depend on the rare earth ionic radius r . Compounds with small ionic radius Y, Dy and Tb are spin glass (SG) insulators, whereas those with Gd, Sm and Nd are ferromagnetic metals. $(\text{R},\text{R}')_2\text{Mo}_2\text{O}_7$ series with different substitutions on the R^{3+} site show a universal dependence of the transition temperature versus r [1], suggesting that Mo-Mo interactions change sign at a critical value r_c , which controls the SG-F threshold. Band structure calculations and photoemission experiments [2] point out that the concomitant changes of the transport and magnetic properties come from strong electron correlations in the Mo t_{2g} band nearby the Fermi level. Up to now, there has been no microscopic investigation of the SG/F threshold, so as to follow the changes in the magnetic correlations and spin fluctuations. To understand the role of interatomic distances in this transition, the most direct way is to combine applied pressure and chemical pressure. We studied the $(\text{Tb}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$ system, allowing us to cross the critical threshold by both chemical and applied pressure. By using three microscopic probes, namely neutron diffraction, μSR and synchrotron X ray diffraction, this study provides the first and complete characterization of the SG-F threshold [3].

Magnetic diffraction patterns were recorded on the powder diffractometers G61 and G41 of the Laboratoire Léon Brillouin (LLB) at ambient pressure, and under pressure on G61. Starting from the spin glass $\text{Tb}_2\text{Mo}_2\text{O}_7$, the dilution by *non magnetic* La ion expands the lattice, inducing long range magnetic order (LRO), which is further destroyed under pressure (Fig.1). Clearly, negative chemical pressure and applied pressure have reversed effects on the magnetic order. The magnetic structure (Fig.2) was solved by a systematic search, using the program BasReps and symmetry-representation analysis combined with Fullprof. We searched for a solution in the in the space group $I41/amd$, the highest subgroup of the $Fd-3m$ space group allowing F and AF components simultaneously. In the ordered structure with $\mathbf{k}=0$ propagation vector, the four tetrahedra of the cubic unit cell are

equivalent, for both Tb and Mo lattices. In a given Tb tetrahedron, the Tb^{3+} moments orient in the local spin ice (2in-2out)

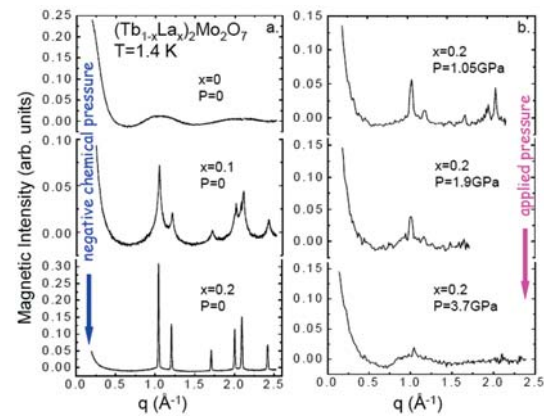


Figure 1. Magnetic intensity of $(\text{Tb}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$ at 1.4 K versus the scattering vector $q=4\pi\sin\theta/\lambda$. The neutron wavelength is $\lambda=4.741 \text{ \AA}$. A spectrum in the paramagnetic phase (70 K) was subtracted and the magnetic intensity was scaled to the (222) nuclear peak intensity.

structure, with a small angle qt with the local $\langle 111 \rangle$ anisotropy axes. Their F component orders along a $[001]$ axis. The Mo moments align close to a $[001]$ axis, with a slight tilting θ_m towards the local $\langle 111 \rangle$ axis (inset Fig. 2). Mo and Tb moments are F coupled.

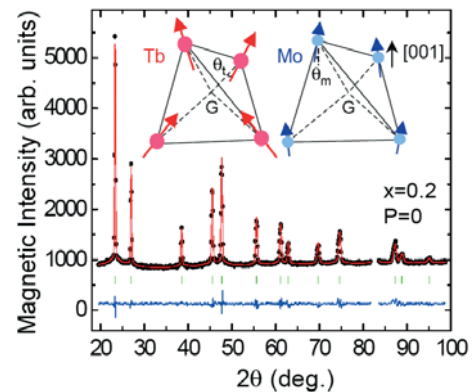


Figure 2. Magnetic intensity for $x=0.2$ at 1.5 K versus the scattering angle $2q$, $\lambda=2.426 \text{ \AA}$. A 70 K spectrum was subtracted. Solid lines show the best refinement and the difference spectrum (bottom). In inset: magnetic structure of the Tb- and Mo- tetrahedra.

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As a striking feature, the long range order (LRO) is induced by diluting the Tb lattice with a non magnetic ion. It proves that the main effect of dilution is the lattice expansion. From the variation of the lattice constant, a small La content ($x=0.06$) is expected to induce the SG-F transition. The SG-F transition is mostly determined by the change in sign of the Mo-Mo exchange interactions and the onset of F interactions like in $\text{Nd}_2\text{Mo}_2\text{O}_7$ [4]. We notice that Tb magnetism should still play a role since $(\text{Y}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$ compounds do not show LRO. The non collinear structure for both Tb^{3+} and Mo^{4+} comes from the uniaxial anisotropy of the Tb^{3+} ion, which brings spin ice frustration in the ferromagnetic region. The ground state moments are strongly reduced with respect to the free ion values.

Under pressure, the ordered moments ($x=0.2$) decrease and reorient. At 1.05 GPa, LRO and SRO phases coexist. The ordering temperature decreases under pressure. At 3.7 GPa the Bragg peaks disappear (see Fig. 3a). When fitting the 3.7 GPa data with a SRO model [5] involving correlation parameters up to the fourth neighbours, we find short range F Tb-Tb spin correlations and AF Tb-Mo spin correlations. So the Tb-Mo correlations change sign at the threshold. The strong intensity at small angles, not taken into account by the SRO model was fitted by a Lorentzian, yielding a mesoscopic correlation length between Tb moments of $18(7)$ Å. All parameters are close to the values in $\text{Tb}_2\text{Mo}_2\text{O}_7$ spin glass.

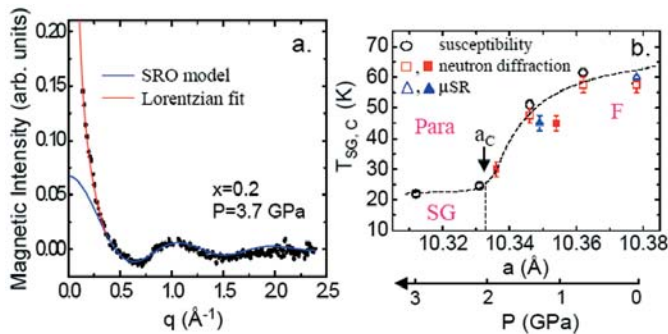


Figure 3. a. Magnetic intensity for $x=0.2$ sample at 1.4 K and 3.7 GPa. Lines are fits using SRO model and Lorentzian fit respectively. b. Phase diagram for $(\text{Tb}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_7$ in the threshold region: ambient pressure (open symbols) and under pressure (full symbols).

μSR measurements (Fig. 4) shed a new light on the magnetic order by probing the spin fluctuations and the static local field below T_C . We measured the $x=0.2$ sample at ambient pressure on GPS and GPD at the Paul Scherrer Institute (PSI) and at 1.3 GPa on GPD. Data analysis allows us to separate the dynamic term λ_z and static terms $\langle B_{\text{loc}} \rangle$ and λ_T (see [3] for a complete description). The longitudinal relaxation rate λ_z which reflects the spin fluctuations shows a critical peak at T_C then a broad maximum at a lower temperature T^* . The static

terms reflecting the static local field “seen” by the muon spin, scale with the Tb moment measured by neutrons. The dynamical anomaly at T^* , akin to that observed in $\text{Sm}_2\text{Mo}_2\text{O}_7$ and re-entrant spin glasses, suggest a freezing of short range correlated moments. It occurs without any anomaly in the static terms, which means that it does not break the LRO.

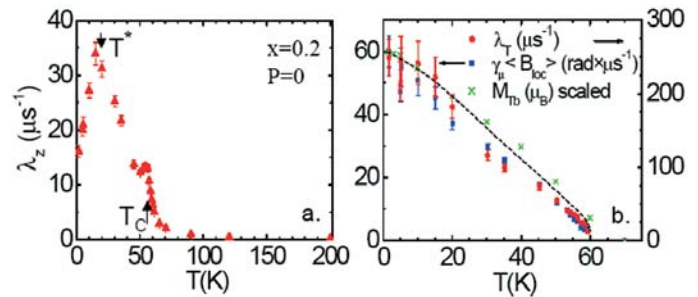


Figure 4. μSR ambient pressure results for $x=0.2$. Temperature dependence of: a. λ_z . b. $\langle B_{\text{loc}} \rangle$, λ_T and M_{Tb} (scaled).

The phase diagram (Fig. 3b) shows the transition temperatures determined by all probes versus the lattice constant. The equation of state $a(P)$ measured by X ray synchrotron diffraction at ID31 (ESRF) allowed us to combine ambient pressure data on compounds with different x , with high pressure data for $x=0.2$. The critical lattice constant agrees with previous determinations [1].

The fact that high pressure and ambient pressure data merge in a single curve supports a dominant mechanism induced by a change in the Mo-Mo interactions. But our microscopic study also shows important features not taken into account by current theories: i) the role of rare earth magnetism at the threshold should be taken into account. ii) the mechanism by which Mo-Mo interactions change sign should be different under chemical pressure and applied pressure. In the first case, it reflects the aperture of a Mott-Hubbard gap, yielding an insulating spin glass. In the second case, it is likely connected with the increase of the Mo bandwidth, yielding a metallic spin glass. iii) the role of Tb anisotropy in the spin correlations and fluctuations is clarified thanks to a comparative study in $\text{Gd}_2\text{Mo}_2\text{O}_7$. In $\text{Gd}_2\text{Mo}_2\text{O}_7$, with isotropic Gd ion, the ferromagnetic ground state is collinear and the transition at T^* is strongly suppressed [6]. The rare earth anisotropy also plays a role on the conductivity, leading to a giant abnormal Hall effect in the ferromagnetic region.

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H4. NEUTRON DIFFRACTION STUDY OF THE BROKEN SYMMETRY PHASE IN SOLID DEUTERIUM AT THE PRESSURE OF 38 GPa

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The solid hydrogen H_2 , HD and D_2 exhibit intricate quantum phenomena, which have been the subject of numerous experimental and theoretical studies. Studying these phenomena is considered as essential to understand the quantum many-body effects of density. Various exciting scenarios have been suggested for high-pressure dense hydrogens, for example, room temperature superconductivity in monoatomic hydrogen or quantum melting at $T=0K$ at the onset of the transition to the monoatomic state [1]. Despite enormous theoretical and experimental efforts, there was no unambiguous information on nature of the pressure induced phases in solid hydrogen. Optical probes detected a phase transition in solid D_2 at the pressure of 25 GPa and low temperatures [2]. A similar transition occurs in H_2 at much higher pressures of 70-100 GPa [3]. The giant isotopic effect reveals the quantum nature of the pressure-induced phase. The transition was interpreted as a transition to a rotationally ordered state. In the ground state at low temperature and low pressure, hydrogen molecules are in the $J=0$ spherical rotational states and exhibit a rotational disorder down to $T=0$ K. At high pressures, a trade-off between two tendencies, going higher in kinetic energy (that is, to $J \neq 0$ rotational levels) and gaining a negative potential energy through a orientational ordering that minimizes electric quadrupole–quadrupole energy might lead to a breaking of the spherical symmetry and the stabilization of an orientationally ordered state (the so-called broken symmetry phase or BSP). In H_2 , the contribution of the kinetic energy is higher than in D_2 , which explains the isotopic effect on the pressure of the transition. The crystal structure of the quantum pressure-induced phases in solid hydrogen is a challenge for modern density-functional theory (DFT) and molecular dynamic simulations (MD). Various theoretical models proposed different crystal structures, most of them suggesting an orthorhombic lowering of symmetry in the basal plane of the initial h.c.p. lattice (see, for example Refs. 4,5). Until the present study, there was no direct evidence of the structural transition in high-pressure solid hydrogen, neither proof of its crystal structure. The optical data on vibron modes provides only indirect information on crystal structure. X-rays are scattered by electronic shells, and therefore almost insensitive to the orientations of hydrogen molecules having no internal electronic orbitals. Contrarily, neutrons are scattered by nuclei and therefore can “see” the orientations of the molecules. While the advantages of neutron techniques in studies of high-pressure hydrogen are obvious, such study is a challenge from an experimental point of view. At pressures above 25 GPa the sample volume is measured in small fraction (10^{-3}) of cubic millimetre. It seemed almost

impossible to obtain high-quality structural information from such a small sample at the pressure of 38 GPa (the pressure was chosen well above the phase boundary) and low (down to 1.5K) temperatures. To carry out the study, we used a new approach, based on a combination of neutron and synchrotron probes. A high-quality single-crystal of D_2 was grown from He- D_2 mixture (Fig. 1). The crystal was surrounded by He pressure transmitting medium, which preserved it from shattering as pressure was increased to 38 GPa.



Figure 1. Single crystal of solid D_2 surrounded by He pressure transmitting medium.

New pressure cells (Fig.2) allowed to combine neutron and X-ray diffraction on the same sample. The quality and orientation of the crystal were checked at the ESRF (ID27 and ID9 beamlines) by X-ray diffraction. This saved many weeks of neutron time. Then the pressure cell was brought to the LLB and installed on the lifting-counter diffractometer 6T2, equipped by a He-flow cryostat. The neutron data on (100), (0-10), (-110), (110), (-210), (1-20) and (101) reflections were collected in the temperature range 1.5-70 K. The present study sets a new record for the maximal pressure in single-crystal neutron measurements.

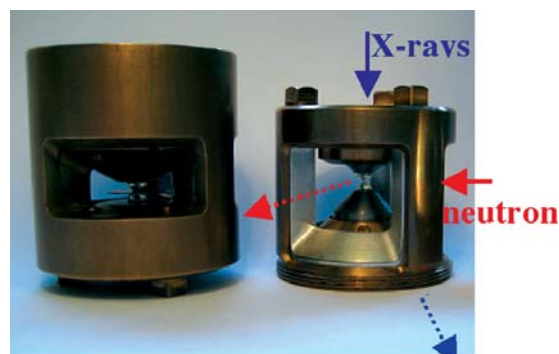


Figure 2. New “hybrid” low-temperature cells compatible with neutron and X-ray scattering at the LLB.

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Fig. 3 and 4 show the first direct diffraction evidence of the BSP transition in solid D_2 under pressure. As temperature decreases, a small ($\sim 5\%$) decrease in intensity indicates a pressure-induced structural transition. The temperature (~ 45 K) of the transition exactly coincides with the temperature at which a shift in vibron modes was detected by optical spectroscopy and a tiny change in c/a ratio by X-ray scattering. The analysis of the obtained data revealed rather surprising results [6]. Firstly, we did not observe any significant difference ($>5\%$) in the measured intensities from the reflections which are linked by the P-3 symmetry (and therefore equivalent) in the initial h.c.p. structure, but should become different in the orthorhombic cells predicted by theory. Secondly, the observed variation of intensities at the phase transition are much smaller than those predicted by the theoretical models [4,5].

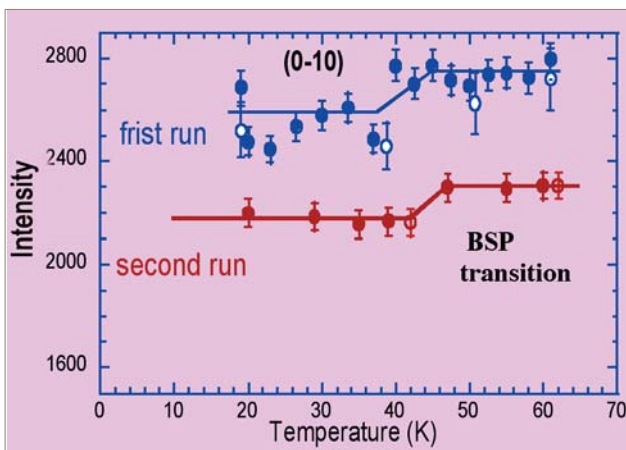


Figure 3. Integrated intensity of the (0-10) reflection versus temperature at the pressure of 38 GPa. Another interesting feature is the presence of incommensurate satellites (1-x, 0 0) in neutron and X-ray diffraction patterns.

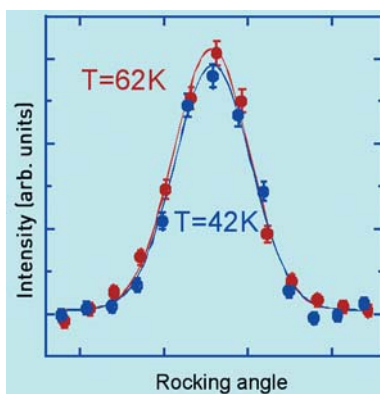


Figure 4. Rocking curves of the (0-10) reflection measured at different temperatures.

Based on our observations, and a proposition of local ordering from a MD simulation by Cui et al [7], we suggest

another type of orientational ordering which is similar to that in metastable ortho-para mixtures having cubic f.c.c. structure (so called Pa3 structure). This structure minimises the electric quadrupole-quadrupole energy. It has P-3 symmetry. If developing in a h.c.p. structure, it exhibits a topological frustration (Fig. 5): the molecules have to choose 3 orientations from 6 possible directions along the body diagonals in a bi-pyramid. Stacking faults between different possible orientations might result in a short-range ordered structure or a long-range incommensurate modulation, similar to that observed experimentally. The obtained results should stimulate further theoretical works on orientational ordering and quantum phenomena in dense hydrogen.

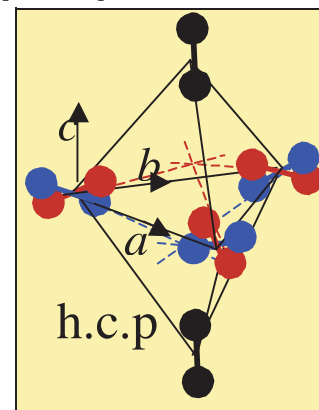


Figure 5. Two possible “frustrated” types of orientational ordering in the BSP phase. The orientations shown in red and blue colours have the same quadrupole-quadrupole energy.

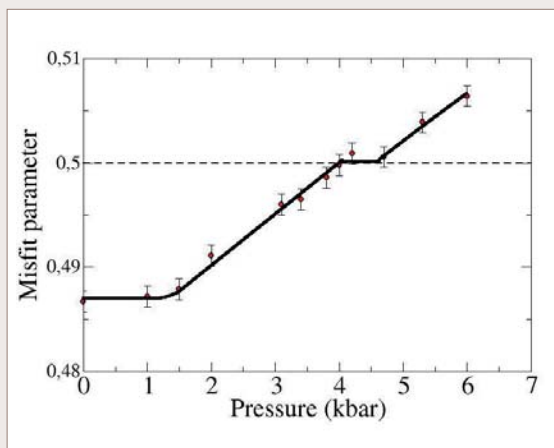
Finally, by a combination of state-of-art synchrotron and neutron techniques, we carried out the first direct diffraction study of the quantum BSP phase in solid D_2 , which was a mystery for about 25 years. Forthcoming neutron experiments in an extended \mathbf{q} range and also similar measurements in solid H_2 at the pressure of 70 GPa should help to improve the understanding of the crystal structure of the BSP phase and to study the isotopic effect on the structure.

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[C1. B. Toudic] First evidence of a pressure induced lock-in in an aperiodic composite crystal

Nanometer-sized containers have huge potential for use in molecular manipulation and chemical reactions. In the frame of this work, we report the first pressure-induced lock-in in an aperiodic nanoporous crystal [1]. This result is based on the concept of free sliding applied to aperiodic materials, allowing striking nanotribologic properties. The studied compound, urea-alkane, is a self-assembled nanoporous crystal made of a host urea lattice with hydrogen bonds and a confined guest sublattice non-covalently bounded, like in many biophysical model systems. Neutron diffraction measurements performed on a triple axis spectrometer with cold neutron, 4F, give a unique opportunity to get very high spatial resolution with the precise hydrostatic environment to very carefully measure the different lattice parameters. The retained urea-hexadecane has the period of the guest just slightly larger than twice the one of the host.



Colossal Magneto resistance (CMR) compounds

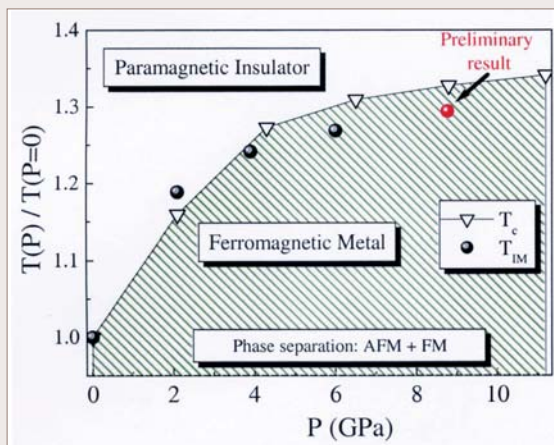
Selective compressibility allowed a commensurate lock-in at the value . Then, the two sub-systems are 'attached' as in normal crystals giving a direct proof of a lock-in energy term in such self-assembled supramolecular crystals. The continuous control of the guest repeat gives a unique tool for tuning one-dimensional properties of confined compounds. These results open a broad field of scientific subjects that can be tackled combining the low friction of incommensurate nanoporous materials with the conformational, optic and electronic properties of guest molecules.

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[Collaboration: B. Toudic, F. Aubert, C. Ecolivet, GMCM Rennes 1; P. Bourges, LLB; T. Brezewski, Bilbao]

[C2. M. Baldini] Pressure effects in $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ studied by neutron and optical methods

CMR compounds exhibit a close relation between magnetic and electronic properties [1]. Optical studies revealed a rapid increase of temperature of insulator-metal transition in the prototypical CMR manganite $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$. In order to establish the relation between the insulator-metal transition and the magnetic ordering, we studied the magnetic structure of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ by neutron diffraction. We obtained the magnetic phase diagram and the $T_C(P)$ line over a wide pressure range (0-8 GPa). The $T_C(P)$ and the $T_{IM}(P)$ [2] behaviour under hydrostatic pressure is the same up to (at least) 8 GPa. This result provides the important evidence that the Double Exchange mechanism, responsible for the close connection between magnetic and electronic transition, still holds in the high pressure regime. On the other hand, an antiferromagnetic peak was observed at pressure above 4 GPa and T 100 K, revealing the onset of a phase separation between FM and AFM. This result gives an unambiguous answer to the hypothesis of a reinforced role of the SE coupling between the t_{2g} core spins and explains the $T_C(P)$ and the $T_{IM}(P)$ saturation observed at higher pressure [3].



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[2] A. Congeduti, P. Postorino, E. Caramagno, M. Nardone, A. Kumar, D. D. Sarma, *Phys. Rev. Lett.* **86**, 1251 (2001)

[3] A Sacchetti, P Postorino and M. Capone, *New J. of Phys.* **8**, 3 (2006)

[Collaboration: M. Baldini, E.Arcangeletti, P. Postorino, Universita di Perugia Italy, L. Capogna CNR-OGG Grenoble, I. Goncharenko, LLB.]

Magnetic pressure-temperature phase diagram of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$

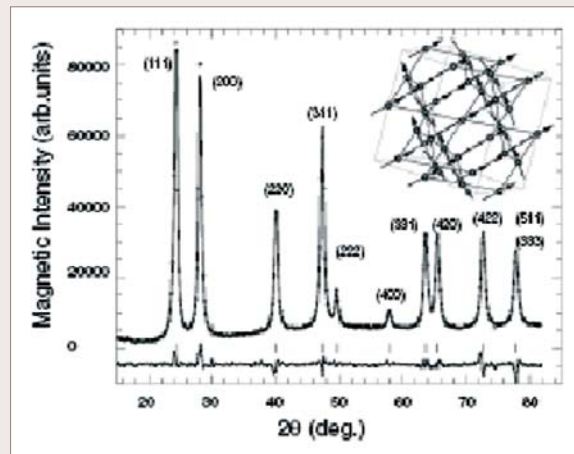
STRUCTURE AND PHASE TRANSITIONS

[C3. I. Mirebeau] Ordered spin ice state and magnetic fluctuations in $Tb_2Sn_2O_7$

$Tb_2Sn_2O_7$ is a geometrically frustrated pyrochlore showing antiferromagnetic liquid like correlations down to 4 K. Below 1.3 K we have observed by neutron diffraction a “two steps” transition towards a new magnetic structure, with both ferromagnetic and antiferromagnetic character [1]. The local structure in a Tb tetrahedron is akin to a spin ice [2], but the four tetrahedra of the unit cell are identical, yielding ferromagnetic component. The ordered ground state, previously predicted by theory [3] but not observed before, seems to result from the combined influence of dipolar interactions and finite anisotropy. We have also indirectly observed *fluctuations of the ordered moments* below T_c , by comparing the ordered moment measured by neutron diffraction to that derived from specific heat. These abnormal fluctuations were recently probed by muons, at such extend that they completely wash out the static field felt by the muon spin [4]. Their precise nature and the way how they coexist with the ordered state remains a mystery, opening a new field of investigation for both experiment and theory.

[1] I. Mirebeau, A. Apetrei et al *Phys. Rev. Lett.* **94**, 246402, (2005).; [2] S. T. Bramwell and M. J. P. Gingras, *Science* **299**, 1495, (2001); [3] J. D. M. Champion et al *Europhys. Lett.* **57**, 93, (2002). ; [4] P. Dalmas et al *Phys Rev. Lett.* **96**, 127202, (2006); F. Bert et al condmat 0603434 to appear in PRL (2006).

[Collaboration: I. Mirebeau, A. Apetrei (LLB); P. Bonville, D. Colson, A. Forget (SPEC); V. Glazkov, J. P. Sanchez (CEA-Grenoble) ; O. Isnard, E. Suard (ILL)].



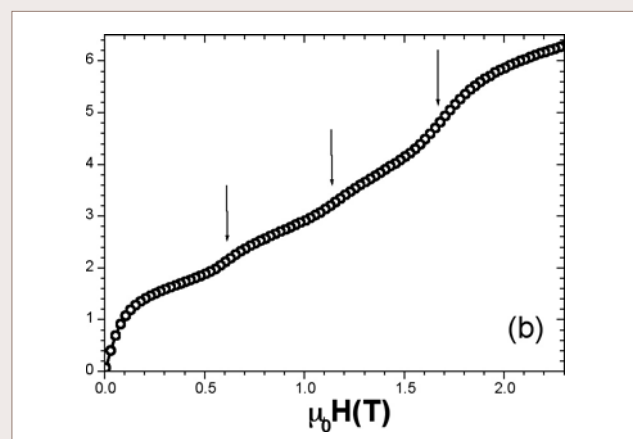
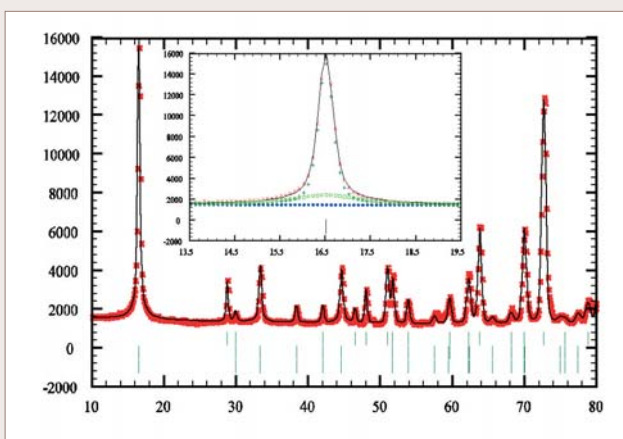
Magnetic neutron diffraction spectrum at 0.10 K, with the ordered spin ice structure in inset. From ref. [1]

[C4. V. Hardy] Magnetism of the geometrically frustrated spin-chain compound Sr_3HoCrO_6 : Magnetic and heat capacity measurements and neutron powder diffraction

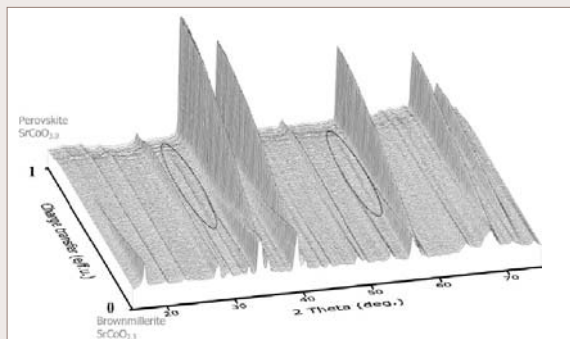
Sr_3HoCrO_6 has been investigated versus temperature by combining magnetic and specific heat capacity measurements, as well as neutron powder diffraction, by using the G4.1 diffractometer. The structure, refined in R-3c with $a=9.78$ and $c=11.30$ Å, can be described as a triangular lattice that consists of chains, running along the c-axis, alternating face-shared HoO_6 prisms and CrO_6 octahedra, the Sr cations lying between the chains. Long-range antiferromagnetic order occurs around 1 K but this magnetic state has features consistent with partially disorder antiferromagnetism, a state theoretically expected in quasi-1D compounds experiencing geometrical frustration. Two of the three chains on the triangular lattice are found ferromagnetic along c, with an antiferromagnetic coupling between them, the third chain remaining incoherent (Fig. a). This leads to unusual temperature dependence of the magnetic Bragg peaks, with a maximum of intensity at 9K, and a broadening at lower temperature. It also gives rise to puzzling behaviours as exemplified with the pattern of steps on the M(H) curves at low temperature (Fig.b).

V. Hardy et al, *Physical Review B* **74**, 064413 (2006)

[Collaboration: C. Martin and V. Hardy, CRISMAT, UMR6508, CAEN ; G. André, LLB]



[C5. R. Le Toquin] Time-resolved in situ studies of oxygen intercalation into SrCoO_{2.5}, performed by neutron diffraction and X-ray absorption spectroscopy



Evolution of the neutron powder diffraction pattern obtained in situ during the electrochemical oxidation of SrCoO_{2.5} vs charge transfer. The diffractogram of the brownmillerite SrCoO_{2.5} is represented at the bottom, whereas that of the perovskite SrCoO_{3.0} is shown at the top. The dotted ellipsoids show the positions of the superstructure reflections.

reaction product (SrCoO_{3.0}) does not proceed continuously but gives evidence for the formation of O⁻ species for stoichiometries corresponding to SrCoO_{2.82}(0.07)[1]. The use of neutrons (vs X-rays) in the diffraction experiments and the choice of the transmission (vs fluorescence) mode in the XAFS experiment guarantee that the obtained data well represent bulk and not just surface properties.

[1] R. Le Toquin, W. Paulus, A. Cousson, C. Prestipino, C. Lamberti, JACS 128 (2006) 13161-13174

[Collaboration : R. Le Toquin, W. Paulus, Université de Rennes 1, A. Cousson, LLB, C. Prestipino, C. Lamberti, Université de Turin]

[C6. V. Paul-Boncour] Structural and magnetic properties of RMn₂D₆ compounds (R=Y, Dy, Er) synthesized under high deuterium pressure

Hydrogen absorption in RMn₂ Laves Phases (R= Rare Earth) modifies significantly their magnetic properties. For x ≈ 4.5, the RMn₂H_x hydrides crystallize in a structure derived from that of the parent intermetallic, with H atoms in tetrahedral interstitial sites. Applying a hydrogen pressure of several MPa to YMn₂ led to the formation of YMn₂H₆ [1]. According to X-ray (XRD) and neutron powder (NPD) diffraction experiments, YMn₂D₆ crystallizes in a disordered fluorite structure (K₂PtCl₆ type) with a = 6.709(1) Å at 300 K (Fig. 1). In the Fm3m space group, the Y and half of the Mn atoms (Mn1) occupy randomly the 8c site whereas the remaining Mn atoms (Mn₂ in 4a site) are surrounded by 6 H atoms (24e site). This structure is not derived from that of the C15 YMn₂ and the H atoms form covalent bonding with Mn atoms. RMn₂D₆ phases, isostructural to YMn₂D₆, were also obtained starting either from C15 (R =Dy, Ho) or C14 (R=Er) Laves phases. YMn₂D₆ displays a modified Curie Weiss behaviour and the NPD study shows the absence of long range magnetic order. The M(H) curves of the RMn₂D₆ compounds (R=Ho, Dy and Er) at 4.2 K show a ferromagnetic behaviour but the saturation magnetization is only half that of the parent compound. NPD studies on ErMn₂D₆ [2] revealed only local magnetic order of Er moment below 5 K, with ferro and antiferromagnetic correlations (Fig. 2). This has been related to the chemical disorder of R and Mn atoms on the 8c site.

[1] V. Paul-Boncour, S. M. Filipek, M. Dorogova, et al. J. Sol. State Chem., 178 (2005) 356

[2] V. Paul-Boncour, S. M. Filipek, G. André, F. Bourée et al., J. Phys. : Cond. Mat., 18 (2006) 6409

[Collaboration: V. Paul-Boncour, LCMTR Thiais; S.M. Filipek (Poland), G. André, LLB ; F. Bourée LLB]

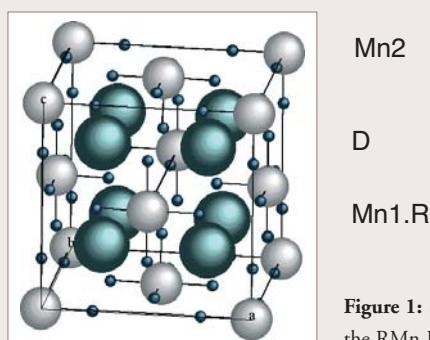


Figure 1: Structure of the RMn₂D₆ compound

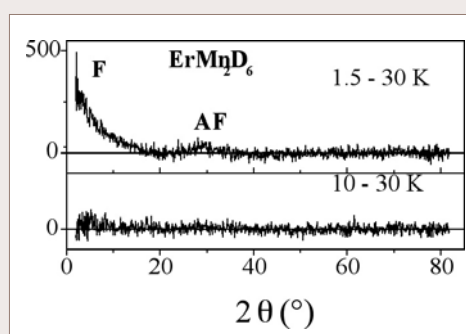


Figure 2: Difference NPD patterns of ErMn₂D₆

STRUCTURE AND PHASE TRANSITIONS

[C7. O.L. Makarova] Role of topology on the magneto-structural coupling in new Laves hydrides

Intricate magnetic and structural phenomena in the Laves phases (RMn_2) and their hydrides come from the magnetic instability (transition from localized to itinerant states) in the Mn sublattice, which is governed by the value of the first-neighbor Mn-Mn distance. On the other hand, the topological frustration in the Mn sublattice could contribute to an unusually strong magneto-structural coupling [1-5]. Recently, progress in high-pressure high-temperature synthesis offered the opportunity to study the magnetic and crystal structures of the same chemical compounds, having the same Mn-Mn distances, but different crystal structures: cubic or hexagonal. Our results show that topology plays a dominant role in the formation of the magnetic ordering (short-range or long-range) and also affects the transition from the localized to the magnetic itinerant state.

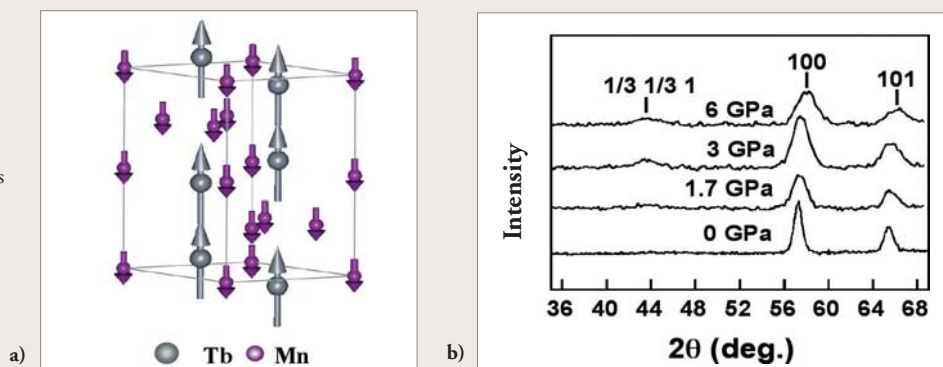
[1] I.N. Goncharenko et al Phys. Rev. B, **56**, 2580, (1997) ; [2] I.N. Goncharenko et al Phys. Rev. B, **59**, 9324, (1999)

[3] O.L. Makarova et al Phys. Rev. B, **66**, 104423, (2002) ; [4] O.L. Makarova et al Phys. Rev. B, **67**, 134418, (2003)

[5] O. L. Makarova et al Solid State Com., **132**, 329, (2004)

[Collaboration: O.L. Makarova, RRC « Kurchatov Institute », Moscow, Russia ; I.N. Goncharenko, I. Mirebeau, F. Bourée, LLB ; A.V. Tsvyaschenko, IHPP, Troitsk, Russia ; L.N. Fomicheva, IHPP, Troitsk, Russia]

Figure: a) Magnetic structure of the hexagonal hydride $\text{TbMn}_2\text{H}_{2.9}$.
b) Magnetic neutron diffraction spectra of $\text{TbMn}_2\text{D}_{2.9}$ measured at different pressures and $T=1.4\text{K}$ at the G6.1 diffractometer. The presence of the $(1/3\ 1/3\ 1)$ reflection indicates a pressure-induced long-range antiferromagnetic component.

**[C8. J. Cambedouzou] Tunable intertube spacing in single-walled carbon nanotubes**

The structure of ternary compounds made of alkali, tetrahydrofuran (THF) and single-walled carbon nanotubes (SWNT) have been investigated using the G6-1 powder diffractometer at LLB [1]. Hydrogen-deuterium substitution in THF allows a layered structure around the nanotubes to be determined. The important changes in the neutron diffraction profile of ternary compounds by comparison with pristine SWNT (figure a) can be understood and simulated assuming that the alkali cations form a monolayer surrounding each tube of the bundle, while THF molecules intercalate between the decorated tubes and at the surface of the bundles (figure b). The structural model we propose also allows to state that the vanishing of the diffraction feature at $0.6\ \text{\AA}^{-1}$ in the $\text{LiC}_{5.88}$ -TDF compound is integrally due to isotopic contrast effects, the structure of both hydrogenated and deuterated compounds remaining exactly the same. In spite of this insertion, the triangular bundle structure is preserved, albeit with a much larger lattice parameter, which depends on the size of the inserted cation.

[1] J. Cambedouzou et al., Phys. Rev. B **72** (2005), 041404(R)

[Collaboration : J. Cambedouzou, S. Rols, N. Bendiab, R. Almairac and J.L. Sauvajol (LCVN Montpellier), P. Petit and C. Mathis (ICS Strasbourg), I. Mirebeau (LLB Saclay), M. Johnson (ILL Grenoble)]

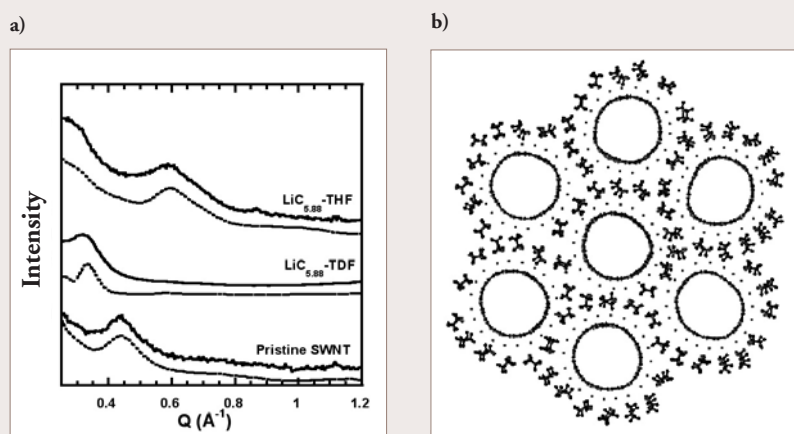


Figure : a) Experimental (plain lines) and calculated (dotted lines) neutron diffraction profiles of hydrogenated (top) and deuterated (center) ternary compounds, and pristine SWNT (bottom). b) Representation of a LiC_6 -THF bundle of seven tubes.

[C9. C. Doussier-Brochard] Magnetic structure of an antimony manganese chlorosulfide MnSbS₂Cl

Relatively to chalcogenides or halogenides, mixed compounds of the halogeno-chalcogenide type have been poorly studied up to now. Among them, quaternary compounds combining a transition metal *TM* with another cation are of special interest for their physical properties, due to the dilution of *TM* in the crystal matrix and the competition of the two types of cations versus the two ligands.

The crystal structure of MnSbS₂Cl can be described as edge-sharing MnS₄Cl₂ octahedra along the *b*-axis, and corner-sharing along the *a*-axis, forming waved layers separated by Bi atoms. The magnetic susceptibility versus temperature, shows a large maximum, around 39 K, characteristic of a low-dimensional anti-ferromagnetic behaviour, following by an increase at 27K.

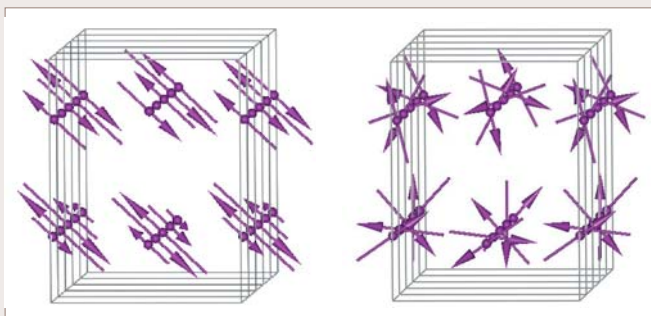
To elucidate this magnetic behaviour, powder neutron diffraction experiments were performed on the multi-detector G4.1 and allowed us to solve the magnetic structure and its thermal evolution [1]. Below T_N=35 K, a complex 3D long-range antiferromagnetic ordering takes place, characterized by an incommensurate 1D propagation wave-vector along the *b*-axis, equal to $k = [0, 0.3838, 0]$. The Rietveld refinements give two possible modulation models, sinusoidal and helicoidal, with similar magnetic reliability factors and a moment of 4.5 μ_B on Mn at 1.5 K.

MnSb₂S₄ and MnPb₄Sb₆S₁₄, which present chains of MnS₄ octahedra separated respectively by 6 and 16 Å, have been also studied to show the evolution of magnetic structure versus 2D or 1D organization [2].

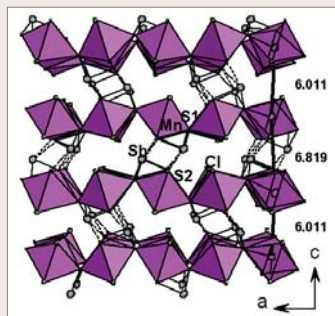
[1] C. Doussier, G. André, P. Léone, E. Janod, Y. Moëlo, Journal of Solid State Chemistry, 179 (2006) 486

[2] C. Doussier, thesis, Université de Nantes (2006)

[Collaboration : C. Doussier, P. Léone, E. Janod, Y. Moëlo Université de Nantes, G. André, LLB]



Magnetic structure with sinusoidal (left) or helicoidal (right) modulation



Crystal structure of MnSbS₂Cl

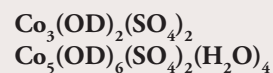
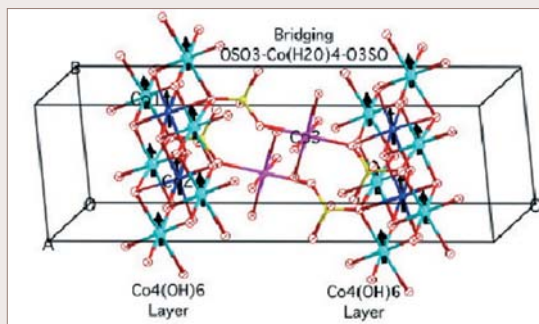
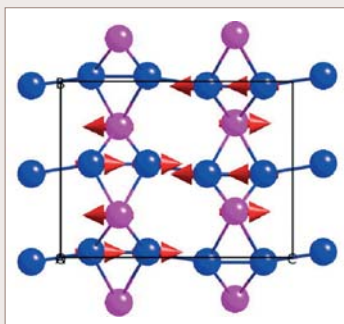
[C10. S. Vilminot] Magnetic structures of the synthetic magnetic minerals based on hydroxysulfates of divalent metals, Co₃(OD)₂(SO₄)₂, Co₅(OD)₆(SO₄)₂(H₂O)₄, Cu₄(OD)₆SO₄

High-resolution (3T2) and high-flux (G4.1) neutron powder diffraction (NPD) data have been used to determine the nuclear and magnetic structures of a series of M^{II}-hydroxysulfates, M = Mn, Co, Ni and Cu, as part of an ongoing project to understand short-range (SRO) and long-range (LRO) magnetic ordering and geometrical frustration caused by μ₃-OH bridges. For the M₃(OD)₂(SO₄)₂ series which are canted antiferromagnets [T_N = 42 (Co), 26 (Mn) and 29 K (Ni)], the Ni exhibits collinear moments along *b* while for Co and Mn the moments lie in the *ac*-plane with a rare co-existence of SRO and LRO.[1]

Co₅(OD)₆(SO₄)₂(H₂O)₄ consists of triangular Co^{II}-OH layers pillared by ...O₃SO-Co^{II}(H₂O)₄-OSO₃...and it behaves as a ferromagnet below 14 K.[2] Extensive magnetization by varying temperature, field and pressure and heat capacity measurements and NPD reveal an easy-plane XY-magnet where the moment of the pillaring Co remains random. Due to slight anisotropy in the layer the moments are oriented along *b*. These results demonstrate, for the first time, the existence of LRO in a single layer.

Cu₄(OD)₆SO₄ has a complex corrugated layered structure and it behaves as a canted AF. NPD was modelled with the moments oriented collinearly perpendicular to the corrugated planes with alternation along ±*a* for neighbouring chains within double chains building up the planes [3].

[Collaboration : S. Vilminot, IPCMS, Strasbourg; G. André, F. Bourée-Vigneron, LLB; M. Kurmoo, ULP, Strasbourg]



[1] M. Ben Salah *et al.*, Chem. Mater. 17 (2005) 2612-2621.

[2] M. Ben Salah *et al.*, J. Am. Chem. Soc. 128 (2006) 7972-7981.

[3] S. Vilminot *et al.*, Dalton Trans., (2006) 1455-1462.

STRUCTURE AND PHASE TRANSITIONS

[C.11. M. Giot] Magnetic structure of the charge ordered $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ manganites.

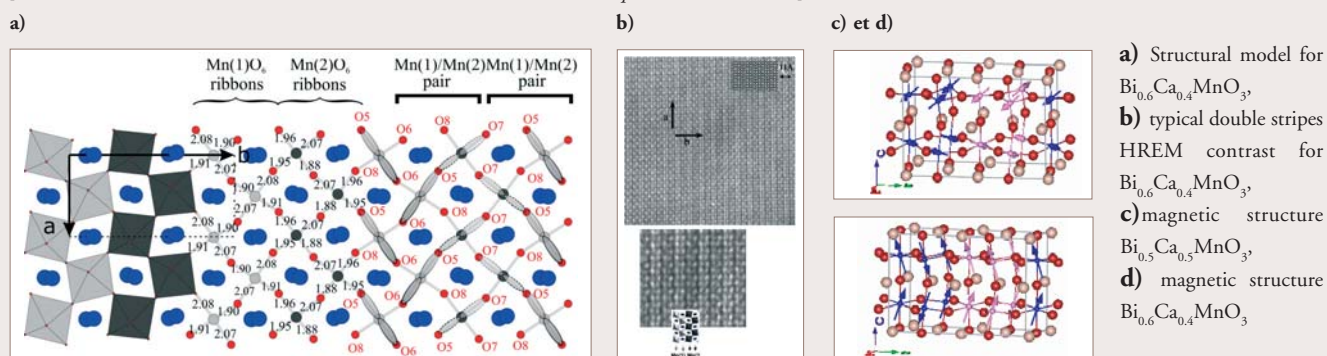
Within the thesis of M. Giot [1], crystals and polycrystalline sample were synthesized to study the magnetic and nuclear structure of the charge ordered $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ $0.5 \leq x \leq 0.64$ manganites. The “Zener polaron ordering” model based on the $P2_1nm$ space group and the “classical $\text{Mn}^{3+}/\text{Mn}^{4+}$ ordering” model based on $P2_1/m$ space group were refined from single crystal X-Ray diffraction [2]. For the three crystals ($x = 0.55, 0.60, 0.64$) the $P2_1nm$ space group allowed the best fitting. A common model for the charge ordered structure (Fig. a) was proposed: the two Mn site have a valence equal to 3.5 and the structure consists on the alternation of double ribbons of $\text{Mn}(1)\text{O}_6$ and $\text{Mn}(2)\text{O}_6$ octahedra. The HREM images were well simulated with this model (Fig. b). The evolution of the anti-ferromagnetic structure with the Bi/Ca ratio study was performed on the powder diffractometer G4.1 at LLB. The data can be refined with different physical models, in particular the classical CE-type model is one of the solutions for $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ manganites with $x = 0.5$ (Fig. c). The moments tend to establish a ferromagnetic coupling with increasing x (Fig. d).

[1] « Etudes structurales et magnétiques de manganites $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ présentant des mises en ordre complexes »

co-financed by CEA and Region BASSE-NORMANDIE : performed between LLB CEA Saclay and CRISMAT Caen.

[2] M. Giot et al Chem. Mat. 18 (14): 3225-3236 (2006).

[Collaborations : LLB, CRISMAT-Caen, M. Nevřiva and K. Knize-Czech Republic, P. Roussel-Lille]

**[C12. D. Bazin] Structural study of pathological calcification : the case of kidney stones**

Urolithiasis constitutes a serious health problem that affects 3 to 20% of the population. Calculi may be composed of various inorganic and/or organic compounds. Ca oxalate (70% of the cases), Ca and Mg phosphates (15%) and uric acid (10%) are the main common components. A site of initial crystallization has been described in the 1930's by Randall. Due to their contribution to the pathogenesis of calcium urinary stones, Randall's plaques (fig. 1) have been the subject of numerous researches. The aim of this study was to determine the structural characteristics of kidney stones which have similar chemical formula i.e. the carbonate apatite. Powder Neutron Diffraction (P.N.D.) indicates that apatite crystallites contain a very small number of units cells in which Ca and phosphate groups have the spatial arrangement of apatite (fig. 2). Moreover, a significant anisotropy in the morphology of these entities is observed. Then, these "nanobiocrystals" may constitute needles-like and finally spherical objects as observed by Scanning Electronic Microscopy (S.E.M.) (fig. 3). The complete set of data give thus major structural information on these biological entities which lead to an understanding of the first steps of the genesis of the Randall's plaques.



Figure 1. "Giant" Randall's plaque

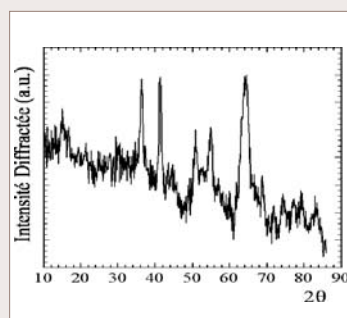


Figure 2. P.N.D. of an urinary stone

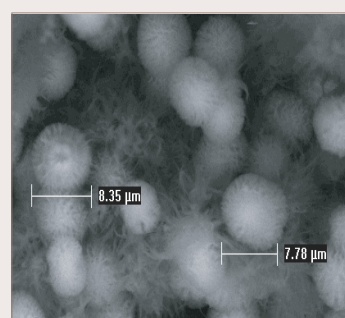


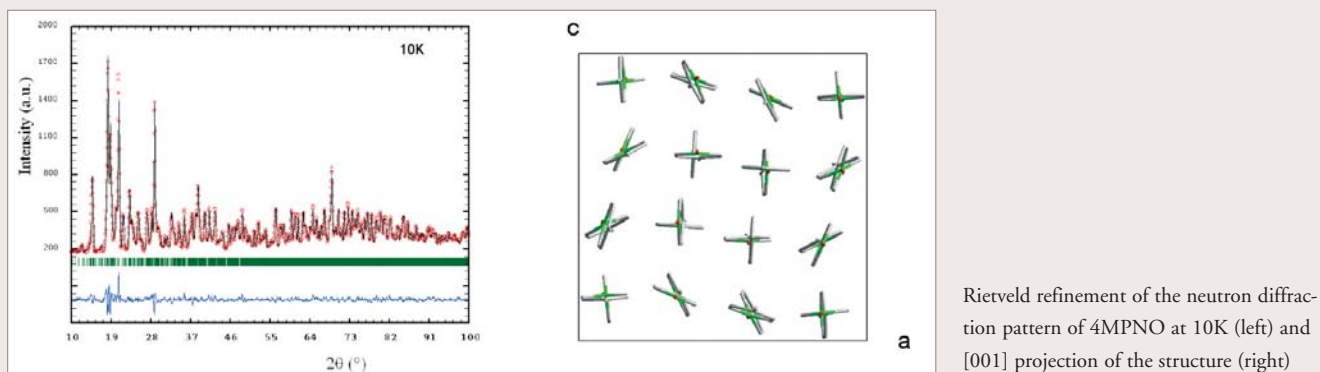
Figure 3. S.E.M. micrograph of an urinary stone

D. Bazin et al. Ann Biol Clin 2006 ; 64 (2) : 125-39. [Collaboration M. Daudon (AP-HP, Necker), D. Bazin (LPS), A. Mazouyes (Ecole Centrale Paris, LPS), P.A. Albouy, A. Thiaville, S. Rouzière, O. Stephan, A. Glotter (LPS), G. André, A. Cousson (LLB), E. Foy, P. Chevalier (Lab. P. Sue), G. Matzen, E. Veron (CRMHT), E. Elkaim, D. Thiaudiere (Soleil)].

[C13. F. Damay] Synchrotron and neutron diffraction structural study of 4-methylpyridine-N-oxide (4MPNO) at 10K
 Combined synchrotron and neutron powder diffraction have been used to solve the structure of fully deuterated 4MPNO at 10 K. Using a simulated annealing algorithm on the synchrotron data, we were able to propose a structural model for 4MPNO, which involves a tetragonal cell with space group $P4_1$ ($a = b = 15.410(2)\text{\AA}$, $c = 19.680(3)\text{\AA}$). This model gives an excellent fit to both sets of diffraction data (Figure 1, left), even though it is impossible to rule out entirely other molecular arrangements. In our model, the asymmetric unit contains 8 molecules exhibiting a complex pattern of reorientations around the three cell axes (Figure 1, right). Along c , two columns of roughly perpendicular molecules alternate with two columns of molecules tilted by about 40° . This pattern is actually reminiscent of a combination of the 250 K and 100 K structures of 4MPNO, respectively [1]. Moreover, in sharp contrast with the simpler structure of parent compound 4-methylpyridine (4MP) at 10 K, the fourfold symmetry for methyl pairs and the translational invariance of the methyl sites are destroyed, as the molecular site symmetry in $P4_1$ is 1. The thermal ellipsoids calculated from the TLS matrix also show that the methyl groups are now largely localised. As a consequence, unlike 4MP, rotational dynamics in 4MPNO cannot be described by the quantum sine-Gordon model in 1D. Our results suggest two kinds of methyl-methyl interaction: along infinite chains parallel to a and b on the one hand, and between perpendicular chains through pairs of face to face methyl groups along c on the other [1].

[1] F. Damay et al, Acta Crystallogr. B 62, 627-633 (2006).

[Collaborations: F. Damay, A. Carretero-Genevri, A. Cousson, J. Rodriguez-Carvajal, LLB, F. Fillaux, LADIR, W. Van Beek, ESRF].



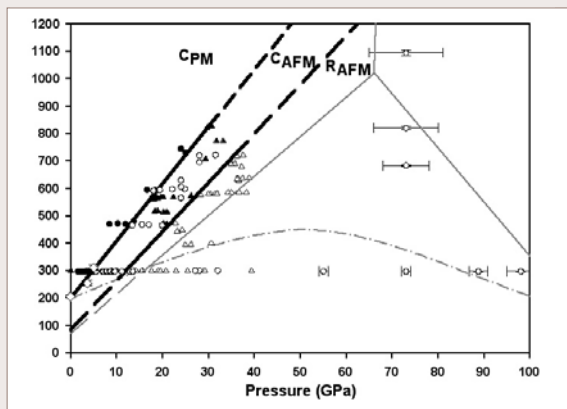
[C14. L. S. Dubrovinsky] High-pressure magnetism in geophysically important materials FeO and MnO

Magnetic ordering influences the density, bulk modulus, and elastic constants of materials. Developments of models of the Earth and analysis of the acoustic data, which provide the main experimental information on the Earth's interior, require direct information on magnetic properties of geophysical materials. Wüstite (FeO), the end-member of the magnesiowüstite MgO-FeO solid solution and the second abundant mineral in the Earth's lower mantle, is a good example of such a "geomaterial". Our combined Mössbauer, acoustic and neutron diffraction studies [1] show that the magnetic ordering temperature rapidly increases with pressure (Figure) and that pressure results in a considerable softening of the elastic modulus. The study established the existence of a magnetically ordered cubic phase of wüstite (Figure). This behavior differs from the other prototype antiferromagnetic oxide, MnO [2]. Below 3.5 GPa the magnetic ordering transition coincides with the structural transition, whereas at higher pressures the two transitions decouple, and the lattice distortion occurs at higher temperatures than the magnetic transition. Our results show that the structural transition (rhombohedral distortion) in transition metal monoxides is not directly coupled with the long-range magnetic ordering.

[1] A. P. Kantor, S. D. Jacobsen, I. K. Kantor, L. S. Dubrovinsky, C. A. Mc. Cammon, H. J. Reichman, I. N. Goncharenko, Phys. Rev. Lett. 93, 215502 (2004).

[2] A.P. Kantor, L. S. Dubrovinsky, N. A. Dubrovinskaia, I. Y. Kantor, I. Goncharenko, J Alloys Compounds 401, 42-45 (2005).

[Collaboration : L.S. Dubrovinsky, I.Yu. Kantor, A.P. Kantor, (Bayerisches Geoinstitut), N. A. Dubrovinskaia (Lehrstuhl für Kristallographie, Universität Bayreuth), I.N. Goncharenko (LLB)]



Phase diagram of non-stoichiometric wüstite. Black lines – phase boundaries between cubic paramagnetic (C_{PM}), cubic antiferromagnetic (C_{AFM}), and rhombohedral antiferromagnetic (R_{AFM}) phases obtained in this study. Circles – Mössbauer spectroscopic runs: solid circles – paramagnetic phase, open circles – magnetically ordered phase. Triangles – X-ray diffraction studies: solid triangles – cubic phase, open triangles – rhombohedral phase. Diamonds are T_N values obtained from neutron diffraction studies. The structural phase boundary of Fei and Mao (Fei and Mao, 1994) and the magnetic phase boundary proposed by Badro et al. (Badro et al., 1999) are also shown for comparison in gray color. Letters C, R, and B8 designate cubic, rhombohedral and NiAs-like hexagonal phases, PM and AFM – paramagnetic and antiferromagnetic phases, respectively.

