

## **AXIS 1 Research: Strongly Correlated Quantum Materials and Magnetism**

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### **Scope**

This scientific axis encompasses research activities on a large variety of magnetic and/or strongly correlated electron systems (SCES). Included are studies of unconventional superconductors (cuprates, pnictides), geometrically frustrated pyrochlore magnets (spin ices), novel magnetic orders in 4f-electron systems (heavy fermions, Kondo insulators), multiferroic compounds with interplay between electric and magnetic orders, manganites with giant magnetoresistance properties, and molecular magnets. The techniques involved are neutron diffraction and inelastic neutron scattering, with the optional use of polarized neutrons.

During the period from 2008 to 2010, 144 publications have been produced on these topics, and 18 invited reports have been given at international conferences. This scientific area also involves 3 ANR projects, 4 RTRA projects (“Triangle de la Physique”), and 1 JRA project (NMI3-7th Framework Program of the European Commission).

## Current Research

The field of strongly correlated electron systems (SCES) covers a wide range of materials and physical phenomena which go beyond the standard theory of a Fermi gas of non-interacting electrons. The composition of these compounds usually involves transition metals or rare earth oxides, hydrides or intermetallics. The interactions between electrons allow several degrees of freedom such as spin, charge, lattice, or orbital to be simultaneously active. Original features in SCES are studied at LLB, both through experiment and theory. The competition between different phases and interactions induces a great variety of magnetic phenomena, ground states, and phase transitions, ranging from **unconventional superconductivity** or **multipolar orders** to **photomagnetism**. When interactions are short-range, the specific geometry of the lattice plays a crucial role, which raises the possibility of fine-tuning the magnetic states through geometrical frustration or spin-lattice coupling (**spin ices**, **multiferroics**). Because of their complex energy balance, materials from this class can exhibit anomalously large responses to small perturbations, such as the **giant magnetoresistance in manganites**, and open the way to new functionalities (e.g., spintronics and photoswitchable compounds). Interesting states may also occur under extreme conditions (e.g., very low temperatures, high magnetic field or high pressure). The neutron probe is likely the best tool to study their properties from a microscopic standpoint, since it is sensitive to spin and lattice ordered states and low-energy excitations, and its polarization state can further be controlled and monitored by appropriate techniques. The main areas of research studied in LLB are summarized below.

### **Unconventional superconductivity: neutron spectroscopy and theory**

In the last two decades, new superconducting (SC) compounds, exhibiting surprisingly high critical temperatures ( $T_c$ ), have been discovered. In contrast to conventional superconductors, the SC order parameter is not isotropic, neither in cuprates nor in Fe-based systems. This ignited a search for new SC pairing mechanisms based on the existence of rather strong electronic interactions. These interactions further render the materials extremely unstable against long-range ordering, which can either favor or compete with superconductivity, and thus give rise to extraordinarily rich phase diagrams

## Organization

The experimental work on SCES carried out at the LLB is based on a versatile instrument suite implementing different neutron-scattering techniques.

- I. Inelastic scattering on triple-axis spectrometers: study of the lattice and magnetic excitation spectra. The LLB operates two thermal-neutron (1T, 2T) and three cold-neutron (4F1, 4F2, G4-3) triple-axis spectrometers. The 2T and 4F1 instruments can be equipped with a polarized neutron setup (linear polarization analysis).
- II. Single-crystal neutron diffraction: study of crystalline and magnetic ordered states. These instruments include a four-circle diffractometer on a hot neutron source (5C2); a four-circle diffractometer on a thermal beam (6T2), which can also be operated in a two-axis mode with a lifting detector; and a two-axis diffractometer with polarized hot neutrons (5C1), specially designed for measuring spin density maps. The 6T2 instrument was recently equipped with a 2D multidetector.
- III. Powder neutron diffraction: characterization of crystalline and magnetic orders. This instrument suite consists of one high-resolution diffractometer with thermal neutrons (3T2) devoted to crystalline studies, one diffractometer (G4-1) on a cold neutron guide for the determination of magnetic structures, and one long-wavelength diffractometer (G6-1) optimized for high-pressure studies.

Three groups with specific experimental expertise are in charge of the above spectrometers. This responsibility involves the operation and upgrade of the instruments and their sample environments, as well as providing the technical and scientific support to visitors who perform experiments at the LLB. The research projects described hereafter involve close collaborations between members of the different groups since most studies actually require the use of several types of spectrometers. Collaborations with external teams are also essential. In particular, chemistry laboratories can supply new materials, in the form of powder or single crystal samples. Obtaining large, high-quality, single crystals is generally a prerequisite for undertaking inelastic neutron experiments. Other collaborations make it possible to study or characterize the same samples by probes other than neutrons (e.g., x-rays, bulk magnetization, resistivity, Mössbauer or NMR spectroscopy, etc.). These close relationships both inside and outside LLB, together with a constant effort to optimize the performance of the instruments, are the keys to meeting the standards of top level research in the present international context.

### The spin resonance-mode scenario in high- $T_c$ cuprates

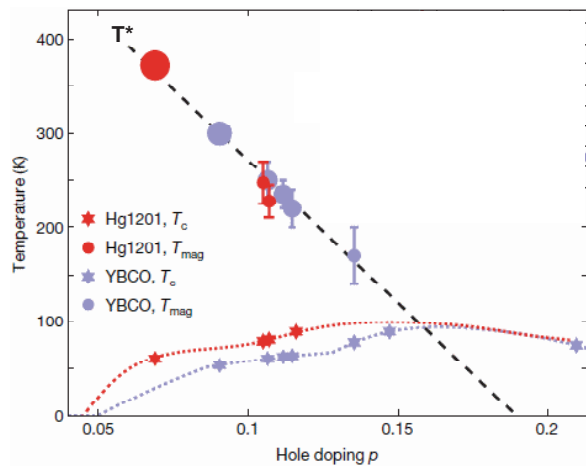
In conventional superconductors, the electron pairing interaction is mediated by an exchange of phonons. In the framework of Eliashberg theory, anomalies in the charge excitation spectrum, probed by tunneling and optical conductivity measurements, were directly connected to the density of phonons, measured by inelastic neutron scattering, thereby providing evidence for the leading role of electron-phonon coupling in these materials. In high- $T_c$  cuprates, on the other hand, the mechanism responsible for superconductivity is still unknown despite 20 years of intensive research. Nevertheless, the observed structure of the low-energy electron spectrum is often considered to be the fingerprint of a strong electron coupling to some boson, which in turn is suspected to be a mediator of the SC pairing. In those materials, strong antiferromagnetic (AF) spin fluctuations, termed “spin-resonance” modes, were observed in the SC state by inelastic neutron scattering. Following early theoretical studies carried out at LLB, these excitations are now well understood as triplet excitons. The theory group has recently developed an improved version of the Eliashberg theory, and has shown<sup>1</sup> that spin-resonance modes could explain significant anomalies observed in the SC high- $T_c$  cuprates: the d-wave SC pairing, the U-shaped angular dependence of the SC gap, the anomalous form of the electron density of states, and the renormalization of the electronic dispersion. This work establishes the scenario of spin-resonance-mediated superconductivity on solid theoretical grounds.

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<sup>1</sup> *Superconducting Pairing through the Spin Resonance Mode in High-Temperature Cuprate Superconductors*  
F. Onufrieva and P. Pfeuty, Phys. Rev. Lett. **102**, 207003 (2009).

## Unconventional magnetic order in the pseudogap state of high- $T_c$ cuprates

Whereas ascertaining the origin of superconductivity in cuprates remains one of the major challenges posed to condensed matter physics, the anomalous electronic properties of those materials outside the SC state constitutes another, equally elusive, mystery. In particular, the low-energy electrons become partially gapped well above  $T_c$  in the so-called pseudogap phase (Figure 1.1). Recent, highly accurate, polarized neutron diffraction measurements have demonstrated the existence of a long-range magnetic order developing below the pseudogap-opening temperature  $T^*$ . This pioneering work performed at LLB has stimulated international



**Figure 1.1.** Universal pseudogap phase diagram: dependence on hole doping ( $p$ ) of the superconducting critical temperature  $T_c$  and the ordering temperature  $T_{mag}$  associated with the appearance of an unconventional magnetic phase in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (YBCO) and  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg1201).  $T_{mag}$  matches the temperature  $T^*$  (dashed line), corresponding to the opening of the so-called pseudogap state, as derived from other types of measurements. From Ref. [2].

collaborations with several groups in the USA (H. Mook, Oak Ridge National Laboratory; M. Greven's group, Stanford University). Our observation was subsequently confirmed in two distinct families of cuprates,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  and  $\text{HgBa}_2\text{CuO}_{4+\delta}$ <sup>2</sup>. The magnetic phase breaks time-reversal symmetry, but preserves the lattice translation invariance. This implies the existence of staggered magnetic moments within each unit cell. The observed magnetic correlations are distinct from the usual antiferromagnetic spin-correlation, which are well documented from previous inelastic neutron scattering (INS) measurements. Here, in contrast, they are thought to possess an orbital-like character and could originate from nanoscopic current loops, as initially proposed by C.M. Varma in his theory of the pseudogap phase. The neutron scattering measurements indeed provide the first experimental evidence that the pseudogap phase is a long-range-ordered phase, competing with superconductivity in cuprates. The search for this novel magnetic phase is now being extended to other cuprate families, such as  $\text{La}_{2-x}\text{SrCuO}_4$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  through new collaborations with other groups in France (I. Laffez, LEMA, Université de Tours) and Switzerland (J. Mesot, Paul Scherrer Institute, Villigen).

## Instability towards a so-called electronic nematic state in cuprates.

Recent INS measurements, carried out in strongly underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$  ( $T_c = 35$  K), have demonstrated the existence of quasi-one-dimensional (1D) incommensurate spin fluctuations, developing spontaneously below 150 K<sup>3</sup>. This observation highlights the spontaneous breaking of rotational invariance in the system. On cooling down, the lattice translation invariance is further broken, while incommensurate spin fluctuations freeze at short distance. Static correlations can be enhanced by applying an external magnetic field. In addition to INS measurements, electrical transport properties exhibit a significant 1D anisotropy, while quantum oscillation measurements in high magnetic fields suggest a folding of the electronic band structure, which is associated with a state which breaks the lattice translation invariance. All these findings point toward the existence of an electronic nematic instability, where rotational symmetry is spontaneously broken at long distance as a result of strong electronic interactions. This instability leads to an electronic smectic state when the translation invariance is further broken. Such mechanisms are also regarded as likely candidates for explaining the anomalous electronic properties of cuprates in the pseudogap phase. These results are the fruit of a long-standing collaboration between the LLB and the MPI in Stuttgart.

<sup>2</sup> Unusual magnetic order in the pseudogap region of the superconductor  $\text{HgBa}_2\text{CuO}_{4+\delta}$

Y. Li, V. Balédent, N. Barišić, Y. Cho, B. Fauqué, Y. Sidis, G. Yu, X. Zhao, P. Bourges, M. Greven, Nature **455**, 372-375 (2008).

<sup>3</sup> Electronic Liquid Crystal State in the High-Temperature Superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$

V. Hinkov, D. Haug, B. Fauqué, P. Bourges, Y. Sidis, A. Ivanov, C. Bernhard, C. T. Lin, B. Keimer, Science **319**, 597 (2008).



## Magnetic superconducting “glue” for Fe-based superconductors?

Non-superconducting  $M\text{Fe}_2\text{As}_2$  ( $M$ : Ca, Fe) shows a crystallographic transition from a tetragonal phase to an orthorhombic phase, accompanied with an AF spin-density wave order. Upon doping with either electrons or holes, the structural and magnetic transitions vanish and the system becomes superconducting. The unconventional “ $s+/-$ ” SC order parameter is believed to reflect an attractive interaction mediated by the exchange of strong AF fluctuations inherited from the spin-density-wave state. Within a collaboration between the MPI Stuttgart (B. Keimer’s group), FRM-II Munich and the LLB, the AF spin excitation spectrum in electron-doped  $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$  was recently mapped out at temperatures spanning the transition from the normal to the SC state. Furthermore, the dynamic spin susceptibility could be determined in absolute units<sup>4</sup>, providing highly valuable information for theories and allowing the coupling strength between electrons and spin fluctuations to be quantitatively evaluated. The role of lattice vibrations in superconductivity was also investigated in non-SC  $M\text{Fe}_2\text{As}$  by the Karlsruhe group at LLB in collaboration with Th. Brückel and his collaborators (Forschungszentrum Jülich, Germany). INS measurements of the phonon dispersions and comparison with density functional theory (DFT) calculations indicate that theory correctly reproduces most phonon frequencies, but fails to account for the anomalous temperature dependence of some modes.<sup>5</sup> The coupling of vibrational and electronic degrees of freedom appears stronger than predicted by DFT and the role of phonons in the superconductivity of Fe-based superconductors could be more significant than anticipated. The importance of both magnetic and lattice degrees of freedom is further supported by first-principle calculations carried out at LLB<sup>6</sup> for FeSe, another newly-discovered iron-based superconductor. Spin-polarized calculations of all frozen phonons at the Brillouin zone center show a significant deformation of the electronic band structure near the Fermi level for several modes involving a displacement of the chalcogen. The particular  $B2u(\text{Se})$  phonon mode shows a strong linear coupling with the AF order parameter, leading to a substantial electron-phonon coupling, which can partly account for the superconducting critical temperature  $T_c$  when the weak coupling BCS theory is used. Nevertheless, the strong linear coupling of this  $B2u(\text{Se})$  mode with the magnetic order parameter strongly suggests that magnetic fluctuations are another necessary ingredient to fully account for the high  $T_c$  observed in this system.

## Novel electronic and magnetic properties in 4f-electron systems

4f electrons are known to be more localized than d electrons and subject to strong spin-orbit coupling. Instabilities of otherwise magnetic 4f states occur mainly in metallic compounds as a result of hybridization with conduction band states, as described in the well-known Anderson model. This approach basically describes a competition between exchange interactions and Kondo-type magnetic fluctuations, producing renormalized Fermi-liquid quasiparticle states, heavy effective masses and, in some cases, “heavy-fermion superconductivity”. Some materials do not fit into this framework, however, because other degrees of freedom (such as the multipole moments) are involved, or because the renormalization leads to a semiconducting ground state (“Kondo insulators”).

## Unconventional ordered states: competing dipole and multipole interactions

Whereas neutron diffraction techniques remain unchallenged in solving intricate magnetic structures, systems in which spin and orbital degrees of freedom are intimately coupled require more diversified approaches. This type of situation occurs in  $f$ -electrons exhibiting various types of “multipole orders” at low temperature, such as skutterudites or hexaborides. The best-known example is  $\text{CeB}_6$ , which shows a mixed order of Ce quadrupole and octupole moments in a narrow temperature range (“phase II”:  $2.3 < T < 3.2$  K in zero field), prior to developing a long-range order of magnetic dipole moments. A field-induced ( $H \parallel [001]$ ) magnetic contribution ascribed to the ordered  $T_{xyz}$  octupole moments was observed

<sup>4</sup> Normal-state spin dynamics and temperature-dependent spin-resonance energy in optimally doped  $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$   
D. S. Inosov, J. T. Park, P. Bourges, D. L. Sun, Y. Sidis, A. Schneidewind, K. Hradil, D. Haug, C. T. Lin, B. Keimer, V. Hinkov, Nature Physics **6**, 178 (2009).

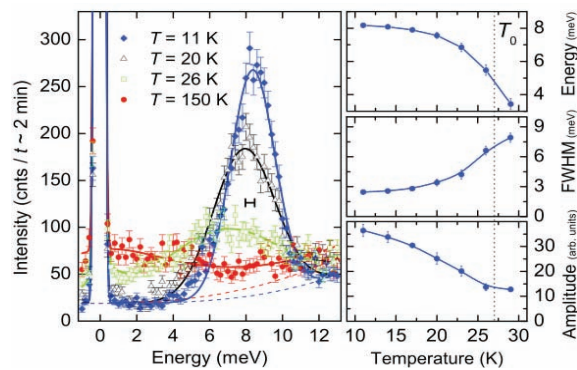
<sup>5</sup> Measurement of Anomalous Phonon Dispersion of  $\text{CaFe}_2\text{As}_2$  Single Crystals Using Inelastic Neutron Scattering  
R. Mittal, L. Pintschovius, D. Lamago, R. Heid, K-P. Bohnen, D. Reznik, S. L. Chaplot, Y. Su, N. Kumar, S. K. Dhar, A. Thamizhavel, and Th. Brueckel, Phys. Rev. Lett. **102**, 217001 (2009).

<sup>6</sup> Strong electron-phonon coupling in  $\text{Be1-xB2C2}$ : ab initio studies  
A.H. Moudden, Eur. Phys. J. B **64**, 173 (2008).

for the first time in neutron diffraction experiments performed at LLB (collaboration with Tohoku University, Sendai and JAEA, Tokai). Substituting Ce by other lanthanide elements with different ground state multiplets ( $2S+1L_J = {}^1S_0, {}^2F_{5/2}, {}^3H_4, {}^4I_{9/2}$  for La, Ce, Pr, and Nd, respectively), one can selectively tune the different multipole moments and study the effect on the ordering properties of the material. Studies of the (Ce,Pr)B<sub>6</sub>, (Ce,Nd)B<sub>6</sub>, and (La,Pr)B<sub>6</sub> series, carried out in a collaboration between the LLB (neutron diffraction), Hiroshima University (bulk properties), and Spring-8 (synchrotron x-ray diffraction), led to the characterization of several new ordered phases in the temperature–magnetic field phase diagrams for different compositions, whose relative stability ranges can be traced back to the interplay between multipole interactions of different orders and symmetries.<sup>7,8</sup>

Recently a new material, CeRu<sub>2</sub>Al<sub>10</sub>, became the focus of considerable attention: despite being a seemingly innocuous intermetallic Ce compound, it appears to be on the verge of a semiconducting state, which can be stabilized under a moderate pressure of ~ 1 GPa, but subsequently collapses above 3 GPa. This dramatic effect is directly connected to an elusive phase transition occurring at  $T_0 = 27$  K, whose order parameter remains controversial. Superstructure satellites were observed in a powder diffraction experiment on G4-1,<sup>9</sup> and proven to be magnetic (wave vector  $\mathbf{k}_{AF} = [1,0,0]$ ) using neutron polarization analysis on 4F1. However, the simplest antiferromagnetic structure suggested by the neutron measurements fails to explain the recent results from Al NMR. Furthermore, INS data performed on powder (Figure 1.2) indicate that the main peak developing at about 8 meV below  $T_0$  has a mixed (magnetic + nuclear) character. This suggests that the transition does not reduce to a conventional antiferromagnetic ordering, and more detailed investigations have been undertaken to clarify this important question.

### Kondo insulators and related boride compounds



**Figure 1.2.** Constant-Q scans ( $Q = 1.5 \text{ \AA}^{-1}$ ) measured on CeRu<sub>2</sub>Al<sub>10</sub> powder as a function of temperature, showing a broad excitation peak around 8 meV in the ordered state below  $T_0 = 27$  K, whose spectral weight transfers to a quasielastic signal in the paramagnetic state. Right frames (top to bottom): energy, full width at half maximum, and peak intensity of the inelastic peak. From Ref. [9].

“Kondo insulators” (KIs) form a unique class of strongly correlated *f*-electron compounds, in which the renormalization of electronic states occurring at low temperature causes the opening of a narrow gap in the density of states, rather than an enhancement of Fermi-liquid quasiparticle masses as found in heavy-fermion systems. They are the subject of a long-standing collaboration with the Russian Research Center “Kurchatov Institute” in Moscow. In previous INS studies, the archetype compound YbB<sub>12</sub> was shown to develop a peculiar magnetic response in its KI state below  $T^* \approx 50$  K, dominated by a spin gap and three distinct magnetic excitations. The lower peak, in particular, was ascribed to a spin-exciton (in-gap) mode due to antiferromagnetic correlations and mapped out in *Q* space using both polarized and unpolarized triple-axis measurements. Lutetium dilution experiments subsequently showed that the spin gap opening is not primarily a coherence effect, as assumed in the usual “hybridization-gap” picture, but could reflect the formation of an array of local singlet-states. Recently, substitution of (trivalent) Yb by (tetravalent) Zr was used to probe the contribution of *d*-electron states to the latter mechanism. The results indicate that, at variance with the Lu

<sup>7</sup> *Magnetic order and multipole interactions in Ce<sub>x</sub>Pr<sub>1-x</sub>B<sub>6</sub> solid solutions*

J.-M. Mignot, G. André, J. Robert, M. Sera, and F. Iga, Phys. Rev. B 78, 014415 (2008)

<sup>8</sup> *Effect of Nd substitution on the magnetic order in Ce<sub>x</sub>Nd<sub>1-x</sub>B<sub>6</sub> solid solutions*

J.-M. Mignot, J. Robert, G. André, M. Sera, F. Iga, Phys. Rev. B 79, 224426 (2009)

<sup>9</sup> *Long-range order and low-energy magnetic excitations in CeRu<sub>2</sub>Al<sub>10</sub> studied via neutron scattering*

J. Robert, J.-M. Mignot, G. André, T. Nishioka, R. Kobayashi, M. Matsumura, H. Tanida, D. Tanaka, M. Sera, Phys. Rev. B, Rapid Commun. 82, 100404R (2010).

case, the spin gap is partially filled, entailing a stronger suppression of the exciton peak than with Lu.<sup>10</sup>

Other intriguing aspects of these dodecaborides concern their lattice dynamics. In these materials, the rare-earth ions are rather loosely bound inside a rigid boron network. It was shown previously for YbB<sub>12</sub> that the phonon modes associated with Yb vibrations occur at an energy close to that of the “exciton” peak, and that their intensity is anomalously enhanced on cooling in the temperature region where Kondo properties develop. This might result from a coupling between low-energy magnetic and phonon excitations. Recently, *ab-initio* calculation and INS measurements performed on superconducting ZrB<sub>12</sub> revealed that similar “quasiloal” Zr vibration modes exist and make an appreciable contribution to the electron-phonon interactions.<sup>11</sup> They might thus play a role in the rather high transition temperature  $T_c = 6$  K of this compound.

### Geometrical frustration in the pyrochlore lattice: spin liquids and spin ices.

In chemically ordered compounds with short-range magnetic interactions, geometrical frustration appears when all interactions cannot be satisfied simultaneously due to the lattice geometry. A well-known example is a triangle of antiferromagnetically coupled spins. This frustration results in a strong degeneracy of the ground state, since many configurations have the same energy. It now appears as a powerful ingredient for designing materials or tuning physical properties, since frustrated magnetic states may be easily switched by small changes in the energy balance. Pyrochlores R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (where R<sup>3+</sup> is a rare earth ion) are model systems showing exotic short-range magnetic orders called “spin liquids” and “spin ices”, with unconventional excitations akin to magnetic monopoles, and a huge sensitivity to perturbations. Various aspects have been studied in collaborations with P. Bonville and A. Forget (IRAMIS/SPEC, Saclay), G. Dhalle and C. Decorse (ICMMO, Orsay), and H. Mutka (ILL, Grenoble).

### Local susceptibility in R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores (R = Tb, Ho, Yb, Er)

Rare earth titanate pyrochlores of *Fd-3m* space group, where the R<sup>3+</sup> ions occupy the summits of corner-sharing tetrahedra and the Ti<sup>4+</sup> ions are nonmagnetic, show very different ground states, such as spin-liquid (Tb) and spin-ice (Ho) states, short range orders, planar antiferromagnetism (Er), and 2D ferromagnetism (Yb). Their physics is governed by the exchange and dipolar interactions between the R<sup>3+</sup> ions, together with the crystal-field anisotropy along the  $\langle 111 \rangle$  axes. The study of the paramagnetic state under applied fields points to precursor effects of these ground states. Single-crystal polarized neutron diffraction gives access to the local susceptibility tensor in the Gukasov-Brown model,<sup>12</sup> which reduces to 2 components  $\chi_{\parallel}$  and  $\chi_{\perp}$  with respect to the  $\langle 111 \rangle$  local axis, owing to the high symmetry of the R<sup>3+</sup> site. This allows one to describe the complex field-induced structures using only two parameters. This tensor cannot be derived from the bulk magnetization due to the equivalent  $\langle 111 \rangle$  axes. Measurements performed in four typical cases where the R-R interactions may be F or AF, and the crystal-field anisotropy either Ising- or XY-type, showed that the local susceptibility is highly anisotropic (Figure 1.3). This is the first determination of the local susceptibility in the Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> spin ice with (F, Ising) behavior. Comparison with a calculation of the non-interacting susceptibility deduced from the crystal-field scheme (measured independently by inelastic neutron scattering) yields the tensor of exchange interactions, which is also found to be anisotropic.<sup>13</sup> As a surprising consequence, in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with (F, XY) behavior, crystal-field and exchange anisotropies nearly compensate,

<sup>10</sup> Spin dynamics in the electron-doped Kondo insulator Yb<sub>1-x</sub>Zr<sub>x</sub>B<sub>12</sub> (x=0.2)

K. S. Nemkovski, P. A. Alekseev, J.-M. Mignot, E. A. Goremychkin, A. A. Nikonov, O. E. Parfenov, V. N. Lazukov, N. Yu. Shitsevalova, A. V. Dukhnenko, Phys. Rev. B **81**, 125108 (2010).

<sup>11</sup> Lattice dynamics in ZrB<sub>12</sub> and LuB<sub>12</sub>: Ab initio calculations and inelastic neutron scattering measurements

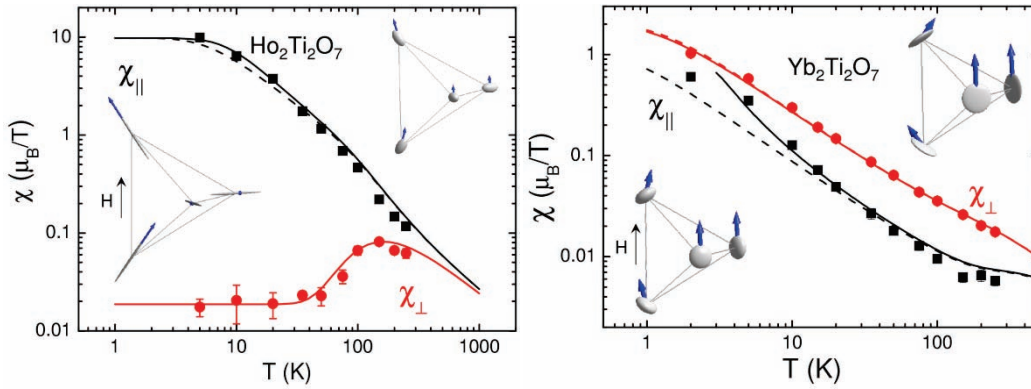
A. V. Rybina, K. S. Nemkovski, P. A. Alekseev, J.-M. Mignot, E. S. Clementyev, M. Johnson, L. Capogna, A. V. Dukhnenko, A. B. Lyashenko, V. B. Filippov, Phys. Rev. B **82**, 024302 (2010).

<sup>12</sup> A. Gukasov and J. Brown, J. Phys. Condens. Matter **14**, 8831, (2002).

<sup>13</sup> Ising versus XY Anisotropy in Frustrated R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> Compounds as “Seen” by Polarized Neutrons

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, C. Decorse, G. Dhalle, Physical Review Letters **103**, 056402 (2009).

yielding a Curie susceptibility and ground state fluctuations in an original “exchange spin-ice” ground state.<sup>14</sup>



**Figure 1.3.** Susceptibility components  $\chi_{||}$  and  $\chi_{\perp}$  versus  $T$  in  $\text{Ho}_2\text{Ti}_2\text{O}_7$  (left) and  $\text{Yb}_2\text{Ti}_2\text{O}_7$  (right). Dashed lines: CEF-only calculation; solid lines: calculation including an effective exchange. In  $\text{Yb}_2\text{Ti}_2\text{O}_7$ , the anisotropy of the molecular field due to the exchange ( $\lambda_{||} \gg \lambda_{\perp}$ ) is reversed with respect to the crystal field anisotropy (XY type). From Ref. [13]

### Evolution of the spin liquid $\text{Tb}_2\text{Ti}_2\text{O}_7$ ground state under applied field

$\text{Tb}_2\text{Ti}_2\text{O}_7$  realizes the (AF, uniaxial) case with a highly tunable spin-liquid ground state, which is easily destabilized by an applied field, pressure, or magnetic substitution. This tunability results from the peculiar  $\text{Tb}^{3+}$  crystal field scheme, with two low-energy doublets easily populated by temperature, or mixed by the magnetic field, and from  $R$ - $R$  effective (dipolar + exchange) interactions at the border between the F and AF characters. Starting from the spin-liquid ground state, a magnetic field close to a  $\langle 110 \rangle$  axis splits the system into two sublattices ( $\alpha$  and  $\beta$  chains) and induces spin-ice-like local structures with  $\mathbf{k} = 0$  propagation vector, but with different moment values on the two sublattices.<sup>15</sup> Above 2 teslas, magnetic structures with  $\mathbf{k} = 0$  and  $\mathbf{k} = (001)$  propagation vectors coexist. The high sensitivity of the spin structures to a small disorientation of the applied field results from the anisotropic susceptibility. In true spin ices ( $R = \text{Ho}$  or  $\text{Dy}$ ), this feature was used as a trick to tune the concentration of magnetic monopoles.<sup>16</sup>

### An ordered spin ice $\text{Tb}_2\text{Sn}_2\text{O}_7$ under high pressure

Starting from the  $\text{Tb}_2\text{Ti}_2\text{O}_7$  spin liquid, substitution of Ti by Sn yields a lattice expansion and the onset of an ordered spin-ice state. The change in the energy balance is understood as follows: the lattice expansion favors the dipolar (F) Tb–Tb interactions at the expense of the (AF) superexchange interactions, since superexchange depends more strongly on interatomic distances. The ordered or “soft” spin ice, whose anisotropy is reduced in comparison with the true spin ice, has the local spin ice spin structure (mathematically identical to proton order in water ice) but not its degeneracy, since all tetrahedra of the pyrochlore structure have the same orientations. This leads to long-range order, ferromagnetic magnetization, and intricate spin dynamics.<sup>17</sup> What happens when one pressurizes a soft spin ice? We observed three effects: a reorientation of the spin-ice structure, the onset of antiferromagnetic order, and the enhancement of spin-liquid fluctuations.<sup>18</sup> It is worth noting that only the soft spin ice  $\text{Tb}_2\text{Sn}_2\text{O}_7$  is sensitive to pressure (Figure 1.4). In the true spin ice  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , although theory predicts a pressure tuning of the magnetic monopoles, it was not observed up to now. Very high pressures are likely necessary to disturb the crystal- field scheme and exchange interactions.

<sup>14</sup> Anisotropic exchange in frustrated pyrochlore  $\text{Yb}_2\text{Ti}_2\text{O}_7$

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, J. Phys. Cond. Mat. Fast Track, **21**, 492202 (2009).

<sup>15</sup> Field-Induced Spin-Ice-Like Orders in Spin Liquid  $\text{Tb}_2\text{Ti}_2\text{O}_7$

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, Phys. Rev. Lett. **101**, 196402 (2008).

<sup>16</sup> T. Fennell et al. Nature Physics **3**, 566 (2007); D. J. P. Morris et al., Science **326**, 411, (2009).

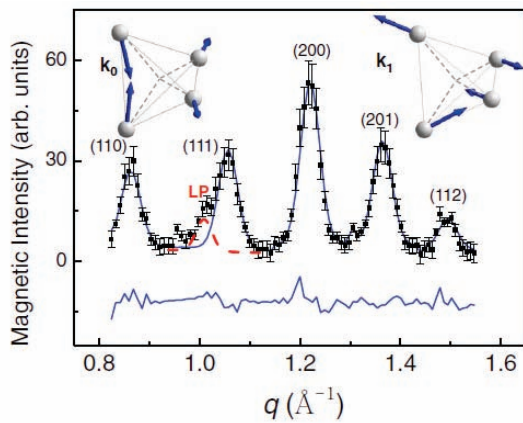
<sup>17</sup> Investigation of magnetic fluctuations in  $\text{Tb}_2\text{Sn}_2\text{O}_7$  ordered spin ice by high-resolution energy-resolved neutron scattering

I. Mirebeau, H. Mutka, P. Bonville, A. Apetrei, A. Forget, Phys. Rev. B **78**, 174416, (2008)

<sup>18</sup> Magnetic order in  $\text{Tb}_2\text{Sn}_2\text{O}_7$  under high pressure: From ordered spin ice to spin liquid and antiferromagnetic order

I. Mirebeau, I. Goncharenko, H. Cao, A. Forget, Physical Review B, Rapid Commun. **80**, 220407R (2009).





**Figure 1.4.** Magnetic diffraction pattern in  $Tb_2Sn_2O_7$  ordered spin ice, at 0.06 K under a pressure of 4.6 GPa. Together with the Bragg peaks of the ordered spin ice [ $k_0 = 0$  propagation vector, fcc lattice], new antiferromagnetic Bragg peaks [ $k_1 = (0,0,1)$  propagation vector, simple cubic lattice] appear under pressure. Top: the spin structures corresponding to the refinement (solid lines). From Ref. [Erreur ! Signet non défini.].

### Strong correlations in CMR manganites

Among the many novel phenomena encountered in strongly-correlated electron systems, specific effects originating from the interplay of different degrees of freedom (lattice, electron charge, spin and orbital angular momentum) have aroused particular interest. One prominent example is the manganites, which are well known for their colossal magnetoresistance (CMR) properties, associated with a phase transition from a high-temperature insulating phase to a low-temperature metallic phase.<sup>19</sup>

In these perovskite manganese oxides  $La_{1-x}B_xMnO_3$  ( $B = Ca, Sr$ ), the number of electrons on each manganese ion can be tuned by the partial substitution of a concentration  $x$  of Ca or Sr atoms on the La site. For  $x = 0$ , there are 4 electrons per manganese site, whose spins are aligned because of a large Hund coupling. The system shows orbital ordering, owing to the  $Mn^{3+}$  Jahn-Teller effect, and is insulating as a result of electronic correlations. In agreement with the Goodenough-Kanamori rules, the spins form ferromagnetic planes that are stacked antiferromagnetically. Upon substitution, the number of electrons per manganese site decreases and the system evolves towards an orbitally disordered ferromagnetic and metallic phase beyond  $x \approx 0.17$ . The latter phase is the one exhibiting the famous CMR properties. The hopping of electrons from site to site leads to a novel type of ferromagnetic coupling ("double exchange"), which is expected to stabilize the ferromagnetic order. However, the way the material evolves towards this new phase is very peculiar and emphasizes the role of charge segregation. The signature of this evolution was characterized by means of inelastic neutron scattering experiments in the course of a longstanding collaboration with the State Steel and Alloys Institute in Moscow (MISIS).

We first showed that, for small  $x$  values, the electronic state can be seen as consisting of hole-rich platelets embedded in a hole-poor matrix within the ferromagnetic planes. Their size ( $\sim 16 \text{ \AA}$ ) and spatial extension could be determined. As  $x$  increases, these platelets grow and percolate for  $x = 0.12$ , where the antiferromagnetic coupling between layers vanishes.<sup>20-23</sup> The system becomes quasi-metallic at room temperature but, in a small range of concentrations around  $x \sim 1/8$ , the ground state remains insulating owing to charge localization. Our study in this regime revealed very unconventional spin dynamics: the magnetic excitation spectrum consists of a dispersive branch near the zone centre, and several discrete modes at the zone boundary.<sup>24</sup> The former indicates long-range ferromagnetically coupled spins, while the latter were attributed to standing spin waves within small ferromagnetic domains. By assuming that the system forms weakly-coupled ferromagnetic clusters, we were able to explain the data successfully, and to obtain a very good agreement between the experiment and the model (Figure 1.5).

<sup>19</sup> *Nanoscale Phase Separation and Colossal Magnetoresistance*, edited by E. Dagotto (Springer-Verlag, Berlin, 2002).

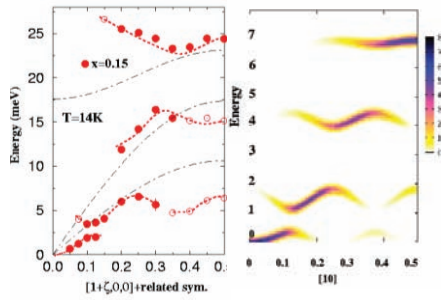
<sup>20</sup> M. Hennion *et al.*, Phys. Rev. Lett. **81** 1957 (1998).

<sup>21</sup> M. Hennion *et al.*, Phys. Rev. B **61**, 9513 (2000).

<sup>22</sup> F. Moussa *et al.*, Phys. Rev. B **67**, 214430 (2003).

<sup>23</sup> M. Hennion *et al.*, Phys. Rev. Lett. **94** 057006 (2005)

<sup>24</sup> M. Hennion *et al.*, Phys. Rev. B **73**, 104453 (2006)



**Figure 1.5.** Experimental (left) and theoretical (right) dispersions obtained at low temperature ( $x = 0.15$ ).

Beyond  $x = 0.17$ , the system enters the ferromagnetic and metallic phase. Pioneering measurements revealed standard cosine laws, although with strong anomalies at the zone boundary, which were described in terms of softening, broadening and flattening of the dispersion. These anomalies were tentatively explained on the basis of a phenomenological Heisenberg model with Mn-Mn magnetic couplings extending up to the fourth neighbors. Subsequently, we revisited these experiments with improved statistics and resolution, and collected data for a number of doping contents ( $x(\text{Sr}) = 0.175, 0.2, 0.3, 0.35, 0.4$  and  $x(\text{Ca}) = 0.3$ ).<sup>25,28</sup> We found that in all cases the spin-wave spectra consisted of a quadratic dispersive branch at the zone centre, characteristic of a three-dimensional (3D) ferromagnetic state, and wave-vector independent (flat) levels at the zone boundary, which were reminiscent of the  $x \sim 1/8$  spectra. The characteristic energies of these levels remain approximately identical, while their intensities show a peculiar temperature and doping dependence. Actually, as the temperature decreases or  $x$  increases, the upper modes become very intense at the expense of the lower ones (

Figure 1.6). At low temperature, this creates the illusion of a cosine law (the quadratic branch) with a softened zone boundary (the upper flat mode), which is in agreement with earlier reports (

Figure 1.7). It is worth emphasizing that, as soon as temperature increases, this effect vanishes as all modes have comparable intensities. Considering the resemblance between the spectra in the  $x \sim 1/8$  region and in the metallic phase, it is tempting to propose a picture where the levels would reflect quantized spin waves in ferromagnetic clusters, embedded in a 3D ferromagnetic matrix. As both insulating and metallic regimes have similar spin-wave spectra, we may speculate that the same physics is at play here and that the existence of such clusters is an important ingredient for the appearance of the CMR phenomenon. However, the stability of these clusters for doping as large as  $x = 0.35$  or  $0.40$  is probably difficult to justify, and casts some doubt on the proposed interpretation. Up to now, the unconventional spin dynamics remain unexplained and new experimental efforts are needed to extend our understanding of these compounds and their puzzling properties.

<sup>25</sup> F. Moussa *et al.*, Phys. Rev. B **76**, 064403 (2007)

<sup>26</sup> *Intralayer and interlayer exchange tuned by magnetic field in the bilayer manganite  $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  probed by inelastic neutron scattering*

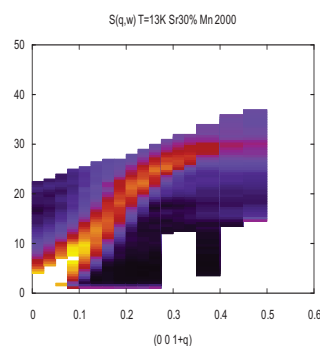
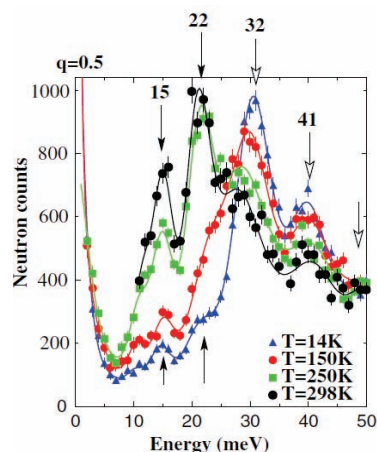
F. Moussa, M. Hennion, A. Gukasov, S. Petit, L. P. Regnault, A. Ivanov, R. Suryanarayanan, M. Apostu, and A. Revcolevschi, Phys. Rev. B **78**, 060406 (2008).

<sup>27</sup> *Spin waves and metallic state of magnetoresistive manganites*

S. Petit, M. Hennion, F. Moussa, D. Lamago, A. Ivanov and Y. Mukovskii, J. Phys. Conf. Ser. **200**, 012159 (2010).

<sup>28</sup> *Quantized Spin Waves in the Metallic State of Magnetoresistive Manganites*

S. Petit, M. Hennion, F. Moussa, D. Lamago, A. Ivanov, Y. M. Mukovskii and D. Shulyatev, Phys. Rev. Lett. **102**, 207201 (2009).



**Figure 1.6.** Energy scans at the zone boundary  $Q = (1.5, 0, 0)$  for different temperatures ( $x = 0.30$ ). Arrows indicate the different flat modes. **Figure 1.7.** Color map of  $S(Q, \omega)$  recorded at low temperature ( $x = 0.30$ ).

The bilayer counterpart of the pseudo-cubic manganites,  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ , is also famous for its colossal magnetoresistance. Here, broad charge-order peaks due to large polarons are found to disappear at the CMR insulator-metal transition. These polarons survive as fluctuations in the metallic phase, which strongly broaden and soften certain phonon modes near the wave-vectors where the charge-order peaks appeared in the high-temperature phase.<sup>29</sup> Again, these findings confirm the amazing entanglement of lattice, charge and spin degrees of freedom in this class of systems.

## Multiferroic materials

Studies conducted over the past few decades came to the conclusion that ferroelectricity and magnetism tend to be mutually exclusive, and interact only weakly with each other when they do coexist. The recent discovery of multiferroic materials, in which ferroelectricity and magnetism are intimately coupled, has completely changed these established views, opened routes to new technological applications, and has forced physicists to reconsider some long-accepted ideas.<sup>30</sup>

Coupling between magnetic and electric orders makes it possible to design promising devices, such as high-speed memories with magnetically and electrically addressable states, magnetically tunable tunnel-junctions, sensors, filters, transducers, etc. For instance, the control of magnetization by an applied electric field via the magnetoelectric coupling offers an opportunity to combine the respective advantages of FeRAMs (ferroelectric random access memories) and MRAMs (magnetic random access memories) in the form of non-volatile magnetic storage bits, which can be switched by an electrical field and thus combine the merits of MRAMs in terms of access time and endurance with a low writing energy.<sup>31</sup>

Meanwhile, a major effort is currently underway to revisit the ferroelectric-ferromagnetic dichotomy and to understand the multiferroic properties on fundamental grounds. The multiferroic compounds are scarce, as symmetry considerations impose severe constraints. Indeed, their space group should be non-centrosymmetric, to accommodate ferroelectricity, but also compatible with a magnetic ground state. Last but not least, all multiferroic materials found to date exhibit a certain amount of magnetic frustration. This, together with a strong spin-lattice coupling, seems to be a basic physical ingredient for multiferroicity. For example, the orthorhombic  $\text{RMnO}_3$  compounds, where R is a rare-earth element ( $R = \text{Eu, Gd, Tb, Dy}$ ), are archetypes of multiferroic materials. Magnetic frustration arises from competing magnetic exchange interactions, yielding an incommensurate spiral magnetic structure. As proposed in the “spin-current” model, the spin-lattice coupling is a result of the Dzyaloshinskii-Moriya

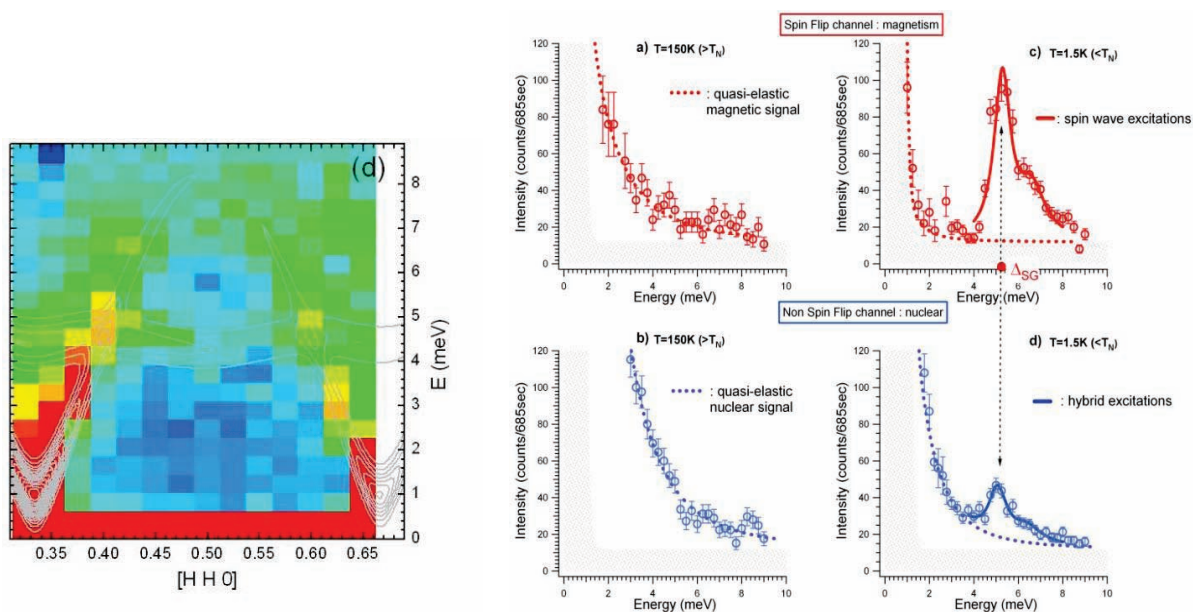
<sup>29</sup> Signature of checkerboard fluctuations in the phonon spectra of a possible polaronic metal  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$   
F. Weber, N. Aliouane, H. Zheng, J. F. Mitchell, D. N. Argyriou & D. Reznik, *Nature Materials* **8**, 798 (2009).

<sup>30</sup> S-W Cheong *et al.*, *Nature Materials* **6**, 13 (2007).

<sup>31</sup> A Barthélémy and M. Bibes, *Nature Materials* **460**, 81 (2009).

interaction: minimizing the corresponding term in the Hamiltonian of the system results in a relaxation of atomic positions and, in turn, in an electric polarization.<sup>32</sup>

A rapid survey of the literature shows that there also exist a large number of multiferroic materials with a triangular-based geometry. Much work at LLB was thus devoted to the study of delafossite-type materials, such as  $\text{CuCrO}_2$  and  $\text{CuMnO}_2$ , in close collaboration with the CRISMAT in Caen (Figure 1.8). These studies showed that the ground state properties of these compounds can be very different, even if the required basic ingredients are present. In  $\text{CuCrO}_2$  the magnetic ground state is an incommensurate  $120^\circ$  magnetic structure, with spin dynamics that is close to that of a 2D Heisenberg triangular lattice; it is multiferroic in its antiferromagnetic phase, but no unambiguous structural distortion was observed so far at  $T_N$ .<sup>33</sup> There are, however, anomalies in the spin-wave spectrum, which can be assigned to additional in-plane interactions, and could be an indication of a magnetoelastic coupling in this material. In contrast, the collinear antiferromagnetic ordering in  $\text{CuMnO}_2$  occurs simultaneously with a symmetry-lowering structural transition, which releases the frustration inherent to the triangular lattice. Below the magnetoelastic transition,  $\text{CuMnO}_2$  is an improper ferroelastic, but is not magnetoelectric.<sup>34</sup> Even though the basic ingredients of multiferroicity (magnetic frustration and spin-lattice coupling) are at play, the balance between the two is subtle and remains unknown. More studies are in progress, focusing in particular on the role of the ligand ions on the magnetic interactions.



**Figure 1.8.** Experimental (color map) and calculated (grey lines)  $S(\mathbf{Q},\omega)$  along the  $[HHO]$  direction in delafossite  $\text{CuCrO}_2$  at 10 K.

**Figure 1.9.** Energy scans performed at the zone center  $\mathbf{Q} = (0,0,6)$  in  $\text{YMnO}_3$ , in the spin-flip (red) and non-spin-flip (blue) channels. Left and right curves correspond to temperatures above and below  $T_N$ , respectively. The spin wave is in reality a hybrid mode, as evidenced by its “lattice” counterpart (bottom right).

Hexagonal  $\text{RMnO}_3$  with  $R$  elements having smaller ionic radii, ( $R = \text{Ho, Er, Yb, Lu, Y}$ ) form another class of triangle-based multiferroic materials, which has been widely studied at LLB in recent years, in collaboration with the Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO University of Paris-Sud 11).<sup>35-38</sup> The Néel order at  $120^\circ$  imposed by the geometric

<sup>32</sup> H. Katsura *et al.*, Phys. Rev. Lett. **98**, 027203 (2007).

<sup>33</sup> Spin dynamics in the geometrically frustrated multiferroic  $\text{CuCrO}_2$   
M. Poienar, F. Damay, C. Martin, J. Robert, and S. Petit Phys. Rev. B **81**, 104411 (2010).

<sup>34</sup> Spin-lattice coupling induced phase transition in the  $S=2$  frustrated antiferromagnet  $\text{CuMnO}_2$   
F. Damay, M. Poienar, C. Martin, A. Maignan, J. Rodriguez-Carvajal, G. André, and J. P. Doumerc, Phys. Rev. B **80**, 094410, (2009).

<sup>35</sup> Spin-Phonon Coupling in Hexagonal Multiferroic  $\text{YMnO}_3$   
S. Petit, F. Moussa, M. Hennion, S. Pailhès, L. Pinsard-Gaudart, and A. Ivanov, Phys. Rev. Lett. **99**, 266604 (2007).

<sup>36</sup> Magnetic order in  $\text{YbMnO}_3$  studied by neutron diffraction and Mössbauer spectroscopy  
X. Fabrèges, I. Mirebeau, P. Bonville, S. Petit, G. Lebras-Jasmin, A. Forget, G. André, and S. Pailhès, Phys. Rev. B **78**, 214422 (2008).



frustration is accompanied by an isostructural transition: each ion “moves” inside the unit cell when Mn moments get ordered. This effect provides evidence for a giant magnetoelastic coupling, likely connected with an increase in the ferroelectric polarization. To shed light on these materials, high-resolution neutron diffraction and inelastic neutron scattering were carried out on four  $RMnO_3$  compounds ( $R = Y, Sc, Ho, Yb$ ), with either non-magnetic (Y, Sc) or magnetic (Ho, Yb)  $R$  ions, showing (Ho, Sc) or not (Y, Yb) a spin reorientation at the temperature  $T_{SR}$  (Figure 1.9). We have shown that the isostructural transition is a systematic feature in this series. In addition, we have established a correlation between the atomic positions, the type of magnetic structure, and the nature of the spin-waves, depending on the compound and its magnetic structure. The key parameter is the position of the Mn ions within the triangular plane, which tunes the sign of the exchange interaction. We speculate that, thanks to the magnetoelastic coupling, the atomic motion helps to release the frustration by selecting one particular magnetic structure, depending on the  $x$  value<sup>36</sup>. This process recalls the spin-Peierls states stabilized in several geometrically frustrated 2D or 3D compounds.

Magnetoelastic coupling also results in mixed magnon-phonon excitations, called electromagnons. While their existence has been theoretically predicted a long time ago, their dual lattice and spin nature makes it challenging to observe them experimentally. Due to their dipole electric activity, they could first be detected by optical measurements, especially in  $GdMnO_3$ ,  $TbMnO_3$ ,  $Eu_{0.75}Y_{0.25}MnO_3$ ,  $DyMnO_3$ ,  $YMn_2O_5$ ,  $TbMn_2O_5$  and  $BiFeO_3$ . Recent inelastic polarized neutron scattering experiments provided one of the first direct observations of a hybrid dispersive wave in the hexagonal series of  $RMnO_3$  materials: part of a spin-wave branch is found to be completely dressed by nuclear spectral weight<sup>37</sup>. Again, the Dzyaloshinskii-Moriya interaction could be at the origin of this hybridization.

### Observation of a magnetic “blue phase” in an itinerant magnet

Blue phases often appear in chiral liquid crystals as arrangements of so-called “double-twist cylinders”, characterized by twisting in all directions perpendicular to the cylinder axis.<sup>39</sup> Magnetic moments in chiral magnets tend to form spirals, and one can thus speculate on the existence of magnetic “blue phases”. By combining model calculations with experiments, we show that such a phase does form in MnSi over a large part of the phase diagram, including at ambient pressure.<sup>40</sup>

In chiral magnets, calculations performed in the large-pitch limit show that spirals with a well-defined twist direction (helical order) should have a lower energy in magnets, and that blue phases cannot appear.<sup>39</sup> Despite this result, a blue phase has been suspected to occur in the itinerant chiral magnet MnSi at high hydrostatic pressure, where a so-called partial magnetic order has been observed.<sup>41</sup> In collaboration with A. Hamann, T. Wolf, and H. v. Löhneysen (Karlsruhe Institute of Technology) and D. Reznik (University of Colorado), we have performed calculations starting from magnetic moments of the same fixed magnitude, with random orientations, and placed on simple cubic or B20 lattices. The orientation of each moment was optimized sequentially in random order until the total energy of the system stabilized. A typical spin arrangement obtained by this method is shown in Figure 1.10 (left). The topology is the same as for blue phases of chiral liquid crystals, i.e., with moments twisting away from cylindrical axes. We tested our model via experiments on the 4F cold triple-axis neutron spectrometer and on the PAPHYRUS small angle neutron scattering (SANS) diffractometer. The magnetic correlation length is expected to be reduced by Fe-doping similarly to thermal fluctuations. According to our model, Fe doping should allow the blue phase to persist to lower temperatures. Experiments show that this is indeed the case:  $T_c$

<sup>37</sup> *Hybrid Goldstone modes in multiferroic  $YMnO_3$  studied by polarized inelastic neutron scattering*

S. Pailhès, X. Fabréges, L. P. Régnault, L. Pinsard-Godart, I. Mirebeau, F. Moussa, M. Hennion, and S. Petit, *Phys. Rev. B* **79**, 134409 (2009).

<sup>38</sup> *Spin-Lattice Coupling, Frustration, and Magnetic Order in Multiferroic  $RMnO_3$*

X. Fabréges, S. Petit, I. Mirebeau, S. Pailhès, L. Pinsard, A. Forget, M. T. Fernandez-Diaz, and F. Porcher, *Phys. Rev. Lett.* **103**, 067204 (2009).

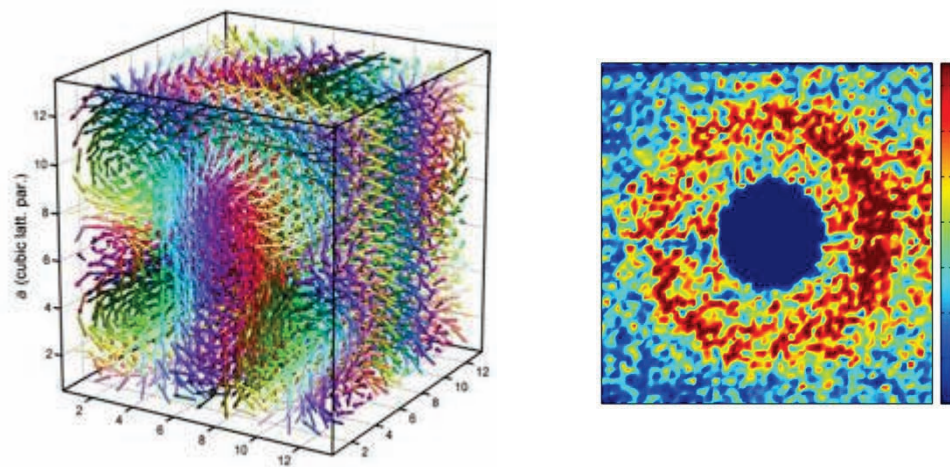
<sup>39</sup> D.C. Wright and N.D. Mermin, *Rev. Mod. Phys.* **61**, 385 (1989)

<sup>40</sup> *Magnetic blue phase in itinerant magnet MnSi*

A. Hamann, D. Lamago, H.v. Löhneysen, D. Reznik, (submitted to *Nature Materials*).

<sup>41</sup> C. Pfleiderer et al., *Nature* **427**, 227 (2004).

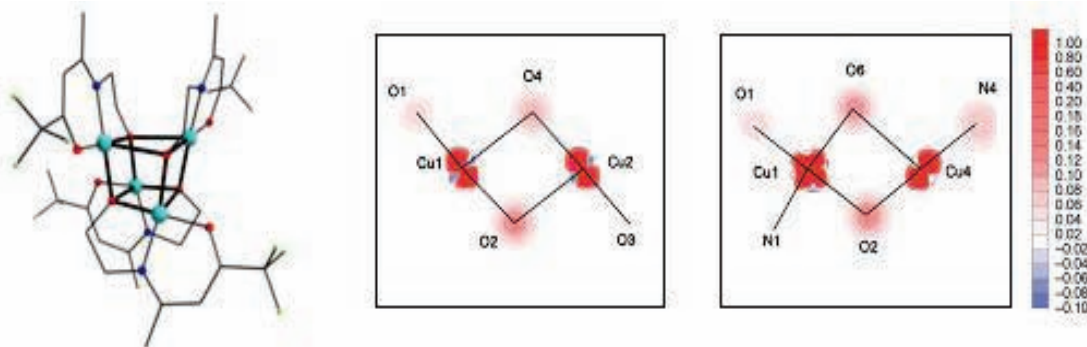
decreases with Fe doping<sup>42</sup> and the SANS spectrum of  $\text{Mn}_{0.8}\text{Fe}_{0.15}\text{Si}$  at 1.5 K is a ring characteristic of the blue phase. The same result was obtained for  $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ ,<sup>43</sup> pointing to a universality of this phenomenon. Our results provide a blueprint for understanding cubic chiral magnets, including MnSi, by showing that the frustrated nature of the magnetic interactions naturally and generically induces complex spin arrangements, which had so far been found only in liquid-crystal blue phases. Controlling special properties of this blue phase with impurities in thin films has a potential for new applications, particularly in electronics and magnetic memory devices.<sup>44</sup>



**Figure 1.10.** (left) Topology of the triple-twist arrangement in a  $12 \times 12 \times 12$  unit-cell cluster containing  $\sim 7000$  spins. (Right) SANS color map for  $\text{Mn}_{0.85}\text{Fe}_{0.15}\text{Si}$  measured at 1.5 K. The scattering intensity ring is characteristic for partial order. The small overall increase in the intensity from left to right results from a sloping background coming from the cryostat.

### Molecular magnetism and photomagnetism

Molecular magnetism is a relatively new field of research, which has attracted growing interest among physicists since the discovery, fifteen years ago, of the first “single molecule magnet” (SMM),  $\text{Mn}_{12}$ -acetate, which behaves as a magnet at the molecular scale below a blocking temperature of 3 K. The present challenges in this field consist in understanding how to control magnetic anisotropy in order to obtain SMM behavior at higher temperatures, and in designing new multifunctional materials possessing other functional properties in addition to magnetism, e.g. magnetic photoswitchable compounds. Optical magnetic switching in the solid state raises questions of fundamental interest as to the mechanisms governing phase separation into magnetic domains or continuous structural changes during photoexcitation.



**Figure 1.11.** Structure of  $\text{M}_4\text{O}_4$  cubane-like complexes.

**Figure 1.12.** Experimental induced spin density in the  $S = 2$  ground state at  $T = 2$  K,  $H = 7$  T, in  $\text{Cu}_4\text{O}_4$  projected onto  $\text{Cu}_2\text{O}_2$  planes with different bridging geometries. Isodensity levels:  $\pm 0.02 \mu_B/\text{\AA}^2$

<sup>42</sup>N. Manyala et al., Nature **404**, 581 (2000).

<sup>43</sup>S.V. Grigoriev et al., Phys. Rev. Lett. **102**, 037204 (2009).

<sup>44</sup>X.Z. Yu et al., Nature **465**, 901 (2010).

## Combined analysis of charge and spin densities in molecular magnets

The goal of the CEDA project, supported by the ANR (2008-2010), on the Convergence of Electron spin, charge and momentum Densities Analysis, is to combine data obtained by different techniques on the electron density in order to refine a unique model, thereby allowing the electronic structure of magnetic molecular compounds to be more accurately described. This work involves theoreticians (SPMS, ECP), x-ray (CRM2, Nancy) and neutron (LLB) diffraction specialists, and chemists (LMI, Lyon). The first step devoted to the joint refinement of charge and spin densities from x-ray and polarized neutron diffraction data sets has been completed. In this approach, the multipole model<sup>45</sup> is used to describe the densities of spin up and spin down electrons, the sum (or difference) of which is the charge (spin) density. The software called MOLLYNX was developed by splitting the electron density model into two spin components. Experimental data were collected by x-ray diffraction at CRM2, and polarized neutron diffraction on 5C1 at LLB on two cubane-like  $[M_4O_4]$  complexes ( $M = \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}$ ), synthesized in Lyon (LMI) (Figure 1.11). The joint refinement of these data is expected to ensure a better characterization of the metal-ligand bonds and a more complete understanding of their role in the intramolecular magnetic interactions and the magnetic anisotropy. The first analysis of the PND data alone<sup>46</sup> shows that the experimental spin distribution in the  $\text{Cu}_4$  complex is mainly located in the basal planes of the  $\text{Cu}^{\text{II}}$  ions and visualizes the magnetic interaction pathways via the bridging oxygen atoms (Figure 1.12).

## Light-induced phase separation in a spin-crossover $\text{Fe}^{\text{II}}$ molecular complex

Progress has been achieved in the investigation of the photoexcitation mechanism in the spin-crossover complex  $[\text{Fe}^{\text{II}}(\text{ptz})_6](\text{BF}_4)_2$  in collaboration with the GEMaC (Versailles). The photoinduced structural transformation between the low spin (LS) ground state ( $S = 0$ ) and the high spin (HS) excited state ( $S = 2$ ) was studied on the neutron Laue diffractometer Vivaldi at ILL, equipped by the in-situ photoexcitation setup developed at LLB.<sup>47</sup> In a previous work,<sup>48</sup> we observed a continuous transformation corresponding to randomly distributed LS and HS molecules during the irradiation of a single crystal by a laser beam (470 nm) at  $T = 2$  K. According to a theoretical model based on the competition between photoexcitation (LS  $\rightarrow$  HS) and relaxation (HS  $\rightarrow$  LS), a light-induced phase separation (LIPS) between HS domains and LS domains was expected in an instability region inside the LITH (light induced thermal hysteresis) loop (Figure 1.13, left). We have provided evidence for this process, as illustrated by the evolution of the photoinduced splitting of one reflection as a function of the irradiation time at 53.5 K (Figure 1.13, right).<sup>49</sup>

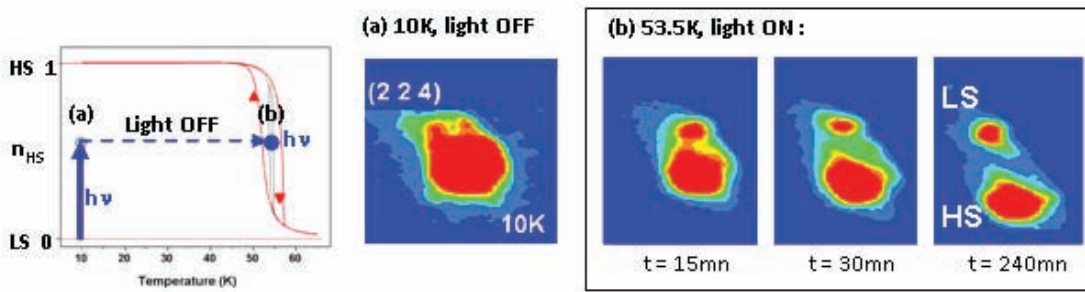
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<sup>49</sup> Light-induced phase separation (LIPS) into like-spin phases observed by Laue neutron Diffraction on a single crystal of  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$   
F. Varret, K. Boukheddaden, A. Goujon, B. Gillon and G.J McIntyre, Z. Kristallogr. **223**, 250 (2008).



**Figure 1.13.** Light induced phase separation (LIPS) in the molecular complex  $[\text{Fe}^{\text{II}}(\text{ptz})_6](\text{BF}_4)_2$ . Left: protocol for the LIPS investigation in the LITH loop (in red),  $n_{\text{HS}}$  is the fraction of photoinduced HS state: irradiation by light at  $\lambda = 470 \text{ nm}$  (10mW) at 10 K, then heating up to 53.5 K with light switched off and again light irradiation at 53.5 K. Right: (2, 2, 4) Bragg reflection on the neutron Laue diffraction diagram (a) after partial photoexcitation at 10 K, light off: (HS, LS) random state; (b) at 53.1 K, light on: evolution of the splitting, as a function of the light irradiation time, towards the LS and HS structural positions.



## Scientific collaborations

The main collaborating institutes in France and abroad are listed below.

Organization	Total
[INST LAUE LANGEVIN GRENoble – FRANCE]	24
[UNIV PARIS 11 - FRANCE]	15
[UNIV BORDEAUX - FRANCE]	12
[LAB CRISMAT - FRANCE]	9
[ESRF GRENoble - FRANCE]	7
[UNIV STRASBOURG - FRANCE]	5
[UNIV GRENoble - FRANCE]	4
[UNIV PARIS 6 - FRANCE]	4
[UNIV NANTES - FRANCE]	4
[UNIV RENNES - FRANCE]	4

Organization	Total
[JULICH - GERMANY]	12
[INST MAX PLANCK - GERMANY]	11
[KARLSRUHE INST OF TECHNOLOGY – GERMANY]	10
[UNIV GOTTINGEN - GERMANY]	6
[UNIV MUNICH - GERMANY]	6
[KURCHATOV ATOM INST MOSCOW – RUSSIA]	5
[PSI - SWITZERLAND]	5
[RUTHERFORD APPLETON LAB - UK]	5
[UNIV DRESDEN - GERMANY]	5
[UNIV COLOGNE - GERMANY]	5
[ARGONNE - USA]	4
[INST ACAD PRAGUE - CZECH REPUBLIC]	4
[JAERI IBARAKI - JAPAN]	4

## Scientific contracts

ANR: CEDA, MAGD0, NEWTOM,

- CEDA: Convergence of electron spin, charge and momentum densities analysis
- MAGD0: magnetism induced by nonmagnetic impurities
- NEWTOM: new transition metal oxides

RTRA (Triangle de la Physique): EXTREME, GLACEDESPIN, CRISPY, MAGCORPNIC

- EXTREME: high-pressure instrumentation.
- GLACEDESPIN: financial support of post-doc, H. Cao.
- CRISPY: crystal growth of rare-earth pyrochlores.
- MAGCORPNIC: magnetism and electronic correlations in superconducting pnictides.

2 JRA: NMI3-7th Framework Programme of the European Commission

## Other

Theses (2008- 2010)

- **Victor Balédent** (2007-10): *Etude de la phase de pseudo gap dans les oxydes de cuivre supraconducteurs à haute température critique.*
- **Sophie Tencé** (2006-30 sept. 2009) (LLB-université de Bordeaux): *Propriétés et structures magnétiques d'hydrures et de composés magnétocaloriques à base de terres rares.*
- **Xavier Fabrèges** (2007-5 oct. 2010): *Etude des propriétés magnétiques et du couplage spin-réseau dans les composés multiferroïques  $RMnO_3$  hexagonaux par diffusion de neutrons.*
- **Julie Bourgeois** (2008-2011) (LLB-Université de Caen): *Les ferrites de type  $RFeO_4$  à valence mixte.*

- **Sonia de Almeida** (2007-2010) (LLB- Lema Tours- IUT Blois): *Synthèse et études neutroniques de la phase sous-dopée du système  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$*
- **Monica Hatnean** (2009-12): (LLB-ICMMO Paris XI): *Etude du composé magnétoélectrique  $\text{GaFeO}_3$ .*
- **Andreas Hamann** ( 2007-10) (LLB-KIT Karlsruhe): *Neutron Scattering on Strongly Correlated Electron Systems:  $\text{MnSi}$ ,  $\text{CeCu}_{5.5}\text{Au}_{0.5}$ ,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{HgBa}_2\text{CuO}_{4+\delta}$*

#### Post-docs

- **Huibo Cao** (2007-09): Neutron studies of  $\text{R}_2\text{Ti}_2\text{O}_7$  pyrochlores: local susceptibility.
- **Andrew Sazonov** (2009-11): Neutron studies of  $\text{R}_2\text{Ti}_2\text{O}_7$  pyrochlores: symmetry analysis.
- **Sergei Kichanov** (post-doc training in 2009-10): Instrumentation under high pressure.
- **Boris Narozhny** (2007-08): Contribution to the study of spin fluctuations and of their role in the pairing of electrons in high- $T_c$  cuprates.

#### Habilitation à Diriger les Recherches defended

- Sylvain Petit, *Neutrons et dynamique de spin,*