2 - MAGNETISM AND SUPERCONDUCTIVITY

Of all physical probes used for studying magnetism in solids, neutrons offer by far the most extended spectrum of experimental techniques. Whereas classical diffraction and inelastic scattering methods remain unsurpassed for disentangling complex magnetic structures or deriving exchange parameters from magnon dispersion branches, neutron scattering has also proved remarkably versatile in targeting new problems at the cutting edge of modern magnetism.

New types of magnetic objects can be studied, such as large-spin clusters in molecular magnets, or transition-metal monoxides in confined geometries. Specific phenomena occurring at magnetic interfaces can be studied in thin-film specimens using neutron reflectometry. Our current understanding of "strongly correlated electron systems", including a variety of transition-metal oxides (ruthenates, high-T_c cuprates, manganites) and unstable *f*-electron compounds (Kondo insulators, heavy-fermion superconductors, quadrupole-order compounds), is based to a large extent on the knowledge of their ground-states and low-energy excitations gained from unpolarized and polarized neutron scattering experiments.

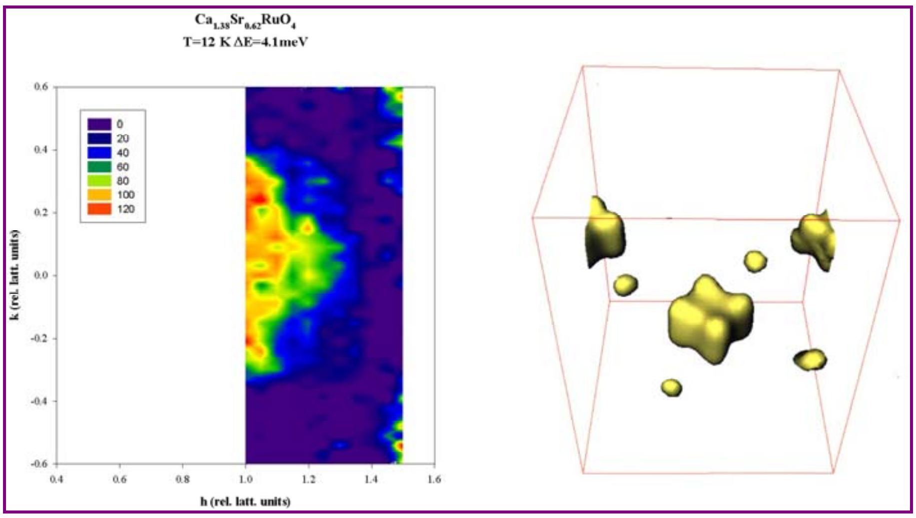
To keep pace with other techniques, neutron instrumentation continuously extends the range of experimental parameters accessible to measurements. To observe new photo-induced phenomena in "switchable" molecular materials, *in situ* illumination by a laser beam has been implemented in a polarized-neutron diffractometer. Various types of materials are studied at the LLB under multi-extreme conditions (high pressure + high field + very low temperature) making it possible to stabilize and investigate novel magnetic states.

1. COMPLEX ELECTRONIC SYSTEMS

1.a. Ruthenates

M. Braden and coworkers (Köln University) - Y. Sidis, Ph. Bourges, O. Friedt (thesis), P. Pfeuty, A. Gukasov, R. Papoular (LLB) - J. Kulda (ILL) - Y. Maeno (Kyoto University).

Sr_2RuO_4 is the only superconducting layered perovskite isostructural with cuprates. It is now well established that its superconductivity is unconventional (spin-triplet, *p*-wave symmetry with line nodes). The supposed pairing via ferromagnetic fluctuations has not been confirmed by inelastic neutron scattering measurements, which show a spin excitation spectrum dominated by incommensurate spin fluctuations. The fluctuations are



Left) Incommensurate spin fluctuations located at wavevectors Q_{inc} = (±0.2,0,0) and (0,±0.2,0) in $Ca_{1.38}Sr_{0.62}RuO_4$. Right) the spin density spreads mainly on $4d_{xy}$ orbital and is partially distributed on O^{2-} ligands in $Ca_{1.5}Sr_{0.5}RuO_4$.

related to a dynamical nesting effect between quasi-1D sheets of the Fermi surface (α and β bands). While the role of these fluctuations is still a subject of debate, it has been shown recently that the strong incommensurate spin fluctuations were induced by a spin-density wave instability nearby. That instability controls non-Fermi liquid properties observed in the normal state of Sr_2RuO_4 (T-linear resistivity, ω/T scaling of the incommensurate spin fluctuation). Furthermore, substituting Ti^{4+} for Ru^{4+} destroys superconductivity and stabilizes the spin-density-wave state. Quantum critical phenomena are under investigation in $Sr_2Ru_{1-x}Ti_xO_4$ ($x = 0.04$).
Substitution of Ca^{2+} for Sr^{2+} gives rise to a tilt and a rotation of oxygen octahedra, leading to deep modifications in both the electronic structure and the magnetic properties. In $Ca_{1.38}Sr_{0.62}RuO_4$, the spin excitation spectrum is dominated by incommensurate spin fluctuations around the ferromagnetic point. These fluctuations are likely associated with a change in the Fermi surface topology, which reinforces the role of the γ band. In $Ca_{1.5}Sr_{0.5}RuO_4$, the spin density, mapped out by polarized neutron diffraction and analysed by the maximum entropy method confirms the dominant influence of $4d_{xy}$ orbitals (γ band) on the magnetic properties.

1.b. High-T_c cuprates

LLB Inelastic group (Ph. Bourges, Y. Sidis, P. Pailhès) - B. Keimer and coworkers (MPI Stuttgart) - L.-P. Regnault (CEA/Grenoble), - A. Ivanov (ILL) - LLB Theory group (F. Onufrieva, P. Pfeuty).

The resonance mode (see highlight)

An unusual spin excitation mode, the so-called magnetic resonance mode, has stimulated numerous theoretical studies on the interplay between charged quasiparticles and collective spin excitations in copper oxide superconductors. The mode had, so far, only been observed in materials with crystal structures consisting of copper oxide bilayers, and was absent in single-layer $La_{2-x}Sr_xCuO_4$. Neutron scattering data have shown that the magnetic resonance mode is present in $Tl_2Ba_2CuO_{6+\delta}$, a single-layer compound with a superconducting transition temperature of ~ 90 K, demonstrating that it is a generic feature of copper oxide superconductors, independent of the layer sequence.
In slightly underdoped $YBa_2Cu_3O_{6.85}$ ($T_c = 89$ K), previous inelastic neutron studies had shown that the magnetic resonance mode displays a downward dispersion. This rather peculiar dispersion was predicted in the “spin-exciton” model by the LLB Theory group. Alternatively, it has been argued that the dispersive magnetic resonance mode could be similar to magnons in incommensurate antiferromagnets. To test this suggestion, the spin excitation spectrum in a stripe-ordered nickelate, $La_{2-x}Sr_xNiO_4$ ($x = 0.31$), was determined using inelastic neutron scattering. The spin excitation spectrum is found to be surprisingly similar to that of a standard incommensurate antiferromagnet. While interesting in their own right, the results do not provide an adequate model for the magnetic resonance observed in several cuprates. (Collaboration: LLB Inelastic Group, M. Braden (Köln Univ.) - J. M. Tranquada (Brookhaven National Lab.)).

Coexistence of antiferromagnetism and superconductivity

J. Hodges (SPEC), LLB (Ph. Bourges, Y. Sidis, M. Hennion, I. Mirebeau), X. Chaud (CRETA).

Weak commensurate antiferromagnetism has been reported in superconducting compounds $YBa_2Cu_3O_{6.5}$ ($T_c = 55$ K) by the LLB group and in $YBa_2Cu_3O_{6.6}$ ($T_c = 63$ K) by other groups. The anomalously fast decrease in the magnetic form factor gave rise to a controversy about the origin of the antiferromagnetic order:

(i) A spin-density wave (LLB Theory Group), or
(ii) A d-wave charge-density wave.

In $YBa_2(Cu_{1-y}Co_y)O_7$ ($y = 0.013$, $T_c = 94$ K), recent neutron scattering measurements have revealed the existence of a commensurate antiferromagnetic order ($T_N = 330$ K, $\mu = 0.14\ \mu_B$). Cobalt substitution leads to a state in which superconductivity and antiferromagnetism coexist, without strong interference, on the microscopic scale. The anomalous magnetic form factor was also observed in a Co-substituted sample at optimal doping. This result brings into question the existence of a d-wave charge-density wave, expected in the underdoped regime only. The exact reason for the observed structure factor remains unclear at present.

Density wave phases and their precursor fluctuations in high T_c cuprates

LLB Theory group (F. Onufrieva, P. Pfeuty).

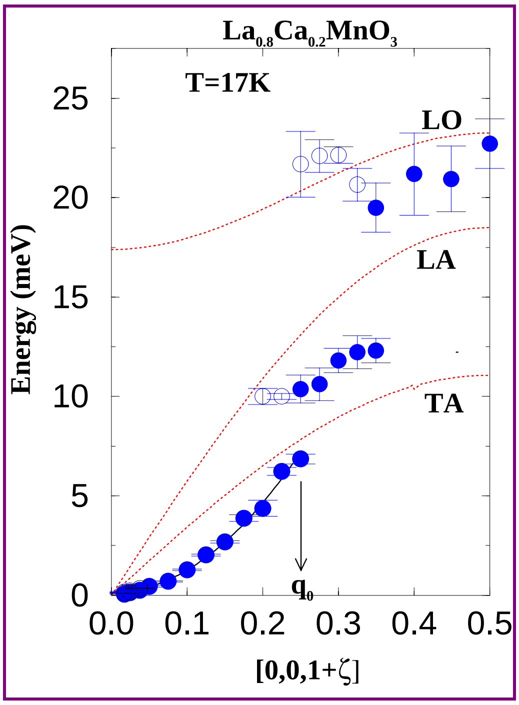
The LLB theory group have analysed different density wave ordered phases (SDW, CDW, Orbital magnetism and Spin current) in 2D strongly correlated metals, their stability in different parts of the T-x diagram (where x is the electron concentration), their compatibility with *d*-wave superconductivity and the precursor dynamic fluctuations associated with these orders. The LLB theoretical work allows one to understand the origin of different phenomena observed in the high T_c hole doped cuprates: namely the magnetic ordered phases observed by neutrons at low hole doping δ as well as their strong sensibility to different external factors, and their disappearance with increasing doping, the spin current phase observed recently by ARPES near optimal doping, the dynamical fluctuations observed by neutrons by NMR and by Raman scattering at intermediate doping and their influence on ARPES spectra as well as recent observation of the coexistence of DW+SC orders.

1.c. CMR Manganites

Hole-doped manganites $A_{1-x}B_xMnO_3$ (A = {La, Pr,...}, B = {Sr, Ca}), display a very rich phase diagram where nuclear and magnetic structures, as well as transport properties, evolve with doping. The purpose of the neutron scattering studies is to shed light on the origin of the "colossal" magneto-resistance observed in the ferromagnetic and metallic state. This paragraph focus on dynamical and large-scale studies complementing the structural work of the previous chapter "Structure and Phase Transitions" of this scientific report.

Spin-charge-lattice interactions in manganites

P. Kober (thesis), F.W. Wang (postdoc), M. Hennion, F. Moussa, J. Rodrigez-Carvajal (LLB) – L. Pinsard, P. Reutler, A. Revcolevschi (LPCES, Univ. Paris-Sud)



Magnon dispersion in (La,Ca)MnO_3 along [001] at 17 K, showing two gaps, at q_0 and q = 3/8. Full (empty) symbols indicate the main (weak) magnons. Phonon dispersions are displayed as red lines). The gap at q_0 is interpreted as a folding of the dispersion curve with an anti-crossing effect due to magnon-phonon coupling.

Experiments performed on triple-axis spectrometers in the canted antiferromagnetic state of $La_{1-x}B_xMnO_3$ (B = Ca, Sr) have brought to light the existence of ferromagnetic platelets of nanometric size. In addition, they have revealed a complex spin excitation spectrum made of two magnon dispersion branches: one reminiscent of the pure antiferromagnetic compound, and the other one showing strong ferromagnetic character. Recent measurements under magnetic field do not indicate any splitting of the antiferromagnetic-like branches, pointing out that the two modes in zero field are actually due to the intrinsic splitting of the antiferromagnetic magnon branch by the inhomogeneous magnetic-field distribution induced by ferromagnetic clusters. The absence of crossing between the two branches might also be related the inhomogeneous character of the system. At the ferromagnetic cluster percolation, the compounds become ferromagnetic and metallic at T_c. However, a new and unexpected metal-insulator transition takes place upon cooling. In two similar compounds, $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.875}Sr_{0.125}MnO_3$, the inelastic neutron scattering studies of the spin excitation spectrum reveal the opening of gaps in the magnons dispersion curve. The gap energies coincide with phonon energies, pointing out a spin-lattice-charge coupling on the microscopic scale that could stabilize a charge order at low temperature. A spin-phonon coupling has been already reported in the metallic state (Ca, Sr: x = 0.3) and ascribed to the coupling between magnons and orbital fluctuations. The comparison between spin excitation spectra in both insulating and metallic ferromagnetic states is in progress.

Spin and charge inhomogeneities in manganites (see highlight)
Ch. Simon and coworkers (CRISMAT), D. Saurel (thesis), G. André, A. Brûlet (LLB)

As a result of the competition between ferromagnetic double exchange, induced by hole hopping, and the antiferromagnetic superexchange coupling, it was originally proposed that a uniform canted antiferromagnetic state should develop as a result of hole doping in manganites. More recent theoretical and experimental studies [M. Hennion *et al., Phys. Rev. Lett. 98*] rather suggest the occurrence of an inhomogeneous electronic phase separation, leading to the appearance of anisotropic ferromagnetic clusters. With increasing doping, the percolation of such clusters could explain the colossal magnetoresistance effect observed in these materials. The dimensions and shape of the ferromagnetic domains of nanometric size, which are embedded in an otherwise antiferromagnetic medium, have been determined by small angle neutron scattering in $Pr_{0.67}Ca_{0.33}MnO_3$.

1.d. Mixed-valence and Kondo systems.
Kondo insulators, mixed-valence semiconductors (see highlight)
J.-M. Mignot (LLB) – P. A. Alekseev, K. S. Nemkovski (RRC Kurchatov Inst., Moscow) – L.-P. Regnault (DRFMC/SPSMS, CEA/Grenoble) – F. Iga (ADSM, Hiroshima Univ.)

One challenging problem in correlated *f*-electron systems is to understand the emergence of an insulating ground state upon cooling in compounds that initially behave as metals near room temperature. The opening of a narrow gap ($E_g \sim 10$ meV) in the electron density of states near the Fermi level is actually predicted by the "periodic Anderson" or the "Kondo lattice" models for the special case of exactly one conduction electron per magnetic 4*f* site, but their applicability to real materials remains controversial. Inelastic neutron scattering can probe subtle changes in the low-energy magnetic response associated with the formation of the gap state. Detailed measurements on the Kondo insulator YbB_{12}, recently made possible by the availability of large single crystals from Japan, confirmed the existence of a spin gap below 10–15 meV at $T = 10$ K, and provided strong evidence that the excitations just near the gap edge have pronounced antiferromagnetic character.
In $Sm_{1-x}Y_xS$ alloys, a mixed-valence (MV) state is achieved by substituting Y into the originally divalent semiconductor SmS. In the latter compound, Sm^{2+}–Sm^{2+} exchange interactions are known to produce a dispersion in the $J = 0 \rightarrow J = 1$ spin-orbit transition. In the MV regime ("black phase"), a remarkable splitting of the dispersion curve into two branches occurs over the entire Brillouin zone. It has been suggested previously that the upper and lower branches might correspond to the localized and extended part of the MV Sm wave function, respectively, as predicted theoretically by Kikoin and Mishchenko. This view is supported by measurements for larger Y concentrations ($x = 0.17, 0.25, 0.33$) showing that, as the Sm valence increasingly deviates from +2, the lower branch gains spectral weight while splitting further apart from the upper one.

Orbital degrees of freedom, quadrupole order
K. Iwasa, M. Kohgi (Tokyo Metropolitan Univ.), J.-M. Mignot, C.P. Yang, A. Gukasov (LLB), M. Braden (LLB and FZ Karlruhe)

Neutron diffraction studies of the unique antiferroquadrupolar (AFQ) phase discovered previously in TmTe (rocksalt structure, divalent magnetic semiconductor) have been extended to include the very-low-temperature ($T \geq 100$ mK), high-field ($H \leq 7$ T) region, where one expects an interplay between quadrupole and magnetic dipole order. The results indicate that the pre-existing order of the O_2^2 quadrupolar components competes with Tm-Tm exchange interactions to produce a canting of the antiferromagnetic magnetic structure formed below $T_N = 0.45$ K. Huge irreversibilities observed at 0.1 K as a function of field denote a peculiar behaviour of the AFQ/AFM domains.
Ce monopnictides Ce*X* (*X*: P, As, Sb), order at low temperature in complex magnetic structures, consisting of long-period stacking sequences of ferromagnetic planes. In each plane, the Ce ions can have either large or small ordered magnetic moments, corresponding to two different crystal-field ground states,

respectively Γ_8-like or Γ_7-like. In this state, the Ce-4*f* orbital order therefore coexists with the magnetic dipole moment order. Inelastic scattering experiments have revealed an extra, nearly dispersionless, lattice excitation at 7 meV. This mode, which appears only in the orbital order phase, is thought to result from a local vibration within the large-moment planes, coupled to a change in the symmetry of the Ce 4*f* orbital due to its mixing with *p* orbitals of Sb neighbours.

The family of "filled skutterudites" RT_4X_{12} (R = lanthanide, T = {Fe, Ru, Os}, X = {P, As, Sb}) combines an exceptional variety of electronic properties with a potential for thermoelectric applications. Among them, $PrOs_4Sb_{12}$ is thought to be the first example of a Pr-based heavy-fermion superconductor. Diffraction experiments performed both at JAERI (Japan) and at LLB in Saclay have established the existence of a small AF moment in the new ordered phase stabilized below 1 K by a magnetic field $H \geq 4.5$ T. This field-induced AF component is ascribed to an AFQ order of the O_{yz} type.

High-pressure studies of magnetic and valence instabilities

In magnetically unstable 4*f* and 5*f* compounds, the decrease of interatomic distances produced by high hydrostatic pressures can induce substantial changes in the electronic structure. Magnetic powder diffraction experiments have been performed on several systems using the dedicated diffractometer G6.1 ("MICRO"). In Ce_2Fe_{17}, pressure modifies the magnetic structure and the magnetic ordering temperature T_N drops from 215 K at ambient pressure to 125 K at P = 7 GPa. (Z. Arnold, O. Prokhnenko, I. Goncharenko). A nonmagnetic state is expected to be achieved in this compound at about 20 GPa. In $YbMn_2Ge_2$, the Yb ions undergo a valence transition at $P \sim 1.5$ GPa. This transition results in a reorientation of the magnetic moments on the Mn sublattice [M. Hofmann P. Link, (IPC Universität Göttingen), I. Goncharenko (LLB).

Dipolar anisotropy of Gd ferromagnetic and antiferromagnetic compounds (see highlight)

In magnetically stable 4*f* compounds, the orbital part of the magnetic moment may be completely cancelled as in Gadolinium compounds and the magnetic anisotropy comes only from very weak dipolar forces or complex exchange mechanisms. Thanks to the high-energy neutrons of the hot source reducing the absorption, the good resolution of the 7C2 spectrometer and the high value of the magnetic moment, a series of Gadolinium magnetic compounds were studied to elucidate their structure and anisotropy. The predominance of the dipolar forces in both ferromagnetic and antiferromagnetic systems is very striking.

1.e. Quantum critical points.

Magnetic filed induced quantum critical point in Pr_2CuO_4

D. Petitgrand, P. Pfeuty (LLB) – A. Ivanov (ILL) – S.V. Maleev (Gatchina)

Pr_2CuO_4 is an insulating parent compound of high-T_c superconducting cuprates. In this system, a pseudo-dipolar interaction gives rise a non-collinear antiferromagnetic state. In a uniform magnetic field applied parallel to the CuO_2 planes, magnetic moments in neighbouring CuO_2 planes rotate and a spin-flop transition occurs. The transition can be either first or second order depending on the direction of the applied field. Studies have first focused on the second-order transition that takes place when a magnetic field H_{c0} = 3 T is applied along the [110] direction. H_{c0} is the end point of the critical magnetic field $H_c(T)$ at T = 0 and therefore corresponds to a quantum critical point, around which strong quantum fluctuations are expected. Neutron scattering experiments are carried out in order to observe these non-classical dynamical effects.

The order parameter, which vanishes at H_{c0}, exhibits a critical exponent $\beta \sim 0.2$, smaller than the expected classical values. Meanwhile, correlation lengths are strongly anisotropic. On the one hand, the out-of-plane spin correlation length decreases slowly from 80 Å down to 9 Å when varying the field from 3 to 5 T, implying the persistence of strong inter-plane spin fluctuations away from H_{c0}. On the other hand, in-plane spin fluctuations remain long range (> 500 Å). The characteristic frequency scale of the critical fluctuations is beyond the 10 GHz experimental detection threshold. Based on neutron scattering measurements, the system can be pictured as a set of long-range, slowly fluctuating, planar antiferromagnetic islands, weakly coupled perpendicular to the CuO_2 planes. In connection with the experiments, a theoretical model is developed by S. A. Maleev in Gatchina and quantum critical phenomena are studied by P. Pfeuty at LLB.

Quantum criticality in MnSi under pressures (see highlight)

C. Pfleiderer, D. Reznik, L. Pintschovius, H. v. Löhneysen (Karlsruhe Univ., FZ Karlsruhe, LLB)).

The transition metal compound MnSi is one of the most extensively studied itinerant-electron magnets. Below 30 K, it orders magnetically in a helical structure. Using hydrostatic pressure one can induce highly reproducible variations of its bulk magnetic properties, in particular its ordering temperature T_C is suppressed above $p_c = 14.6$ kbars. New single-crystal elastic scattering experiments have been carried out just below p_c ($p = 14.3$ kbars, $T_C \approx 3.3$ K) on the cold-neutron triple-axis spectrometer 4F1 using a miniature pressure cell. The results indicate the appearance of a partial order, akin to that found in liquid crystals, with magnetic intensity spread out over a sphere of radius 0.0422 $Å^{-1}$. More generally, this observation is an important step in the search for novel electronic states in intermetallic compounds.

Heavy-fermion superconductors

The study of critical phenomena occurring close to the quantum critical point (QCP) in heavy-fermion superconductors continues to be investigated in connection with possible dimensionality effects.

A careful study of the Q dependence of magnetic fluctuations in $CePd_2Si_2$ by B. Fåk (DRFMC, CEA/Grenoble, and ISIS) and N.H. van Dijk (Delft University of Technology) did not reveal significant anisotropy, contrary to expectations from the electrical resistivity. Experiments on $CeRu_2Si_2$ have been undertaken by S. Raymond and W. Knafo (DRFMC, CEA/Grenoble) to search for scaling laws in the (T,ω) dependence of the dynamical susceptibility. This study of the pure compound will complement measurements performed at the ILL on the solid solution containing 7% La located right at the QCP.

The new family of heavy-fermion superconductors $CeMIn_5$ (M = Rh, Co, Ir) presents a layer structure but it is still unclear whether 2D effects are important for their comparatively "high" critical temperatures. The pressure dependence of magnetic order in $CeRhIn_5$ close to the QCP has been determined by neutron diffraction. [J.-M. Mignot, I.N. Goncharenko (LLB), E. Moshopoulou (National Center for Scientific Research «Demokritos», Athens), A. Llobet-Megias (Los Alamos Nal. Lab.)], and inelastic measurements have been carried out on a (Rh, Ir) solid solution to probe the dynamical response close to the QCP.

2. MOLECULAR MAGNETISM

The design of molecules that could be used for information processing or storage is one of the main topics in molecular magnetism. This branch of material science deals with the magnetic properties of molecules, or assemblies of molecules, containing magnetic centres: spin-crossover systems, magnetic clusters or organic magnetic materials for example. The determination of spin density maps provides crucial information on the mechanisms of magnetic interactions, such as spin polarization and spin delocalisation. Polarized neutron diffraction on single crystals is a unique experimental technique that makes it possible to visualize the spin distribution over a whole complex molecule in its ground or metastable state.

2.a. Photo-induced molecular magnetism (see *highlight*)

A. Goujon, B. Gillon, A. Gukassov (LLB) – J. Jeftic, Q. Nau, (Ecole Nationale Supérieure de Chimie de Rennes) – E. Codjovi, F. Varret (Laboratoire de Magnétisme et d'Optique de Versailles)

In a pioneering experiment, carried out on the 5C1 diffractometer at LLB, the photo-induced magnetization density of the photo-switchable spin-crossover compound $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) could be obtained [A. Goujon et al, Phys. Rev. B 67(2003)220401(R)]. The photo-switching process was observed using a new experimental set-up in which the sample is illuminated in situ during the polarized neutron diffraction (PND) measurement. The photo-excitation kinetics was followed and a complete photo-process was evidenced. These results emphasize the potential of PND for studies of a variety of systems known to exhibit photo-induced magnetic effects. In particular, when the photo-excitation process is due to a charge transfer (metal-metal, metal ligand), PND technique should give an insight into the photo-excitation process and the metastable state. Therefore, new collaborations are starting off in this field: *i*) photo-magnetism has been evidenced in a high-spin molecule ($Mo^{IV}Cu^{II}_6$) in which the photo-excitation process is assumed to involve an electron transfer from a Mo^{IV} site to one of the six Cu^{II} sites. PND experiments should explain the photo-process mechanism and the magnetic nature of the photo-induced state [collaboration: Laboratoire de Chimie des Métaux de Transition, Univ. Paris VI]; *ii*) the technique will also be applied to the study of the photo-excited magnetic state in materials synthesized with the molecular precursor $K_4[Mo^{IV}(CN)_8]\bullet 5(H_2O)$ [collaboration: Laboratoire des Sciences Moléculaires, ICMCB].

2.b. Molecular clusters

The study of molecular clusters with large spins is another important topic in molecular magnetism. Using PND, one can unambiguously determine the magnetic ground state, which is not always possible from bulk magnetic measurements.

The magnetic properties of cyano-bridged (A^{II}, B^{V}) molecular-based compounds (A = {Mn, Co, Ni} and B = {Mo, W}) have been studied [J. Larianova, M. Pilkington, H. Andres, H. Stoeckli-Evans, H.U. Güdel, S. Decurtins]. The measurement of the magnetization density in $Ni^{II}_9W^{V}_6$ has confirmed an $S = 12$ ground state with a collinear spin alignment. In contrast, PND results do not support the proposal of an $S = 51/2$ state for $Mn^{II}_9Mo^{V}_6$ based on magnetization measurements. [Collaboration: Laboratoire de Chimie Moléculaire ET Organisation du Solide, Montpellier].

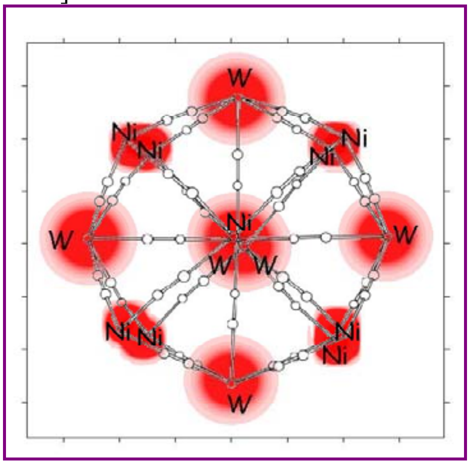


Figure 3. $Ni^{II}_9W^{V}_6$: projected spin density along the Ni1W3 direction (T=1.5 K, H=5 T)

2.c. Mixed compounds

In a system containing a rare earth (Gd) together with semiquinonate radicals, the combined determination of charge and spin densities sheds light on the mechanism of intramolecular magnetic interactions. In the case of the antiferromagnetic interaction between Gd^{3+} and a semiquinonate radical, it could be shown that there exists a spin delocalisation from the organic radical to the rare earth site in an isostructural compound where Y^{3+} substitutes for Gd^{3+}. This result supports an antiferromagnetic coupling involving the overlap of rare earth magnetic orbitals and the π orbital of the radical [collaboration: University of Florence, Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, Nancy].

3. NANOMAGNETISM

Investigations of the magnetic interactions in nanostructured systems will help creating new functionality in artificial magnetic materials. The new physics of magnetic superlattices or confined particles will enable major improvement in ultra-strong permanent magnets and magnetic-based electronics.

3.a. Magnetic ordering and phase transitions in confined media

I. V. Golosovsky (Gatchina), I. Mirebeau, G. André (LLB), and Ioffe Physical Institute of St Petersburg.

The study of magnetic ordering and phase transitions in confined media has been developed in two directions. At first, it has focussed on antiferromagnetic transition metal oxides (MnO, FeO, CoO) embedded in the same porous media (Vycor glass). Then, it has been extended to the antiferromagnet MnO embedded in porous matrices with a different topology such as:

i) porous glass Vycor (irregular matrix with a random interconnected network of pores),

ii) mesoporous materials of [MCM-41]- and [SBA-15]-type (regular hexagonal array of parallel channels with tuneable diameters of 20-90 Å),

iii) natural minerals such as Chrysotile asbestos.

For samples embedded in Vycor glass, the recent measurements in CoO confirm previous results on MnO: persistence of magnetic ordering in confined geometry, type of ordering and structural distortions similar to those in the bulk compound, noticeable reduction of the ordered moment ascribed to finite size effects. For samples embedded in natural (asbestos) or artificial (MCM, SBA) channels, neutron diffraction suggests that MnO is adsorbed at the surface of pores walls. The ordered moment is reduced with respect to the bulk moment, but surprisingly this effect is smaller in the smallest pores. Further measurements by complementary techniques (X-ray diffraction, EPR, magnetization) are in progress to confirm this result.

3.b. Dynamic nuclear polarisation (see *highlight*)

E. Leymarie and H. Glatlli (LLB), Collaboration with CEA, DRECAM/SPEC.

A new tool combining NMR techniques and Small Angle Neutron Scattering (SANS) has been developed to image the dynamic nuclear polarisation of paramagnetic centres. The contrast variation induced by this method can be viewed a new alternative to the standard H-D isotopic substitution, commonly used in soft matter and life sciences to study for example the transient dynamics of these complex systems.

3.c. Magnetic thin films (see *highlight*)

The LLB operates a polarized neutron reflectometer with polarization analysis (PRISM) dedicated to the study of magnetic thin films: multilayers of 3d ferromagnets (Fe, Co, Ni), rare earths (Gd, Ce), ferromagnetic oxides (manganites and magnetite), hard magnets (NdFeB) or magnetic semiconductors (GaMnAs). The polarized neutron reflectivity (PNR) technique allows one to determine fine details at magnetic interfaces (magnetization orientation, magnitude, roughness…) but also to determine the magnetic ordering and coupling in magnetic superlattices such as $[Fe/Si]_n$, $[Fe/Ge]_n$, $[GaMnAs/GaMn]_n$. In such superlattices, the magnetic coupling amplitude and sign depend on the thickness of the non-magnetic spacer and the coupling therefore oscillates between antiferromagnetic and ferromagnetic. A quadratic coupling (90°) is even observed for very specific structures. The trend in these last two years has been to study structures involving semiconducting materials that could be coupled to existing industrial microelectronic devices. Such structures are foreseen as possible candidates for spin-memory cells (MRAMs) and spin-transistors based on spin injection properties (see also ***highlight*** on GMR sensor optimisation)

3.d. Spin dynamics in thin films (see *highlight*)

The spin dynamics in confined structures, at the nanometric scale, is still a topic under investigation. Recently, the measurement of the spin-wave dispersion in semiconducting heterostructures (MnTe/ZnTe) has demonstrated the possibility of studying dynamical properties of magnetic thin films. This study has been performed thanks to the very high performance of the upgraded triple axis spectrometers of the LLB and the high-quality of MBE-grown single crystalline films of metastable Zinc Blende structure.
In parallel, a technique based on grazing incidence geometry has been evaluated on the PRISM reflectometer. The technique couples a surface sensitive technique (reflectivity) together with a selective excitation of the sample by a hyper frequency field. It should allow the characterization of very low energy magnetic excitations in thin films. In the first tests performed on Permalloy thin films, the accessible energy range has been found to be limited to 20GHz corresponding to surface magneto-static spin-waves in thin films.

3.e. Magnetic surface diffraction and Grazing Incidence Small Angle Neutron Scattering (GISANS)

"Grazing Incidence SANS", another technique derived from reflectivity, is presently evaluated on the spectrometer PAPOL. The technique will allow us to study the magnetic correlations in planar structures at a nanometric scale. The spectrometer PAPOL is currently being upgraded in order to implement and offer performing GISANS in the coming year. At the moment, the technique has been demonstrated for magnetic structures in the range 50-100 nm and will be extended to smaller sizes. One of the advantages of this technique is that neutrons can probe in-depth structures and give a quantitative magnetic information inaccessible to surface techniques such as Magnetic Force Microscopy for example. Application fields of GISANS concerns magnetic domains in thin films, self organized metallic clusters or nanometric objects fabricated by modern lithographic techniques to study the confinement and reduced dimensionality effects.
Confinement effects due to the finite film thickness or external strains due to epitaxial growth on a substrate strongly affect the magnetic behaviour of thin films. The precise knowledge of the magnetic ordering in thin films at the atomic level is therefore still a question. A new option of grazing incidence surface diffraction with polarized neutrons has been developed on the reflectometer EROS in order to study the magnetic order in epitaxial thin films (see ***highlight*** for a detailed presentation of this set-up).