MAGNETISM AND SUPERCONDUCTIVITY

The research related to magnetism is progressing steadily as shown by the number of new pertinent results of high quality at the international level and the large number of scientists involved coming from the Laboratoire Léon Brillouin and from other national and international laboratories. Let us mention as an example the "hot" result obtained recently which concerns the new rather unexpected discovery of **strong incommensurate magnetic fluctuations in the ruthenate** Sr_2RuO_4 (brother compound of the cuprate La_2CuO_4), a potent candidate for p-wave superconductivity.
The field covered is rich and in constant evolution with emergence of new subjects (spin ladders, ruthenates). The activities can be grouped into several subfields :
The first one (the largest) is entitled **Strongly Correlated Electron Systems**. After having got a strong impulse from the physics of high T_c cuprates, it progresses rapidly and becomes more unified. It includes the **Mixed Valence** and heavy fermions rare earth compounds, the **Low Dimensional** systems (spin Peierls system $CuGeO_3$ and spin ladder compound $(Sr,Ca)_{14}Cu_{24}O_{41}$), the "colossal magnetoresistance" **Manganites**, and naturally the **High T_c Cuprates** (and related materials such as the **ruthenates**).
The second one is the **Molecular Magnetism** developed in collaboration with the Chemistry group of O. Kahn at Bordeaux University.
The third one concerns **Magnetic Nanostructures,** a rapidly progressing theme which includes small agregates, superlattices and thin layered nanostructures.
The activity concerning **Magnetism in the frustrated Laves hydrides** $RMnH_x$ is rising rapidly .
Finally magnetic structure determination in various families of d and f intermetallic compounds constitutes an important activity in collaboration with several Solid State Chemistry Laboratories.

1. STRONGLY CORRELATED ELECTRON SYSTEMS

There are mainly two classes of strongly correlated electron systems : the rare earth (actinide) systems where the localised f electrons are strongly interacting with themselves and with the conduction electrons, and the d electron oxides where the d electrons are strongly interacting. Because of the strong interactions, Mott insulator-metal transitions are expected, new magnetic properties are obtained and Fermi liquid behavior of metals may break down. These strong interactions can lead to new types of superconductivity, charge and spin orderings. Neutron scattering is a good tool to study the new orderings and the fluctuations in their vicinity or at low dimension when ordering is suppressed and replaced by a **spin liquid** phase. This field is rapidly expanding both experimentally and theoretically. LLB takes part in this adventure.

1.a Mixed valence and Kondo systems (J.-M. Mignot)

This activity is developed by J.-M. Mignot together with postdocs in collaboration with French groups in Grenoble (Boucherle, Fak, Schweizer, Givord), a Russian group at Kourchatov Institute in Moscow (Alekseev, Clementyev, Goncharenko) and two Japanese groups, one at Tohoku University Sendai (Matsumara, Suzuki) and one at Tokyo Metropolitan University (Kohgi, Iwasa).

Antiferroquadrupolar order in TmTe

The most interesting result obtained in collaboration with the Japanese group at Sendai and with a postdoc (P. Link) is the determination by neutron diffraction of antiferroquadrupolar long range ordering in the mixed valence compound TmTe. This determination is indirect. Detailed information of the ordered state of quadrupolar moments is derived from the symmetry properties of the response to an applied magnetic field.

Mixed valence systems

In mixed valence systems such as Yb_4As_3 or Sm_3Te_4, the rare earth ion is not fluctuating between two valences but is either in one valence state or in the other. The number of ions in each valence state is fixed by charge neutrality. At low temperature, **charge ordering** occurs in Yb_4As_3. The ions with the valence corresponding to a magnetic ion order along one-dimensional chains which then behave as **spin 1/2 Heisenberg antiferromagnetic chains.** The excitation spin fluctuation spectrum has been studied by inelastic neutron scattering and the expected two-spinon

continuum spectrum has been recovered (in collaboration with the Tokyo Metropolitan University japanese group (Iwasa, Kohgi)).
In the other mixed valence system Sm_3Te_4, it seems that the different valence ions are not ordered even at very low temperature, but could form a **charge glass** with magnetic properties reminiscent of a spin glass of a new type (collaboration with Grenoble group : Boucherle, Givord, Schweizer).

Kondo systems
YbB_{12} is known to behave as a **Kondo insulator** with a small **charge gap** seen by photoemission. Neutron inelastic scattering on a powder sample have revealed a complex excitation spectrum with a well defined **spin gap**.
In heavy fermion systems (Kondo lattice) the border between the magnetic phase and the non-magnetic one is marked by the presence of a T=0 **quantum critical point (QCP)** which may be responsible for **non-Fermi liquid behavior**. The vicinity of such a QCP has been studied by inelastic neutron scattering in $Ce_{1-x}La_xRu_2Si_2$ with x close to .1 (collaboration with S. Raymond, L.P. Regnault, B. Fak (CENG)). The behavior seems to be different from another well studied compound $Ce(Cu_{1-x}Au_x)_6$ (Schröder)

1.b Low Dimensional systems
The renewal of interest in low dimensional systems is stimulated by the physics of high T_c cuprates for which the active electrons are located in D=2 dimensional CuO_2 planes and where **pseudogap** and non-Fermi liquid phenomena have been observed in the normal state, which are reminiscent of low dimensional electron systems (Luttinger liquid). Two quasi one-dimensional systems have been studied : the spin Peierls system $CuGeO_3$ and the spin ladder system $(Sr,La)_{14-x}Ca_xCu_{24}O_{41}$.

Spin Peierls system $CuGeO_3$
(M. Braden, B. Hennion, M. Ain (LLB), G. Dhalenne and A. Revcolevschi (Laboratoire de Chimie des Solides d'Orsay))
In this quasi one-dimensional system, the spin-Peierls dimerisation structural transition is based on the spin-phonon coupling. This aspect has been investigated in LLB for recent years by M. Braden. Contrary to the usual view which assumes an adiabaticity with fast magnetic excitations and slow phonons (soft modes), the situation has been shown to be the opposite. There are no soft modes, the phonons become harder so that there is non-adiabaticity. The spin excitations are slow and the phonon modes fast so that non-adiabaticity leads to a new effective spin Hamiltonian. This could explain (P. Pfeuty) the **recently discovered new excitation** by inelastic neutron scattering just above the two spinon continuum and independently of the spin-Peierls transition.

Spin Ladder system $(Sr,La)_{14-x}Ca_xCu_{24}O_{41}$
(L.P. Regnault (CENG), H. Moudden (LLB), J.E. Lorenzo (Laboratoire de Cristallographie de Grenoble)).
2-3-n legs ladders are one-dimensional systems which become closer to two dimensions when n becomes large. Such systems may constitute a link between one and two-dimensional electron systems and thus help to better understand the high T_c cuprate two dimensional physics. $(Sr,La)_{14-x}Ca_xCu_{24}O_{41}$ is a doped two-leg ladder system which becomes **superconductor** under pressure. The magnetic excitation spectrum has been studied by neutron scattering with clear evidence of a singlet-triplet excitation. Measurements as a function of doping show that the **spin gap** does not vary with doping. Experiments under pressure in the superconducting phase are expected soon. The samples are prepared by the Laboratoire de Chimie des Solides in Orsay (A. Revcolevschi)

1.c Manganites.
The oxides of perovskite structure with Mn ions have recently attracted a strong interest due to the discovery of a giant negative magnetoresistance. The doping of the family $RMnO_3$ (R: lanthanide) with divalent ions introduces holes in the d band that give rise to interesting interrelated magnetic, transport and structural properties.
Three projects are actually developed :

Inhomogeneities and magnetic excitations in $La_{1-x}Ca_xMnO_3$
(M. Hennion, F. Moussa, G. Biotteau [PhD student])
Pure $LaMnO_3$ is an insulator with a well defined antiferromagnetic structure at low temperature. When hole doping reaches a certain threshold around x=.3, the system becomes metallic and ferromagnetic and acquires new interesting transport properties. In order to understand this state, it is interesting to approach it from the low doping side $0<x<.2$. New unexpected properties have been discovered, some of which are not yet understood.
First, new **well defined low energy excitations** have been discovered from inelastic neutron scattering studies on single crystals (prepared by the Laboratoire de Chimie des Solides in Orsay).

Secondly, from small angle neutron scattering, **magnetic inhomogeneities** have been identified and characterized. These could be associated with **charge inhomogeneities** which are the object of much debate in the scientific community.
The same phenomena have been observed in the brother compound $La_{1-x}Sr_xMnO_3$.
Parallel studies (structural Jahn-Teller transitions) have been pursued on the same samples (J.Rodriguez-Carvajal).

Charge ordering phenomena
(J. Rodriguez-Carvajal, A. Daoud-Aladine [PhD student])
For specific doping elements and specific concentrations of these dopants a **charge ordered** state can be realized. This is the case for **$Pr_{.5}Ca_{.5}MnO_3$** and **$Nd_{.5}Ca_{.5}MnO_3$** which have been studied by neutron diffraction to reveal charge orderings (single crystals were grown by the Laboratoire de Chimie des Solides at Orsay). New experiments are planned with Ca replaced by Sr.
Another project leaded by C. Martin (Crismat-Caen; collaboration LLB: G. André, F. Bourée) deals with the relations between the nuclear and magnetic structures of some GMR manganites and their associated macroscopic (magnetic, transport...) properties. For the family $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ ($0<x<0.5$), the complete nuclear and magnetic phase diagram has been obtained from neutron powder diffraction showing the influence of the A cation size on the magnetic properties of the compounds. The influence of the doping on the Mn site on the charge and orbital ordering of the $Pr_{0.5}A_{0.5}Mn_{1-x}M_xO_3$ (A=Sr,Ca; M=Cr,Al; x=0.05) compounds has been studied for Cr and Al doping.

1.d Magnetism and Superconductivity in cuprates and ruthenates.

High T_c cuprates
LLB Neutron group (Y. Sidis [new CNRS recruitment], P. Bourges, D. Petitgrand, B. Hennion, M. D'Astuto [PhD student]), LLB Crystallogenesis group (G. Collin, P. Gautier-Picard [Postdoc], L. Manifacier [PhD student]), LLB Theory group (F. Onufrieva, P. Pfeuty, M. Kisselev [post doc], F. Bouis [PhD student]))
High T_c cuprates constitute the motor of the actual development of the field of strongly correlated electron systems. After more than ten years of intense experimental and theoretical efforts, the secrets of those highly complex electronic systems are still not yet unraveled and we should pursue our efforts.
High T_c cuprates are characterized by global anomalies : the very existence of high T_c anomalies observed for all properties in the underdoped regime above T_c, anomalies observed in the superconducting state. There are more and more arguments that all of them are somehow related to anomalous magnetism. This is why the study of details of magnetic properties becomes today a key point for understanding the physics of high T_c cuprates.
In LLB we follow a strategy combining three interrelated actions : **preparation** of large good quality single crystals; **inelastic neutron scattering** experiments giving access to the spatio-temporal magnetic response in both the normal metallic state and the superconducting state; **theoretical** developments trying to give a unified picture for both charge and spin properties.
The **underdoped** regime has been extensively studied. In the superconducting state, the existence of a **resonance peak** has recently been confirmed in a new system **$Bi_2Sr_2CaCu_2O_{8+\delta}$ (BiSCO),** in collaboration with B. Keimer and H.F. Fong (University of Princeton and MPI Stuttgart), for which the electronic spectra are known from photoemission experiments. The neutron resonance peak has larger momentum and energy width in BiSCO than in YBCO.
New experiments have been realized with **Zn** and **Ni** doped YBCO samples prepared by the LLB crystallogenesis group (G. Collin, P. Gautier-Picard). The effect of these two impurities seems to be rather different : Zn affects strongly the resonance peak, whereas Ni only shifts it slightly with a broadening in both wave vector and energy .
New results obtained in underdoped YBCO both in LLB and abroad (Mook, Hayden, Aeppli) show that for energy below the energy of the commensurate resonance peak there exists an **incommensurate** dynamic response. This has been explained by the LLB theory group (F. Onufrieva, P. Pfeuty) based on the general theory of two dimensional electron systems close to an Electronic Topological Transition (ETT). It is shown that the superconducting state in the two-dimensional electron system in the proximity of ETT (i.e. a long range ordered state with respect to charge degrees of freedom) is at the same time a **quantum spin liquid** state with respect to spin degrees of freedom and that both the resonance peak and the incommensurability are signatures of such a **mixed state**. As we already noticed, this is only part of a general theory developed by the theory group (F. Onufrieva, P. Pfeuty, M. Kisselev, F. Bouis). This theory being developed for different properties and for both normal and superconducting states allows to understand crucial anomalies observed experimentally in high T_c cuprates by NMR, inelastic neutron scattering, photoemission, tunneling... More generally it shed light on the nature of the new anomalous metallic state observed in the high T_c cuprates and on the very existence of high T_c superconductivity with d-wave symmetry.

Two other important situations remain to be understood : the **overdoped** regime for which actually no neutron scattering study exists; and the case of **electron doped** cuprates for which the phase diagram is different.
The electron doped system $Nd_{2-x}Ce_xCuO_4$ has been investigated (thesis submitted in 1998 by M.D'Astuto (under the direction of D. Petitgrand)). Samples were not good enough to study dynamic magnetic fluctuations in the superconducting state. The magnetism of rare earth Nd has been studied both in the pure non-superconducting sample Nd_2CuO_4 and in the superconducting sample (T_c=10K) $Nd_{1.85}Ce_{.15}CuO_4$. In Nd_2CuO_4, quasi-elastic scattering due to Nd has been measured with the existence of two components : a three dimensional one and a two dimensional one. This could be due to the nature of the interactions between the Nd and Cu ions. To better understand these interactions, magnetic excitations of Nd have been analysed at low temperature. In $Nd_{1.85}Ce_{.15}CuO_4$, magnetic order of Nd has been studied and it is shown that the effect of the presence of superconducting CuO_2 planes is to induce bidimensional order of Nd magnetic moments.
Finally the role of the reservoir planes in the high T_c cuprates has been considered in a recent PhD thesis work (L. Manifacier 1998 under G. Collin supervision) by crystallographic (structural refinements) and magnetic (diamagnetic susceptibility) studies performed on lead and rare-earth substitutions in Bi-2212 systems. The main conclusion reached is that "overdoped", "underdoped", and insulating phases would depend altogether on the carrier concentration in the CuO_2 planes, their mobility, and the physical state of the charge reservoirs.

Ruthenates
(M. Braden, W. Reichardt, (Kf. Karlsruhe) , Y. Sidis, P. Bourges, B. Hennion, G. André (LLB), Y. Maeno (Kyoto University))
A few years after the discovery of superconductivity in CuO_2 systems, a new **oxide superconductor** has been found : **Sr_2RuO_4**. This system has the same layered perovskite structure as La_2CuO_4, but behaves otherwise very differently. In its stoechiometric composition it is metallic and becomes superconductor at 1.5 K. The electronic properties are determined by the three 4d t_{2g} orbitals (d_{yz},d_{zx},d_{xy}) of the Ru^{4+} ion which form the bands that cross the Fermi level resulting in two electron-like quasi-one-dimensional Fermi Surfaces (FS) and one hole-like quasi-two dimensional FS (analogous to the 2D FS of cuprates). Some experiments suggest that superconductivity is rather unconventional of **p-wave symmetry** and could be due to the coupling with ferromagnetic fluctuations. To confirm this view it was essential to study the magnetic fluctuations by neutron scattering on a single crystal which was available (Maeno). Existing NMR results are difficult to interprete making neutron data essential. Recent results reveal unambigously intense dynamic **spin fluctuations** at low energy (8 meV) and for an **incommensurate** wave vector (.3,.3,0) $2\pi/a$. This can be interpreted in an itinerant picture as a dynamic quasi-nesting effect due to the two quasi-one dimensional electron like FS (Mazin, Pfeuty). These experiments have been made in the normal metallic state with temperature 10K<T<300K. Further experiments are planned to explore the superconducting state.
Lattice dynamics has been also explored. If the modes associated with an intra-plane charge ordering behave normally, an anomaly is observed for the vibrations associated with an inter-plane charge ordering .
When Sr is replaced by Ca, the system orders antiferromagnetically at low temperature. With excess oxygen, structural studies by neutron diffraction have shown that **Ca_2RuO_4** presents a first order structural transition associated with a metal-insulator transition.

2. MOLECULAR MAGNETISM

Molecular magnetism is at the borderline between magnetism and organic condensed matter chemistry. It constitutes an activity developed for many years in LLB by B. Gillon in collaboration with O. Kahn and his laboratory at the Institut de Chimie de la Matière Condensée in Bordeaux. Recently an English postdoc (John Stride) joined B. Gillon's group.
The main project developed actually consists in the study of the **ferromagnetic interaction mechanisms** in molecular compounds through the determination of the spin density map which is obtained from diffraction by polarized neutrons. The study of the organic radical triazole nitronyl nitroxide has not been completed because of the lack of sample. A complete study of the bimetallic compound **$MnNi(NO_2)_4(en)_2$** (en=ethylendiamine) has been realized. In this compound ferromagnetic chains are formed. The spin density map has been determined and the main result is the low apparent spin transfer from the metallic ions to the bridge NO_2 with a larger spin delocalization towards the outside atoms. This could be due to a compensation effect between two opposite effects, delocalization and spin polarization. Actually a similar study is in progress with the ferromagnetic bimetallic compound **$Mn_2H_2OMo(CN)_74H_2O$.**
The informations coming from spin density measurements are completed with charge density measurements from X-ray diffraction and compared to quantum chemistry calculations.

3. MAGNETIC NANOSTRUCTURES

Because of new fabrication tools (epitaxy, nanolithography), small size architectures are designed and a study of their fundamental properties is a challenge for future technological applications.

3.a Molecular nanomagnets : low energy excitations of the Mn_{12} acetate spin cluster

(I. Mirebeau, M. Hennion)

Molecular nanomagnets consist of a few (10-20) paramagnetic ions coupled by exchange interactions. The study of these large magnetic molecules has both fundamental and practical interest (information storage).

New data of very high precision concerning the low energy magnetic excitations of the Mn_{12} acetate spin cluster have been obtained by inelastic neutron scattering at LLB and ILL. This enables to separate the energy sublevels of the ground state and determine through a simple quantum mechanical calculation the value of a very small non- diagonal term which presence in the spin Hamiltonian is necessary to explain the excitation spectrum. This term which produces quantum tunneling between the different magnetic quantum levels is then responsible of the observed finite relaxation time of the magnetization at low temperature.

3.b Neutron Diffraction of rare earth superlattices and epitaxial films

(M. Hennion (LLB) and C. Dufour, K. Dumesnil, P. Mangin (Laboratoire de Physique des Matériaux, Nancy))

Spin reorientation in Laves phases (RE)Fe_2 (RE=rare earth).

Laves phases (RE)Fe_2 present a giant magnetostriction effect at room temperature with potential applications. An epitaxial film of the ternary compound $Dy_{.7}Tb_{.3}Fe_2$ has been prepared and studied by neutron diffraction to follow the spin reorientation as a function of temperature. An actual project concerns the polarized neutron study of the superlattice $DyFe_2/YFe_2$ to determine the spin density and follow the spin reorientation as a function of temperature and magnetic field.

Light rare earth films and superlattices

Neutron diffraction of Sm films with thickness of 4000 Å show that the magnetic order of the Sm in the hexagonal sites seems to be the same as in the bulk, but with a higher magnetic moment. The nature of long range interactions between magnetic Sm through non magnetic Nd phase should be studied on superlattices Sm/Nd.

3.c Magnetic structure of superlattices, thin films and regular nanostructures from polarized neutron specular and off-specular reflectometry and surface diffraction

(C. Fermon, F. Ott)

These three different techniques are developed at LLB. When applied together to regular magnetic nanostructures of sufficient size, they give a full 3D magnetic structure determination both parallel and perpendicularly to the surface of the nanostructure. These techniques have been applied to different examples of nanostructures : this necessitates large regular samples (1cm ×1cm) with repetitive motives (alternate lines, alternate layers, lattice of magnetic motives). Only a few laboratories prepare such samples and collaborate with the LLB : SPEC Saclay, CENG Grenoble, CRISMAT Caen, IEF Orsay, IPCMS Strasbourg. The systems studied are Fe/Mn/Fe sandwich structures, $(LaMnO)_m(SrMnO)_n$ superlattices, FePd and Co thin layers with magnetic domains, Pt/Co irradiated interfaces and M/Co/M (M=Au,Pt) sandwiches, Co/Mn superlattices, $La_{.7}Sr_{.3}MnO_3/SrTiO_3$ interface, $La(Sr,Ca)MnO_3/YBa_2Cu_3O_7$ interface, Si/SiO_2/Co systems with an electric field.

4. Magnetism in the frustrated Laves hydrides $RMnH_x$

(I. Mirebeau (LLB), I. Goncharenko and A. Irodova (Kurchatov Institute, Moscow))

The RMn_2 compounds where R is Y or a rare earth metal, have been studied during the recent years for several interests : the magnetism of Mn at the border between localized and itinerant; the interplay between R and Mn magnetism; quantum frustration effects for the Mn sublattice with antiferromagnetic interactions.

When hydrogen is added and occupies the interstitial site in the metal sublattices, new interesting effects can be studied : hydrogen acts as a negative pressure on the magnetism of Mn; hydrogen can order and the H ordering can affect the magnetic ordering of Mn and R.

In recent studies of the magnetic and crystal structures of **$YMn_2H_{4.3}$,** a peculiar interplay between the magnetic and hydrogen order has been observed. Mn magnetic moments and hydrogen atoms order simultaneously through a first order structural transition.

Further neutron diffraction (and eventually inelastic neutron scattering) studies of the interplay between hydrogen and magnetic orders are in preparation using chemical substitution, applied pressure and varying the hydrogen content.

Similar structural and magnetic phase determinations have been pursued on the same hydrides but for lower hydrogen concentration (specifically x=1.1) by M. Latroche, V. Paul-Boncour from CNRS-Thiais and F. Bourée, G. André (LLB).

5. DETERMINATION OF MAGNETIC STRUCTURES IN MAGNETIC SYSTEMS WITH D AND F ELECTRONS

When new families of magnetic compounds are synthesized, it is essential to determine their magnetic structure in order to have access to the microscopic magnetic interaction at work. This is done in close collaboration with solid state chemistry laboratories in France (Bordeaux, Rennes, Paris VI, Clermont-Ferrand...) and abroad (Spain, Germany, Poland, Russia, Switzerland). Many different compounds are studied, ranging from transition metal, rare earth to actinide compounds. Among these, let us consider three typical examples:
With the ICMCB Bordeaux (B. Chevalier) and the LLB (F. Bourée and T. Roisnel), the study of the family R_2T_2X (R=rare earth or U; T=transition metal; X=Sn or In) has been pursued (PhD thesis of D. Laffargue) mainly for X=Sn, T=Pd and R=Tb,Dy,Ho,Er. Two magnetic structures (commensurate and incommensurate) have been determined at low temperature for all of these four compounds but with different magnetic moments depending on the rare earth element and reflecting the competition between the magnetic RKKY exchange and the crystalline field anisotropy.
The magnetic structures of different and new Uranium compounds (UGe_2, U_3Ge_5, U_3TiGe_5, $U_3Ga_2Ge_3$) synthesized by the group of H. Noël at Rennes (collaboration with LLB (G. André and F. Bourée)) have been obtained, stressing the key role of the local Uranium ion environment (nature and ligand position in the cell) on the Uranium magnetic properties.
A study on a new Terbium fluoride family has begun with the compound KTb_3F_{12} (D. Avignant from Clermont-Ferrand in collaboration with the LLB (F. Bourée and G. André)) where Tb is present in two valence states : Tb^{4+} and Tb^{3+} (ratio $Tb^{3+}/Tb^{4+}=1/2$). Neutron diffraction gave two main results : the precise localization of the light F atoms leads to correct the X-ray space-group determination (from I4/mmm to I4/m); the compound is antiferromagnetic below $T_N \approx 3.65K$ with only the Tb^{4+} moments magnetically ordered.

CONCLUSION

Six years after the impulse given by Jean Rossat-Mignod when he joined the LLB from 1991 to 1993, the activity in magnetism is progressing well with a large spectrum of research themes.
It benefits from a close collaboration with chemists : O. Kahn (Bordeaux) for molecular magnetism, A. Revcolevschi (Orsay) for the preparation of single crystals of Strongly Correlated Electron Systems and G. Collin and P. Gautier-Picard (crystallogenesis group at LLB) for the preparation of single crystals of high T_c compounds.
Efforts are made to get better instruments (new polarized neutron triple-axis 2T) with a better environment (high pressure and high magnetic field).
The coupling with theory is good especially on high T_c cuprates and is progressively extending to other subjects.