MAGNETISM AND SUPERCONDUCTIVITY

Magnetism and superconductivity represents a large part of the activity of LLB (8 thesis students present at LLB in 1999 and/or 2000). We have seen the emergence during the last years of several new subjects: topologically frustrated magnetic systems,the first study of a spin flop magnetic quantum tricritical point in Pr_2CuO_4, magnetic ordering in confined media,coexistence of magnetism and superconductivity in high Tc cuprates,the inelastic study of the spinwave spectrum in a thin film of MnTe.

The activities can be grouped into several subfields:
The first one, the largest one, concerns Complex Electronic Systems. It includes ruthenates, high Tc cuprates, manganites, mixed valence and Kondo systems particularly 1D magnetism in the charge ordered mixed valence system Yb_4As_3, non collinear antiferromagnetism and quantum critical effects in Pr_2CuO_4.

This field needs long term tenacious experimental efforts coupled to new theoretical developments to unravel intricate effects due to the interplay between numerous degrees of freedom (charge, spin, lattice). New concepts are emerging: competition between several ordered ground states and the presence of quantum critical points, importance of charge ordering and charge segregation phenomena, low dimensional effects.

The second one concerns Nanomagnetism, a rapidly progressing theme (under pressure from the technology oriented "Spintronics"), with new results such as: the inelastic study of thin films of magnetic semiconductors, the magnetism in confined media and the study of proximity effects in magnetic trilayer systems.

The third one is Molecular Magnetism developed in collaboration with several chemistry groups (Bordeaux, Montpellier, Florence).
The activity concerning the Topologically Frustrated Magnetic Systems constitutes now a new subfield.
Finally, magnetic ordered structure determination in various families of d and f intermetallic compounds constitutes a basic activity in collaboration with several Solid State Chemistry Laboratories.

The activity of LLB on Magnetism and Superconductivity is at the International level and benefits from tight collaborations mainly with Russia, Japan, Germany, Poland and Italy. There is also a close connection with Grenoble (ILL+CENG).

1. COMPLEX ELECTRONIC SYSTEMS

1.a. Ruthenates (see highlight)

(M.Braden, O.Friedt (thesis), Y.Sidis, P.Bourges, P.Pfeuty and Y.Maeno (Kyoto University))

Ruthenate Sr_2RuO_4 is the only superconducting layered perovskite isostructural with the cuprates. There is evidence that the superconducting pairing is unconventional (triplet symmetry) and the coupling mechanism is still subject of debate. A pairing mechanism via ferromagnetic fluctuations has not been confirmed by the inelastic neutron scattering studies developed at LLB. Instead it was found that the magnetic spectrum above Tc is dominated by incommensurate fluctuations which may arise from the quasi one dimensional nature of two of the Fermi surface sheets associated with the orbitals dxz and dyz of Ru. The change of the fluctuation spectrum when the superconducting phase is reached is actually under intense study at LLB.

The temperature dependence of the incommensurate dynamic excitations shows that a characteristic energy scale goes down with decreasing temperature which is the signature of closeness to a magnetic instability, in agreement with the recent finding of static incommensurate order (with the same incommensurability vector) in a compound with a slight Ti doping (x=.09 Ti replacing Sr)

Superconductivity in Sr_2RuO_4 is very sensitive to doping and disappears as soon as Sr is replaced by some doping element. Replacement of Sr by Ca (with smaller size) leads to a very rich phase diagram with a great variety of structural distortions and several magnetic phases (Thesis of O.Friedt). There is a close coupling between structural and magnetic anomalies due possibly to a change of the Fermi surface induced by structural modifications. For instance in $Sr_{1.5}Ca_{.5}RuO_4$ the magnetic susceptibility is enhanced and magnetic dynamical fluctuations have been seen at LLB for a q vector (.2,0,0) close to ferromagnetic q=(0,0,0), which is certainly revealing a change of the Fermi surface.

Magnetism and Superconductivity

1.b High T_c cuprates

LLB Inelastic Neutron group (P.Bourges, Y.Sidis), B.Keimer+collaborators (MPI, Stuttgart), L.P.Regnault (CENG), A.S.Ivanov (ILL), LLB Crystallogenesis group (G.Collin), LLB Theory group (F.Onufrieva, P.Pfeuty))

The resonance mode

Recent studies have shown that the "resonance" magnetic exciton bound state dispersive mode, characteristic of the superconducting state and first seen by J.Rossat-Mignot et al ten years ago, is a generic feature in d-wave superconducting cuprates. This mode had been extensively studied in underdoped and optimally doped YBCO. It has been also found recently in optimally doped BiSCO. The dispersion of this mode, which is rather peculiar and which had been predicted by LLB theorists (Onufrieva, Pfeuty), has been shown experimentally in underdoped YBCO. Very recently, the resonance mode has been observed at 38 meV in overdoped bilayer BiSCO (T_c=83K). Its energy position is smaller than in optimally doped BiSCO (T_c=91K, E_{res}=43meV).

Very recent measurements performed at LLB provide evidence of the magnetic resonance E_{res} =47.5mev at (π,π) in the superconducting state of $Tl_2Ba_2CuO_{6+x}$ (T_c=92K), a single layer system without structural complexity such as copper oxide chains, incommensurate superstructure, or CuO_2 buckling distortions. This is the first evidence of a resonance mode for a single layer system, which rules out that the resonance mode is due to the strong interaction of two closely spaced oxide layers. All the experiments on the resonance mode are made in collaboration with B.Keimer's group (Max Planck Institute, Stuttgart). The sample which was used for this experiment is made of 300 aligned small single very pure crystals prepared in Russia and with a total volume of 100 mm^3.

Coexistence of antiferromagnetism and superconductivity

Commensurate antiferromagnetic ordering has been observed in the very underdoped high T_c cuprate $YBa_2Cu_3O_{6.5}$ (T_c =55K) by polarized and unpolarized elastic neutron scattering (see Figure 1). The form factor decreasing faster at large Q is consistent with more delocalized magnetic states. This could be a spin density wave state which coexists at lower temperature with d-wave superconductivity as shown by theoretical studies (F.Onufrieva, P.Pfeuty, M.Kisselev, F.Bouis (thesis)). This surprising observation of the coexistence of antiferromagnetism and superconductivity had been already made in 1988 (D.Petitgrand, published in J.Phys. (Paris) 49, 1815 (1988)) but not considered seriously at that time. The origin of this antiferromagnetic phase could be associated with impurities or defects acting as a revelator of an intrinsic situation, and more detailed studies are certainly needed. Similar coexistence of magnetism and superconductivity has also been observed in optimally doped YBCO in the presence of a small concentration of Co (with J.A Hodges).

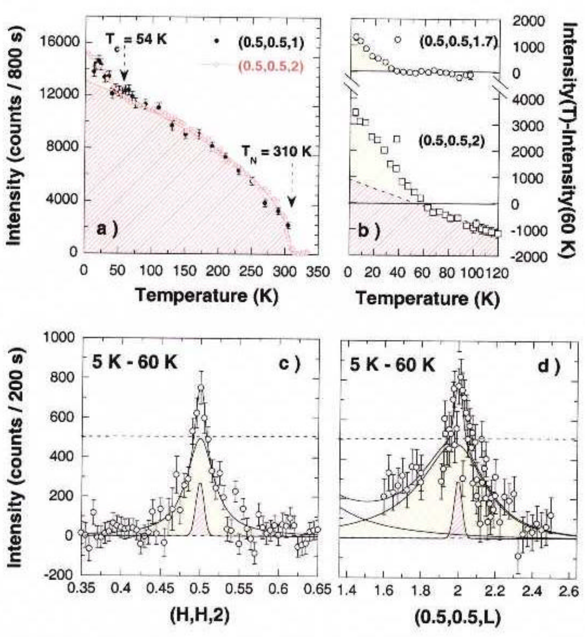

Figure 1. a, b) Temperature dependence of antiferromagnetic superlattice reflexion intensity in $YBa_2Cu_3O_{6.5}$ showing a kink at the superconductivity transition temperature T_c = 54K. c,d) The excess intensity below T_c.

1.c. Manganites

Inhomogeneities and magnetic excitations in $La_{1-x}Ca_xMnO_3$ at low doping

(M.Hennion, F.Moussa, G.Biotteau [thesis])

The study of manganites $La_{1-x}Ba_xMnO_3$ 0<x<.2 (insulator regime) B=Ca and Sr, has been pursued in two directions.

1.The spin dynamics in the low doping regime 0<x<.1 has been studied in the presence of a magnetic field and the picture emerging from the evolution of the different excitation branches with the magnetic field is a picture of ferromagnetic clusters enriched with holes coupled together ferromagnetically through an antiferromagnetically ordered matrix poor in holes.

2. At higher concentration, x>.1 close to the metallic ferromagnetic phase, the magnetic excitation spectrum changes drastically and acquires a magnetovibrational character. For x>.125, diffuse scattering experiments show that the charge segregation changes from a 3D cluster to a 2D lamellar organisation.

Charge orbital spin ordering phenomena

(J.Rodriguez-Carvajal, A.Daoud-Aladine [thesis])

The proposed orbital ordering which explains the complex antiferromagnetic order in half doped $R_5D_{.5}MnO_3$ manganites is concomitant to a charge ordering. New neutron diffraction experiments on $Pr_{.6}Ca_{.4}MnO_3$ allows to discriminate previous proposed models based on a mixed valence charged ordered model with a stacking of small $Mn^{4+}O_6$ and large $Mn^{3+}O_6$ octahedra. A non centro-symmetric structure is obtained having Mn sites in two types of octahedra of very similar size, characteristic of an intermediate valence state.

Structural and magnetic properties of CMR manganites

(C.Autret (thesis CRISMAT-LLB), C.Martin (CRISMAT), G.André, F.Bourée)

Manganites are prepared and their physical properties are studied in Caen; their structural and magnetic properties are obtained in LLB. Three families have been studied.

1. The system $Pr_5Sr_{.5-x}(Ca/Ba)_xMnO_3$ with x=.05,.2, has been first studied with a ratio $Mn^{3+}/Mn^{4+} \approx 1$. As function of decreasing temperature there is a succession of phases from paramagnetic metallic (PM) to ferromagnetic metallic (FM) and finally to antiferromagnetic metallic (AFM).

2. In another family, Mn is substituted by another d element and two systems have been studied: $Sm_{.2}Ca_{.8}(Mn_{1-x}Ru_x)O_3$ and $Ca(Mn_{1-x}Co_x)O_3$. In both cases for x=.1 a drastic change appears with CMR properties and the coexistence of both a ferromagnetic and an antiferromagnetic phase is observed.

3. The properties of the layered 2D manganite $Pr_{2-x}Ca_xMnO_4$ with 1.5<x<2. have been compared with those of a similar (also rich in Mn^{4+}) 2D manganite and in both cases there is a coexistence of a ferromagnetic and an antiferromagnetic phase.

1.d. Mixed valence and Kondo systems (J.M.Mignot, A.Gukasov)

Mixed valence semiconductors/Kondo insulators

(with P.A. Alekseev "Kurchatov Institute")

The spin gap behavior previously observed in the low temperature (T<50K) magnetic spectra of the Kondo insulator YB_{12} was confirmed by new high resolution time-of-flight experiments performed on IN6 (ILL). Above 50K, a broad quasielastic component reappears gradually. Lutetium substitution experiments show that up to x_{Lu}=.25 the gap structure remains similar to that of pure YB_{12}.

The inelastic response of $Sm_{.83}Y_{.17}S$ has been obtained. There are two different excitation branches with comparable dispersions, which appear to exchange their intensities about half way to the zone boundary. The lower branch is ascribed to the extended part of the Sm mixed valence wave function, in line with previous results obtained in SmB_6.

Valence instabilities in Tm monochalcogenides: novel magnetic phases at high pressure

(with I.N. Goncharenko and J.M. Mignot)

Previous measurements on TmTe have been extended to 6 GPa showing a new type I antiferromagnetic phase identical to that occurring at ambient pressure in TmSe.

Magnetism and Superconductivity

TmSe is already in a mixed-valence state at P=0, but pressure changes the magnetic structure from type I to type II near P=3GPa. Recent measurements indicate that the AF I phase can be restored by applying a magnetic field in the direction <001> of about 2 Tesla at P=4.1GPa.

TmS is a metallic Kondo system with a complex incommensurate magnetic structure at low temperature. By applying a pressure of 5.7 GPa, the propagation vector is locked in at the commensurate vector (.5,.5,.5).

All these experiments have been realized in LLB on the spectrometer 6T2

Staggered field effect on the one dimensional S=1/2 antiferromagnet in the mixed valence system Yb_4As_3
(see highlight) (J.M.Mignot and A.Gukasov)

(this theme is under the leadership of M. Kohgi from the Tokyo Metropolitan University with K.Isawa et al)

The study of the mixed valence system Yb_4As_3, which is now pursued for several years, reveals a great richness of unexpected phenomena related to the physics of one dimensional spin chains which are formed at low temperature, when charge ordering takes place with the building of one dimensional arrays of Yb^{3+} carrying spin 1/2.

Recent experiments have shown that by applying a magnetic field perpendicular to the [111] direction, a gap opens in the normally gapless excitation spectrum. This effect has been explained (H.Shiba et al) as due to a "staggered field" on Yb^{3+} induced by the uniform magnetic field perpendicular to the chains in the presence of a Dzyaloshinsky-Moriya interaction.

1.e. A new quantum critical point induced by a magnetic field in Pr_2CuO_4 (see highlight)
(D.Petitgrand with A.S.Ivanov (ILL), theory made by S.V.Maleyev (Gatchina))

In Pr_2CuO_4, the pseudodipolar interaction is responsible for the non collinear antiferromagnetic structure. In the presence of a uniform magnetic field applied parallel to the CuO_2 plane, the directions of the spins in the two adjacent CuO_2 planes rotate and a spin-flop transition takes place. Such a spin-flop transition extends up to T=0 where the order of the transition depends on the angle ψ that the field makes with the direction <100>. This transition is first order when ψ is different of $\pi/4$ and becomes second order when ψ is equal to $\pi/4$. The point ($\psi = \pi/4, H = Hc, T = 0$) is a Quantum Tricritical point of much interest (the first example) which is actually studied in great details from static and inelastic neutron measurements. The theory is developed by S.V. Maleev (Gatchina) and the quantum critical aspect is discussed by P.Pfeuty. Furthermore, the two relevant fields: temperature (a few K) and magnetic field (a few Tesla), are quite easily accessible experimentally, and a good single crystal of reasonable size is available. Results are already obtained and more experiments are programmed.

2. NANOMAGNETISM

Molecular nanomagnets (B.Gillon, D.Petitgrand)
"Giant spin" clusters (Mn+Mo, Co+Mo, Ni+Tu) prepared by J.Larionova (Montpellier) are actually studied by different neutron techniques (polarised neutrons, inelastic scattering...). This constitutes the beginning of a long term program.

Magnetic ordering and phase transitions in confined media (I.V.Golosovsky (Gatchina), I.Mirebeau, G.André (LLB), D.A.Kurdyukov, Yu.A.Kumzerov, S.B.Vakrushev (St Petersburg))

Antiferromagnetic MnO embedded in a porous SiO_2 glass has been studied by neutron diffraction. The type of magnetic ordering and the structural distortion are similar to those of the bulk, but the ordered magnetic moment is strongly reduced (from 4.89 to 3.84 μ_B per ion) and the Neel temperature is enhanced (from 118K to 124K). The magnetic transition is **second order** in contrast to the first order transition in the bulk. These results are not well understood. The MnO samples were prepared in situ (Russian collaboration) from a manganese nitrate solution by chemical bath deposition method. The glass matrix has a random interconnected network of elongated pores with a narrow distribution of pore diameters of 7 nm (see Figure 2).

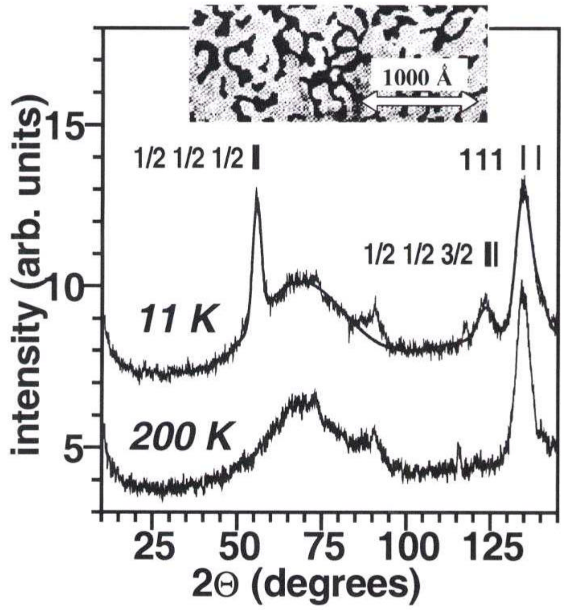

Figure 2. Neutron diffraction pattern of MnO embedded in a porous glass, measured at 11K and 200K on the G6.1spectrometer (λ=4.732 Å). The solid line corresponds to the calculated profile. In the top insert, a typical fragment of the pores network (in dark) viewed by electron microscopy.

Spin dynamics in thin film and multilayers of a magnetic semiconductor (B.Hennion and W.Szuszkiewicz (Poland))

This is the first inelastic neutron study of very thin 2D magnetic samples (thickness of a few microns, volume of the order of $1mm^3$). The rapid development of spin electronics or "spintronics" with potential technological applications, pushes the study of magnetic semiconducting films. In this perpective, the MnTe films and MnTe+ZnTe multilayers have been studied by inelastic neutron scattering. Spin wave dispersion spectra have been obtained which give access to the magnetic interaction microscopic parameters.

Magnetization measurements in thin films and multilayers from neutron reflectivity (C.Fermon and F.Ott)

Neutron reflectivity allows the study of the surface and interface magnetism in magnetic multilayer systems. In artificial structures of very thin magnetic films (of the order of few nanometers) one can observe magnetic behaviors not observed in bulk materials. Non collinear magnetic coupling has been observed in $Fe_{1-x}Co_x$ Mn $Fe_{1-x}Co_x$ trilayer systems (see highlight, E.Kentzinger, S.Nerger, U.Rücker (Jülich)). There is also a great industrial interest in these magnetic multilayer systems because of the giant magneto-resistance effect which appears in these structures. Last year a collaboration has began with On-Stream, a company which develops high density magnetic tape storage. Reflectivity has allowed to characterize the magnetic switching behaviour of the GMR structures used in the read-heads of theses systems.

Another field of interest is the surface magnetism. These last three years, great hopes have been put into half-metallic ferromagnets which have an almost fully polarized conduction band. These materials would be especially suitable for spin injection in electronic devices (such as Magnetic-Rams or spin-transistors). These materials are mainly ferromagnetic oxides (Fe_3O_4, $La_{.7}Sr_{.3}MnO_3$). However, problems have arised related to the surface magnetism of these oxide thin films. They present a magnetic order which departs from the behaviour of bulk materials. Among these, are the finite size effects (which appear to be especially important in superexchange or double-exchange ferromagnets), the surface strains or epitaxial strains in the films or the proper control of the oxides stoichiometry at the interfaces. A lot of reflectivity work has been devoted to the study of these oxide surfaces to be able to distinguish between these different effects.

3. Molecular Magnetism

(B.Gillon with J.Stride (post doctorate))

Magnetic structure of cyano-bridged (Mn^{II}, Mo^{III}) molecular-based compound (see highlight) (J.Stride, B.Gillon, A.Gukasov, O.Kahn (Bordeaux), J. Larionova (Montpellier))

Magnetism and Superconductivity

The spin density in the ordered magnetic phase of the compound $K_2Mn_3(H_2O)_6[Mo(CN)_7]_2 6H_2O$ ($T_c = 40K$) was determined from polarised neutron diffraction data at 4K with an applied field of 3 Teslas. The spin densities upon the two metals were found of opposite sign which reflects an antiferromagnetic Mn^{II}-$M0^{III}$ interaction through the cyanobridge. This shows that this compound actually orders ferrimagnetically (and not ferromagnetically as it was previously proposed). There is a theoretical support from S.Alvarez (Barcelona).

Intramolecular ferromagnetic coupling between organic radicals (D.Gatteschi, A.Caneschi, L.Sorrace (University of Firenze) and B.Gillon)

The intramolecular ferromagnetic coupling between two semiquinonate radicals in the triplet ground state of the complex formed by the non magnetic Ti^{4+} ion and two semiquinonate ligands, may be due to direct overlap between the ligand magnetic orbitals or/and to superexchange mediated by the metal empty orbitals. From the determination of the spin distribution it has been demonstrated that the ferromagnetic interaction between the semiquinonate radicals is due to a superexchange mechanism via the d-orbitals of the Ti^{4+} diamagnetic ion.

In another system containing a rare earth (Gd) together with semiquinonate radicals, a study focusing on the nature of the interaction between the rare earth and the organic radical is under way in collaboration with the Italian group and with C.Lecomte (Nancy) for charge density measurements.

4. TOPOLOGICALLY FRUSTRATED MAGNETIC SYSTEMS

In regular magnetic lattices showing "topological frustration" (which is different from disordered spin-glass-like frustrated systems), no long range ordered spin arrangement is able to minimize the energy. This pecularity results in original magnetic behaviors such as spin "liquid", spin "glass", or even the recently discovered spin "ice" state. The most common "topologically frustrated lattices" are the hexagonal (triangular) and Kagome lattices in 2D and the FCC and the pyrochlore lattices in 3D. Two examples of pyrochlore lattices are discussed.

Magnetic properties of paramelaconite (Cu_4O_3) (A.Gukasov, J.Rodriguez-Carvajal, L.Pinsart-Gaudart (Orsay))

Paramelaconite is the first S = 1/2 pyrochlore lattice to be studied from the magnetic point of view. The sample studied is a natural single crystal of Cu_4O_3 ($5mm^3$) provided by the Smithonian Institute of Washington DC. It is a magnetic insulator with a magnetic transition at 40K. Magnetic order is characterized by magnetic reflections at k=(1/2,1/2,1/2). The critical exponent for the appearance of magnetic order is low (β=.23). The magnetic moment carried by Cu^{2+} is small (.14 μ_B). More work is needed to a better understanding of this interesting new system, with the development of synthesis of paramelaconite.

Magnetic instabilities in Laves Hydrides RMn_2D_x: New ordered magnetic phases induced by pressure and hydrogen order} (I.Goncharenko, I.Mirebeau, P.Cadavez-Peres (thesis),O.Makarova (Kurchatov Institute thesis))

1. Effect of hydrogen order

In the hexagonal Laves hydride $ErMn_2H_x$, different hydrogen superstructures (with hydrogen content x=3, 4.2, and 4.6) release the topological frustration (Mn moments being located on a pyrochlore lattice, a lattice of corner sharing tetrahedra) and impose different types of long range or short range magnetic orders.

2. Effect of applied pressure

Applying pressure allows one to modify the energy balance between the different types of magnetic interactions. In the H disordered hydride $Tb(Mn_{.9}Al_{.1})_2D$, Mn magnetism disappears above a pressure of 6 GPa and the compound recovers a long range ferromagnetic state between rare earth moments.

5. MAGNETIC STRUCTURES IN SYSTEMS WITH D AND F ELECTRONS

Magnetic structures in the Ce-Ni-Ge system

(L.Durivault (thesis LLB-ICMCB), F.Bourée, B.Chevalier (ICMCB), G.André)

Neutron powder diffraction studies have been performed in the Ce-Ni-Ge system in order to establish correlations between chemical composition, crystal structures, magnetic properties and Cerium valence state.

Ternary germanides containing more than 50% atomic percentage of germanium are antiferromagnetic and when the percentage in germanium diminishes, the ordering temperature also diminishes together with the value of the ordered magnetic moment.

Magnetic ground states of the tetragonal UFe_2Sn-type structure from anisotropic RKKY exchange
(S.Bordère, B.Chevalier, J.Etourneau (ICMCB), F.Bourée)

Magnetic structures observed in $(Ce_{1-x}U_x)_2Pd_{2.05}Sn_{.95}$, $U_2Pd_{2+x}Sn_{1-x}$ and $U_2(Ni_{1-x}Pd_x)_2Sn$ have been explained on the basis of a general RKKY model based on a non-spherical Fermi surface to account for the magnetic interactions involved in these systems.

Crystal and magnetic structures, and superexchange interactions in condensed phosphates
(G.André, N.Blanchard, F.Bourée, G.Collin, J.Rodriguez-Carvajal, T.Roisnel, A.Boukhari, R.Cherkaoui, El Moursli (Rabat),N.El Khayati (thesis LLB-Rabat))

Phosphate materials are quite close to oxides but there is a stronger trend towards charge localisation. Two families of magnetic insulator phosphates have been selected: $CuFe_2(P_2O_7)_2$ and $MFePO_5$ (M=divalent transition metal). Information on the super and the supersuperexchange through phosphate groups $(PO_4)_n$ has been obtained from the determination of the magnetic structures by neutron diffraction on powder samples.

Applications of polarized neutrons (A.Gukasov)

1. Magnetic anisotropy in UNiGa and UCoGa determined by polarized neutrons (K.Prokes, V. Sechovsky (Prague), A.Gukasov)

As proposed by G.Lander et al, magnetic anisotropy can be determined by measuring flipping ratios of **polarized neutrons** on the sample oriented with the easy-magnetization direction making some angle with the applied field. Such an experiment has been performed recently in LLB on 5f isostructural antiferromagnets UNiGa and UCoGa. The results of neutron-scattering studies give extremely high magnetic anisotropy in UNiGa and UCoGa, an anisotropy which is comparable to those of the strongest rare-earth-based permanent magnet materials.

2. Spin and orbital moments in Uranium pnictides. (P.Wisniewski, Z.Henkie (Poland), A.Gukasov)

Polarized neutron diffraction technique allows to determine the ratio of orbital and spin components of magnetic moments. This ratio in uranium compounds is usually considered as a measure of the degree of hybridization (the smaller the ratio, the stronger the hybridization). A systematic study of a series of U_3X_4 pnictides (X=N,P,As and Bi) was performed which demonstrated an important hybridization of 5f-electron states with the conduction band for all four compounds. The hybridization plays a significant role in the appearance of local anisotropy in U_3X_4 pnictides, which in turn has a strong influence on the magnetic structure in these compounds. For another ferromagnetic uranium compound UAsSe, where the strong anisotropy of the hybridization has been predicted, the value of L/S ratio obtained from the polarized neutron data favours nearly free ion U^{4+} state, which indicates rather weak hybridization of 5f-electrons.

3. Spin density on ligands O^{2-} and covalency of Fe^{3+} ions in antiferromagnets garnets. (V.Plakhty, O.P.Smirnov (Gatchina), A.Gukasov, R.Papoular)

Magnetism in ionic crystals appears owing to covalency, a partial redistribution of electrons between the magnetic cation and surrounding anions-ligands. All the mechanisms of superexchange between magnetic ions via the ligands can be expressed in terms of covalency. Usually the covalency parameter is estimated from the comparison of the magnetic ion moment determined from the Bragg intensities with that of the free-ion for the zero- point spin fluctuations. However, the covalent moment transfer can be obtained directly using polarized neutron diffraction. The measurement consists in the determination of the magnetic moment induced on the ligand itself in an antiferromagnet subjected to an external magnetic field. In this method no corrections for the zero-point spin fluctuations are needed and, which is more important, the corrections for the moment reduction caused by frustration due to magnetic impurities is avoided. This method evidenced unambiguously significant (.025) positive spin density transfer on the ligand ion O^{2-}, this value being consistent with the theory prediction for the covalent reduction of moment in Fe^{3+}.