I SYNTHESE du PROJET

Titre : XMCD and XMLD beam line on SOLEIL in the 350 to 2000 eV range

Promoteurs : Philippe Sainctavit[1,2] et Philippe Ohresser[2]

[1]Laboratoire de minéralogie et cristallographie de Paris

[2]Laboratoire pour l'utilisation du rayonnement électromagnétique

Caractéristiques Principales de la ligne

Source	**Gamme d'énergie**	**Principe du schéma optique**	**Résolution spectrale (E/ΔE) et flux dans la tache focale (HxV)**	**Station(s) expérimentale(s)**
Deux Onduleurs HU50 : - un Apple II à polarisation accordable linéaire horiz. et verticale et circulaire droite et gauche - un onduleur électromagné-tique pour la polarisation circulaire avec une fréquence d'inversion droite/gauche de 100 Hz	**350 eV-2000 eV**	**Monochromateur avec fente d'entrée :** **-miroir de focalisation verticale sur la fente d'entrée** **- 3 réseaux plans de 600 à 2000 traits par mm** **- miroir sphérique de focalisation verticale sur la fente de sortie fixe** **Insertion possible d'un système KB pour une tache focale de 10x20μm^2 (microscopie)** pour la réjection d'harmoniques à basse énergie plusieurs stratégie sont possibles (études à faire)	**6000 à 10000 sur toute la gamme,** **10^{11} Ph/s sur l'échantillon** **très haute pureté spectrale et stabilité du faisceau nécessaires à la source et sur l'échantillon**	**2 stations de dichroïsme :** **- l'une à haut champ magnétique (7T) et très basse température (50 mK)** **- l'autre à champ magnétique à retournement rapide (2T) et température variable (10 à 1000K)** **Une chambre ultra vide de préparation et de caractérisation d'échantillons reliée aux 2 chambres d'analyse par des SAS d'introduction** **Un microscope X** **Une chambre de réflectivité (développée au laboratoire de cristallographie de Grenoble)**

The community of magnetic x-ray absorption is well identified in France. Several major French schools have been held in Mittelwihr under the supervision of the Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS) where the whole community gathered (1989, 1996 and 2000). Every year a national dedicated workshop is also held in Strasbourg to outline the new trends in the field. Moreover two workshops have been organized by SOLEIL in Strasbourg, first during the Foundation Phase (1997) and at present (May 2001) in order to identify the objectives that should be fulfilled by the SOLEIL beam lines and the expectations of the French community. The magnetism community using synchrotron radiation has also established connections with other scientific communities making use of circular polarization among which one can quote the community gathered under the action of José Goulon in the workshop on gyrotropy: ”X-ray gyrotropy and synchrotron radiation based chiroptical spectroscopies” (ESRF-Grenoble, 21 - 23 September 2000).

The various themes in which the French community is involved concern the emergence of magnetism in exotic compounds (molecular magnets, hybrid organic-inorganic magnets) and in compounds with low dimensionality (magnetism at surfaces, in thin layers and nanostructures, superparamagnetic nanoclusters, high spin molecules, …).

The application of synchrotron radiation to magnetism is related to the development of circularly polarized sources. The main advantage of X-ray Magnetic Circular Dichroism (XMCD) over other techniques addressing magnetic behavior lies in its chemical and orbital selectivity. One can probe the magnetic moment of one specific atom in a compound in which the absorbing atom is not a major component. Due to the electric dipole nature of the Hamiltonian interaction, one can also probe specific shells for which the magnetic orbital and magnetic spin moments can be “independently” measured.

New physical and chemical properties shown by different classes of materials provide the basis for promising applications and challenging scientific investigations. The knowledge of the electronic structure of these materials is of crucial importance for the understanding and tailoring of well defined properties, like transport and photoconductivity, the magnetic behavior, the photocatalytic properties and others. Some of the majors trends in physics, chemistry and Earth sciences for which XMCD and X-ray Magnetic Linear Dichroism (XMLD) should provide new insight are summarized.

Purely molecular magnets : In most magnets, magnetism results from the presence of transition elements (essentially 3d elements), of rare earths or of actinides. There is another class of magnets, called *molecular magnets* that do not contain any of these elements. The magnetism in such compounds does not come from the build-up of a magnetic 3d band, nor from localized 3d, 4f or 5f electrons but from molecular complexes, generally nitroxides, in which the highest occupied molecular orbital possesses only one single electron. These NO groups are in ferromagnetic interaction inside the molecules and the molecules are organized in a three-dimensional network where they are ferromagnetically coupled through magnetic dipole interaction. The first molecular ferromagnetic complexes have been synthesized ten years ago and the physics of magnetism at stake is completely different from what one is used to deal with. In a related class of magnetic compounds, the nitronyl nitroxide group is a mediator of the magnetic interaction between 3d transition elements or rare earths. The site selectivity of XMCD is essential to detect the small although essential magnetic polarization of nitrogen and oxygen.

Langmuir-Blodgett films : In addition to offering a greater ease for the study of 2D phenomena, Langmuir-Blodgett (LB) films provide an outstanding facility for the processing of supramolecular assemblies, allowing for the deposition of compounds in sequences of layers. M. Pomerantz at IBM has processed the first LB films with magnetic properties. Magnetism was the result of the presence of Mn atoms, co-deposited with stearic acid. Since then, many organo-metallic compounds have been processed as LB films. Magnetism is brought in by some metallic ions, and these studies correlate the magnetic properties of the molecules in the bulk and in the LB films. The possibility of creating multilayered LB films in which the metallic planes can be magnetically coupled or decoupled according to the elaboration procedure is also demonstrated. Last, the observation of a phase transition to a magnetically ordered phase has recently been reported for a LB film containing gadolinium. The circular and linear dichroïsm beamline at SOLEIL will give a unique tool to characterize the magnetism of these films.

Hybrid magnetic materials : A large interest is devoted to the study of compounds of low dimensionality intermediate between magnetic chains and magnetic planes. In lamellar compounds where the 3d transition elements are copper and vanadium, ferrimagnetism has been obtained as a consequence of some topological order, also related to magnetic frustration. At low temperature, one assists to the emergence of a three dimensional antiferromagnetic order that is governed by the interplanar interaction monitored by hydrogen bonds. The intercalation of various organic species between the magnetic planes controls the dimensionality of the magnetic order. In this vein, synthesis is developed to produce organic/inorganic compounds in which inorganic planes are related by organic pillars. The organic pillar can be magnetically inactive or active. Nitroxyde radicals have been tested as well as ligands with π conjugated electrons. One expects original magnetic behavior from the presence of localized magnetism inside the planes coupled to strongly delocalized π electrons.

High spin molecules : The synthesis of polynuclear molecules has recently produced a large variety of compounds in which transition elements are magnetically coupled to produce a huge molecular magnetic moment. The perspective concerning this work is inscribed in the conception of materials for the nanotechnologies where the target is to address specifically one nanoparticle or molecule, to store in it a piece of information, to transmit it and to collect it at a molecular level. The high spin molecules can have large magnetic moments. These molecules are in essence monodisperse, carry a well-defined magnetic moment and possess also a well-defined anisotropy. These specific magnetic properties made possible the observation of superparamagnetism and quantum spin tunneling. This is a consequence of their inherent properties: large magnetic moments, large uniaxial or rhombic anisotropy and large exchange coupling and also intermolecular interactions. All these parameters can be tailored by the tools of coordination chemistry so that these types of compounds would be candidates for q-bits in the molecular electronics of the future.

Superparamagnetic nanoparticles : Through various routes of syntheses, one can produce nanoparticles such as magnetite (Fe_3O_4), maghemite ((γ-Fe_2O_3), hematite (α-Fe_2O_3), pyrrhotite ($Fe_{1-x}S$) or greigite (Fe_3S_4). These nanoparticles are present at the surface of the Earth and are responsible for what is called the paleomagnetism. From paleomagnetism one can understand the evolution of the tectonic migration of the various Earth plaques. Paleomagnetic signatures are also geological thermometers and barometers informing on the condition of formation of minerals. The joint point of view of the chemist and the paleomagnetician is essential to unravel the differences between the magnetic properties of natural nanoparticles and their bulk analogs: magnetic surface canting, chemical and magnetic disorder, vacancies ordering.

The recent findings concerning the Martian magnetic map has revealed that an exceptionally large paleomagnetic signature was present at the surface of Mars. The origin of such a signature is still completely unknown. In the perspective of the spatial mission Mars Sample Return in which France is deeply involved, it is essential to furbish our instruments in order to be able to handle and study small quantities of paleomagnetic materials.

Beyond the paleomagnetism, granular systems are of high interest for their technological application since they are a direct extension of the studies performed on multilayers. However up to now, the superparamagnetism character is a technological obstacle for future applications in high density magnetic storage at room temperature, it is interesting to study pure or alloyed nanoparticles prepared by different ways (chemical, thin films lithography, clusters deposition...) in view to repel this limit. An XMCD measurement performed on magnetic nanoparticles assemblies under UHV (to avoid contamination in such reactive systems) and at various temperatures (from a few Kelvin to room temperature) is a unique tool to reach their local magnetic moments.

Surface and interface magnetism - Materials for spin electronics

Magnetic properties without counterpart in the bulk have been discovered in quasi two-dimensional systems, such as ultrathin films and superlattices. Similarly small magnetic clusters, supported on surfaces or embedded in a matrix (see § *Superparamagnetic nanoparticles*), as well as magnetic oxides and semiconductors, will play an important technological role in the near future either in the field of spin electronics or for high density magnetic storage. In this field we can quote the Magnetic Tunnel Junction and the Spin-valve Transistor. In these scientific cases magnetic dichroism will play an important role. Its high sensitivity, its chemical selectivity and its unique capability to separate the spin and orbital contributions to the magnetic moment (using the XMCD sum rules) are ideal to characterize the magnetic properties of low dimensionality systems (evolution of the spin, the orbital magnetic moments, the blocking temperature in the superparamagnetic regime, … with the size of the nanostructures).

XMCD also allows a direct access to the magnetocrystalline anisotropy (through the measurement of the anisotropy of the orbital magnetic moment), and this for magnetic nanoparticles as small as few tens of atoms. This potentiality is very important, since perpendicular magnetocrystalline anisotropy is a key parameter for the high-density magnetic storage technology. The goal is to understand the role of different parameters such as broken bonds or strain, among others, over the magnetocrystalline anisotropy and to be able to use them to favor a particular magnetic anisotropy.

The chemical selectivity of this technique allows to individually follow the magnetic behavior in complex magnetic systems such as alloys, multilayers or particles embedded in a matrix. This is particularly important in the field of spin electronics with the advent of new materials such as complex magnetic oxides (double perovskites with high Curie temperatures) and magnetic semiconductors (II-VI and III-V semiconductors doped with 3d elements). Considering magnetic oxides, even the induced magnetism on oxygen can be measured. In the case of an interface (key parameter in such systems) between a metal and its oxide (e.g. Fe_3O_4/Fe or NiO/Ni), it is possible to take benefit of the different signatures of the XMCD signals between the metal and the oxide to separate those magnetic contributions. Using linear polarization of the X-ray beam, the magnetic moment of antiferromagnetic material is accessible. This makes it useful in the field of magnetoresistive sensors where sandwiches of ferromagnetic and antiferromagnetic materials are used; moreover it would be ideal to understand the interface between the antiferromagnetic and the ferromagnetic layers, for instance the origin of the exchange bias is still not well understood.

Additionally using the time-resolved mode of SOLEIL dynamic studies in the nanosecond range can be performed with XMCD as demonstrated by Bonfin *et al*. from the Laboratoire Louis Néel (Grenoble). Indeed the study of magnetization dynamics in thin magnetic films has become a matter of high interest for the future of magnetic recording and non-volatile magnetic memories. Parallel to the evolution towards smaller magnetic bits and memory cells, writing and reading times approaching the GHz range will be required in a few years from now. The dynamics of the magnetization reversal of each of the layers of complex heterostructures (spin valves or tunnel junctions) can be probed *independently* by tuning the photon energy to the relevant absorption edge.

Less "usual" XMCD experiments can be carried out on "Ferromagnetic metal/Oxides/Ferromagnetic metal" systems by applying bias voltages between the uppermost layer (oxide) and the ferromagnetic metal.

Related techniques

Other techniques based on "reflectivity" using the "magnetic sensitivity" of the polarized X-ray light are possible: XRMS (X-ray Resonant Magnetic Scattering) and DXRMS (diffuse x-ray resonant magnetic scattering).

While it can be expected that magnetic properties of nanoscale magnetic layers are different at interfaces with dissimilar materials than in the center of the magnetic layer, characterizing such differences with adequate depth resolution remains a great experimental challenge. This *q*-space depending technique has been used to directly probe the extension of the induced magnetism from the interface across a spacer layer in Ce/Fe and CeLa/Fe systems. That approach should be of great interest in the investigation of interlayer exchange coupling and exchange bias coupling. Nanoparticles of magnetic transition metals embedded in either a metallic or insulating matrix are also of interest. For potential applications, as high-density magnetic recording media, a fine control of the particle size and inter-particle distance is crucial. Strong efforts are currently undertaken in order to achieve a lateral patterning of magnetic films on a nanometer scale, by electron beam lithography or self-organizing growth mechanisms. In both kinds of system, the magnetic sizes and/or transport properties of the particles are sensitive to factors such as their lateral ordering, as well as to the interaction between them. Therefore, it is essential to develop new methods allowing to investigate directly the structural and magnetic properties of patterned and hybrid magnetic materials. The DXRMS use the large enhancement of the scattering amplitude together with the circular dichroism at the absorption edges of magnetic material resulting in a huge diffuse scattering contribution. This technique is successfully used to study magnetic correlations in sample presenting an in-plane periodicity in the nanometer range.

Communauté concernée

Purely molecular magnet :

- *Laboratoire de Minéralogie et Cristallographie de Paris (LMCP),*
- *Laboratoire de Chimie Inorganique et Matériaux Moléculaires (LCIMM),*
- *Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE).*

Langmuir-Blodgett films :

- *Institut de Physique et Chimie de Strasbourg (IPCMS),*
- *LURE*

Hybrid magnetic materials:

- *LCIMM,*
- *LURE,*
- *IPCMS*

High spin molecules:

- *LMCP,*
- *Dante Gatteschi (from the LCIMM permanent address in Firenze),*
- *Laboratoire Louis Néel de Grenoble (LLN)*
- *LURE.*

Superparamagnetic nanoparticles:

- *LMCP,*
- *Laboratoire de Physique des Matériaux de Lyon,*
- *IPCMS,*
- *LURE,*
- *Institut des Matériaux de Nantes (IMN),*
- *Institut de Physique du Globe (IPGP),*
- *Laboratoire de Chimie de la Matière Condensée (LCMC),*
- *Laboratoire de Chimie Inorganique et Electrochimie des Matériaux Moléculaires,*
- *Laboratoire de Chimie des Matériaux Divisés et Catalyse.*

Surface and interface magnetism - Materials for spin electronics:

- *IPCMS,*
- *LURE,*
- *UMR CNRS/Thalès,*
- *Centre d'Etudes Nucléaires de Grenoble (CENG),*
- *Laboratoire Louis Néel de Grenoble,*
- *Laboratoire de Cristallographie de Grenoble,*
- *Laboratoire de Physique des Matériaux de Nancy (LPMN),*
- *LMCP*

Related techniques:

- *Laboratoire de Cristallographie de Grenoble,*
- *CENG.*

II Recommandations du Comité scientifique consultatif (22/01/02)

Beamline Proposal 4 : Proposal presented by Philippe Sainctavit and Philippe Ohresser
"**XMCD and XMLD beam line on SOLEIL in the 350 to 2000 eV range"**

The SAC acknowledges the good scientific case for this beamline which covers a broad area of expertise and it considers that a first class XMCD beamline should be built at SOLEIL, with a high priority.

To probe the local magnetic properties is very important in many, rapidly growing, scientific areas (bulk magnets, metallic and oxide thin layers of transition and lanthanides elements, spin electronics, giant and colossal magnetic resistances, nanosciences, "exotic" compounds, such as molecular magnets, magnetic properties in geology, biology…). The beamline will clearly support a broad scientific program in magnetism, an area which is traditionally strong in France. Many of the concerned scientific groups already support the beamline and were associated to its conception through various workshops open to the European community in the field. SAC encourages the proponents to continue their endeavours in these directions.

As for the technical aspects, the energy range, covering the L edges of the first line of the transition elements and the M edges of the lanthanides is well adapted for the scientific purpose as well as the proposed resolution. The proposition of recording at very low temperatures in two ways, with a continuous high applied magnetic field or with an alternating weaker field, is also worthy of interest. The possibility of two end stations of the BL equipped with the two kinds of devices should be considered. SAC also recommends that the proposed choice of a scanning type microscope should be reconsidered in favour of an imaging system.

The SAC encourages the team to go ahead with a more precise definition of the beamline layout, which is barely sketched in the present proposal. The layout and the reasons for the corresponding technical choices should be reviewed in one of the forthcoming SAC meetings.

The proponents have already the experience of working on 3rd generation SR centres, even sharing their own equipments (ESRF, Bach line at ELETTRA). SAC encourages them to maintain or strengthen these links, in order to take advantage of the new instrumental opportunities appearing on XMCD lines of third generation synchrotrons and to build an up-to-date first-class XMCD line and to keep its scientific case at the best level.

III Propositions de la Direction de SOLEIL

La direction de SOLEIL demande l'aval du Conseil pour le lancement de la construction de la ligne « **Dichroïsme circulaire et linéaire magnétique des rayons X à SOLEIL dans la gamme 350 à 2000 eV** ». Cette ligne dotera la communauté du magnétisme d'un outil de pointe pour répondre à des questions posées tant en physique fondamentale que pour la définition de systèmes optimisés pour l'électronique de spin ou l'enregistrement haute densité. La gamme d'énergie proposée permet de couvrir les seuils d'absorption K des éléments légers (Azote et au delà), les seuil $L_{2,3}$ des métaux de transition de la première série et les seuils $M_{4,5}$ des terres rares et ainsi de réaliser l'ensemble du programme scientifique proposé. La communauté scientifique française concernée est très diverse, active et ouverte sur la communauté internationale. Elle a largement participé à l'élaboration du projet de ligne que nous présentons ici. L'utilisation de sources étrangères permettra de maintenir une activité pendant la période d'arrêt entre LURE et SOLEIL avec par exemple l'installation du dispositif haut champ-basse température à ELETTRA. Plusieurs laboratoires français ayant développé des expériences pionnières dans le domaine, aussi bien à LURE qu'à l'ESRF, poursuivront cette activité en association avec SOLEIL, tant sur un plan expérimental que théorique.