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Two recent developments in XMCD

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This paper reports on two new technical developments concerning sample environments for X-ray magnetic circular dichroism (XMCD). The first measurements under high pressures of up to 30 GPa are described. The difficulties of combining the techniques of high pressure and XMCD are commented on. The second development involves the use of a fast-switching magnetic field. A new superconducting device is used to perform XMCD measurements on paramagnetic compounds in magnetic fields of up to 6 T. The small amplitude of the XMCD signal imposes, for a given signal-to-noise ratio, a noise less than a few 10^{-5}. The signal-to-noise ratio is improved by the use of a series of acquisitions, switching the magnetic field between each acquisition. A very fast switching mechanism has been built based on mechanical rotation of a superconducting coil, with the sample kept in place inside the coil. The XMCD signals at the $L_{\rm II,III}$-edges of paramagnetic rare-earth compounds have been measured at 4.5 K in fields of up to 6 T with a switching time of 11 s.

Keywords: XMCD; high magnetic fields; low temperature; high pressure.

1. Introduction

We present two new sample-environment developments implemented on the energy-dispersive absorption spectrometer of the DCI storage ring at the French synchrotron facility LURE. This beamline has been completely renewed recently in order to be installed on the future third-generation French synchrotron SOLEIL. These sample environments are dedicated to X-ray magnetic circular-dichroism (XMCD) experiments. The first development allows switching of high magnetic fields (6.5 T) in a very short time, at rates faster than 1 T s^{-1}. The second is a high-pressure cell able to work in a magnetic field.

2. X-ray magnetic circular dichroism

XMCD is the difference between X-ray absorption spectra with right and left circular polarization, and gives a signal proportional to the magnetic moment of the absorbing atom. It is often quite complicated to estimate this proportionality in the hard X-ray domain where atomic calculations fail to describe the spin polarization of delocalized electrons. The value of the XMCD signal can be as small as 10^{-4} of the total absorption. Therefore, to improve the signal-to-noise ratio, quite lengthy statistics are required. From a practical point of view, reversing the photon helicity is equivalent to reversing the external applied magnetic field while keeping the photon helicity fixed. This is true when a ferromagnetic sample is magnetically saturated and is always the case for paramagnetic samples. The problem is obtaining a high-field magnetic environment which can be rapidly switched (which is generally easier than switching the helicity) and making sure that the same part of the sample is probed in both measurements.

3. The XAS dispersive beamline

This scheme combines dispersive optics – reflecting a polychromatic X-ray beam and focusing it on the sample – with a position-sensitive detector such as a photodiode array or a digital CCD camera able to work under high-flux conditions (Fig. 1).

The Bragg angle changes continuously along the footprint of the beam on the bent crystal. The outcome is a polychromatic beam with a correlation between the energy and the direction of propagation. This leads to an energy–position correlation at the detector. Complete spectra can be collected in a very short time, typically a few ms.

4. The fast-switching high magnetic field

The microscopic study of the magnetic phase diagrams (H,T) of rare-earth and transition-metal compounds should be possible using XMCD at the *K*- and *L*-edges of the magnetic atoms. Until now rapid acquisition measurements using magnetic field switching have been limited to ferromagnetic study in 2 T magnetic fields. Nevertheless, for studying numerous physical problems, it is necessary to obtain high H/T values. However, the weakness of the XMCD signal requires the averaging of a great number of absorption spectra while rapidly reversing the magnetic field between each spectral acquisition.

For these reasons it is necessary to obtain magnetic fields of up to 6.5 T, which necessitates the use of superconducting coils with a short current-reversal time. The smallest time achieved for electrical reversal of a 6 T magnetic field is around 2 min. This is time-consuming and poorly effective when compared with the typical acquisition time of 1 s. We chose to mechanically rotate the superconducting coils between each data acquisition, reversing the 6.5 T field direction in less than 11 s. One difficulty of this option is to rotate the heavy superconducting coil without inducing any movement of the sample.

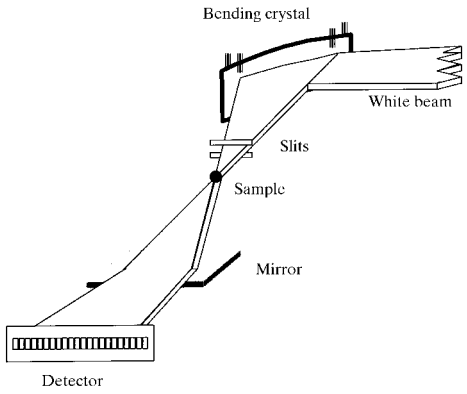

Figure 1
X-ray absorption dispersive spectrometer.

The rotating system is based on a 250 mm-diameter rotating seal with first-stage differential pumping (Fig. 2). The cryostat of the superconducting coil rotates around the fixed cryostat of the sample. The superconducting-coil cryostat is cooled by successive tanks of nitrogen and helium needing around 20 l of helium per day. The sample cryostat is separate and is a continuous-flow cryostat with a heat exchanger small enough to be installed inside the central well of the coil. The superconducting-coil cryostat acts as a radiation shield for the heat exchanger of the sample cryostat. The lowest sample temperature obtained is about 4.5 K using 4 l h^{-1} of helium. We hope to improve this value by reinforcing the radiation shielding of the part of the sample cryostat which is not inside the well of the coil. This scheme preserves a free cylindrical space for the sample with a diameter of about 30 mm and a height of 40 mm. The advantage of using a rotating seal is that the same vacuum is obtained for both cryostats and also that the use of several cryogenic screens is avoided.

On our first prototype the rotation seals used were nitrile O-ring seals with a PTFE ring on one side of the seal. The PTFE ring does not seal but ensures that the cryostat rotates centrally. This centring is not good enough to ensure a correct value of the vacuum better than 10^{-4} during rotation. We are studying an improved centring system based on a 250 mm-diameter ball bearing. It is hoped to obtain faster rotation with a vacuum better than 10^{-4}. The nitrile O-rings have been used for 3 months and have performed about 150000 π or $-\pi$ rotations without any problems.

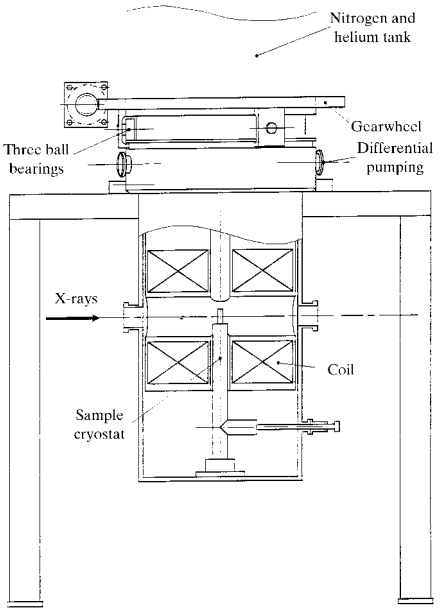

Figure 2
Mechanical rotating system of a superconducting coil.

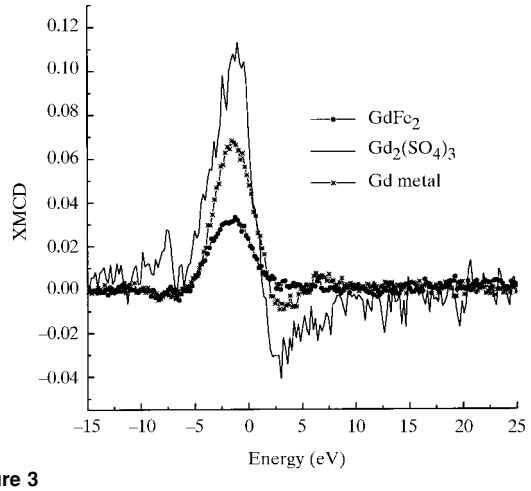

Figure 3
XMCD signal of $Gd_2(SO_4)_3$, Gd metal and $GdFe_2$, with the energy origin taken to coincide with the white-line maximum.

The rotation is driven by a 550 W step motor and a gearwheel. The gearwheel is only half-cogged in order to avoid rotations greater than π and $-\pi$ if misdriving occurs. A larger rotation could destroy the electrical and cryogenic connections. Two double kapton windows of 50 mm are installed along the X-ray photon trajectory. The differential pumping was ensured by a 32 m^3 h^{-1} pump. It is planned to use a 65 m^3 h^{-1} pump in the near future for safety reasons. For the coil and sample vacuum a 150 l h^{-1} turbomolecular pump was used, which gives a vacuum better than 10^{-6} (except during rotation).

The powdered samples are mixed with BN powder and fixed with collodion between two 1 µm aluminium foils in order to achieve optimum rigidity, cooling and transmission. The samples are clamped in a copper sample-holder with a hole of 1.5 mm-diameter for the passage of the beam. Three samples are mounted simultaneously and can be changed rapidly. If there are defects in the homogeneity of the sample, a movement of about 1 mm can lead to artefacts in the XMCD spectra. A clamping of the system support to the floor is sufficient to overcome this difficulty, even with a 100 kg rotating mass.

5. Initial experiments

A good test of the efficiency of the experimental set-up was to measure paramagnetic ionic compounds, *e.g.* $GdCl_3$, Gd_2O_3 and $Gd_2(SO_4)_3$, which require high magnetic fields and low temperatures.

XMCD signals at the Gd L_{III}-edges for these compounds are similar in shape. The different spectra scale with the amplitude of the magnetic field.

In the XMCD spectra of Gd metal and $GdFe_2$, the width of the first peak is always of the order of 7 eV, whatever the width of the absorption white line. There is no correlation between the inflexion point and the XMCD maximum, but when the origin is taken to coincide with the white-line maximum (Fig. 3), each XMCD spectrum has a maximum close to the same relative position, −1.7 eV. In fact, the XMCD maximum and the white-line maximum are close to the same position for all Gd samples. The normalized XMCD amplitude variation with the field at 4.5 K follows the magnetization curve measured at the same temperature, which proves the perfect thermalization of our sample. The analysis of the complete results will be published in a separate paper.

In the near future the safety of the system will be developed in order to control every consequence of a possible leak during the magnet rotation. An automatization of the experiments, allowing several hours of acquisition time, is in preparation. This long acquisition time is crucial in order to obtain highly sensitive measurements and XMCD signals as low as 10^{-4}.

6. The high-pressure XMCD system

XMCD is a useful technique in probing magnetic properties of matter. X-ray absorption spectroscopy (XAS) under pressure is a

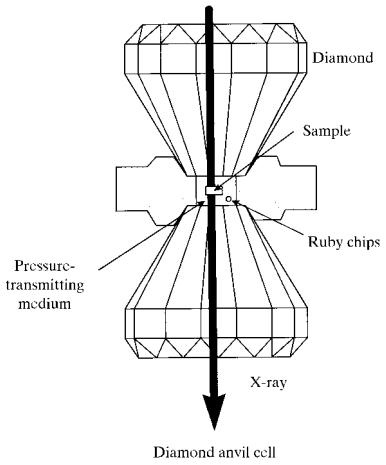

Figure 4
Classical diamond-anvil cell.

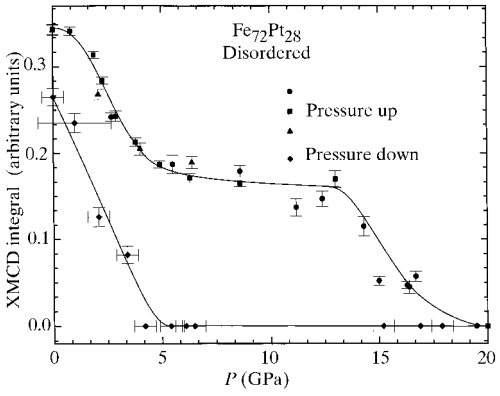

Figure 5
Integral value of the XMCD signal at the L_{III}-edge of platinum in $Pt_{28}Fe_{72}$, as a function of pressure.

commonly performed technique. We combined these two techniques to perform the first high-pressure XMCD. Combining high pressure and XMCD presents difficulties.

The high circular-polarization rate necessary for XMCD can be achieved, with an important loss of intensity, by selecting out-of-orbit emission from the bending magnet. The reduced X-ray intensity becomes a major problem in high-pressure measurements because of the large absorption of the diamond anvil and the sample size. Therefore brighter sources than our first-generation one are needed for most studies. We focus our attention on a study performed at the L_{III}-edge of platinum (11.5 keV), where the diamond-anvil absorption is not too high, allowing the use of our set-up.

The high-pressure dedicated diamond-anvil cell (DAC) (Fig. 4), made of a copper–beryllium alloy, is well known. So that it can be installed in the gap of a dipole magnet, our cell is a small cylinder, 50 mm in diameter and 30 mm in length. The latter value will be reduced to 26 mm in the next prototype. In our DAC, pressure is applied by a gas on a metallic membrane. The ratio of the membrane surface area to the diamond upper surface area gives a pressure of a few hundred kbar on the sample from a gas pressure of a few tens of bars. The pressure is measured by ruby luminescence.

Performing XMCD on a very small sample requires a focused beam. The dispersive XAS station beam spot of our first-generation synchrotron is about 400 μm, which is not the smallest beam presently available, but is small enough to cover the pressure domain up to 30 GPa. The highest pressure achievable is dependent on the sample size. The second very important condition is to obtain a stable beam. We usually collect more than 100 XAS spectra to give a good signal-to-noise statistical ratio. For our purposes, a stable beam is defined by two important parameters: the mean time between two perturbations such as re-injection or feedback, and intensity fluctuations, which must have a frequency higher than that of the data collection of individual spectra. Any noise of frequency smaller than 100 Hz can spoil the XMCD measurement by creating spurious artefacts. As the DCI life time of the storage ring is about 200 h, it delivers a very stable beam allowing continuous collection of data for 20 h. The low flux available is partly compensated by the possibility of obtaining many spectra.

We have performed a series of XMCD experiments under pressure at the L_{III}-edge of Pt in $Pt_{72}Fe_{28}$ invar metal. The invar metals are characterized by their very small thermal expansion coefficients. The natural temperature-dependent lattice expansion is counterbalanced by magneto-volumetric effects. Under pressure the invar metals have a phase transition from a high-spin (HS) state with high volume to a low-spin (LS) state with lower volume (Moruzzi, 1990).

The XMCD signal shows the spin polarization of the 5*d* band of Pt induced by the 3*d* band of Fe. The sign of the signal gives the ferromagnetic coupling between iron and platinum.

The integral value of the XMCD signal is shown in Fig. 5 with increasing and decreasing pressure. The important decrease of the XMCD signal between 2 and 4 GPa indicates a magnetic phase transition. This is the HS to LS transition predicted by theoretical calculations (Moruzzi, 1990; Podgorny, 1989). At the same time a discontinuity of the compressibility coefficient is observed at 4 GPa using high-pressure dispersive-diffraction experiments. This result is in agreement with high-pressure Mössbauer studies (Abd-Elmeguid & Micklitz, 1989). The XMCD signal is stable at pressures between 4 and 15 GPa, above which the beginning of a second magnetic transition to a non-magnetic state (NM; XMCD = 0) at 20 GPa is observed.

When the pressure is released, the XMCD signal only returns at 5 GPa. At ambient pressure, the full HS state is not totally restored. The release of pressure induces a direct transition from the NM to the HS state (Podgorny, 1989) which is evidence of a hysteresis cycle of the magnetic moment with pressure in $Pt_{72}Fe_{28}$ invar metal. Conversely, after the complete pressure cycle the initial lattice parameter returns to its original value. The complete cycle of XMCD *versus* pressure variation will be discussed in a forthcoming paper.

An important improvement to the experiment will be the possibility of cooling the sample to 1 K to obtain a complete magnetic phase diagram. In the near future a cryostat compatible with the DAC will be developed in order to perform high-pressure low-temperature XMCD on the dispersive absorption beamline.

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