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Dispersive XAS at third-generation sources: strengths and limitations

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The experience of two years of operation of the ESRF Dispersive XAS beamline is reviewed. The examples of experiments performed show that the advent of third generation sources has given a new perspective to the field of X-ray absorption in the dispersive mode. The achievement of an aberration-free horizontal focal spot of ~ 20 μm FWHM has opened up unique possibilities for performing X-ray absorption studies in extreme conditions of temperature and pressure. The implementation of quarter wave plates has allowed extremely accurate XMCD and nanosecond-resolved XMCD using the pump-probe scheme to be recorded. However, the reduction of source size combined to the lengthening of beamlines have introduced new problems related to the much higher sensitivity to beam instabilities amplified by phase contrast phenomena. Possibilities for the future have been investigated and shall be discussed.

Keywords: Energy dispersive optics, time-resolved XAS, high pressure XAS, X-ray magnetic circular dichroism.

X-ray absorption spectroscopy using energy dispersive optics has been widely exploited to study dynamical processes as well as very small samples in restrictive environments, thanks to the parallel data collection and to the small and stable focal spot respectively. Moreover, the mechanical stability of the optics during acquisition drastically reduces the sources of noise, thereby opening the way to the study of very small signals, such as those encountered in XMCD (Pizzini, 95).

The dispersive XAS beamline at ESRF, ID24, (Hagelstein 97) has now terminated its first two years of user operation. The tapered undulator source and the chosen optical scheme allow to cover the energy range 5 -25 KeV, with an average flux on the sample of 10^{12} phot/s and a horizontal spot size down to 20 μm FWHM (Pellicer Porres 98).

The first experiments performed on ID24 are representative of the new possibilities which the advent of third generation sources opens up in the field of dispersive XAS. Fig. 1 illustrates the results of the first XAS measurements on single crystals subject to high pressure in a diamond anvil cell (Itié 98). XAS determines the evolution of interatomic distances with pressure. In the past, the study of single crystals was prohibitive due to the extremely small spot required. The dimensions of the GaSe crystal in this experiment were ~ 100x100x20 μm^3. GaSe belongs to the III-VI layered compounds, with an intra layer covalent potential and a Van der Waals potential between the layers: the pressure dependence of the strong and weak bonds is very different.

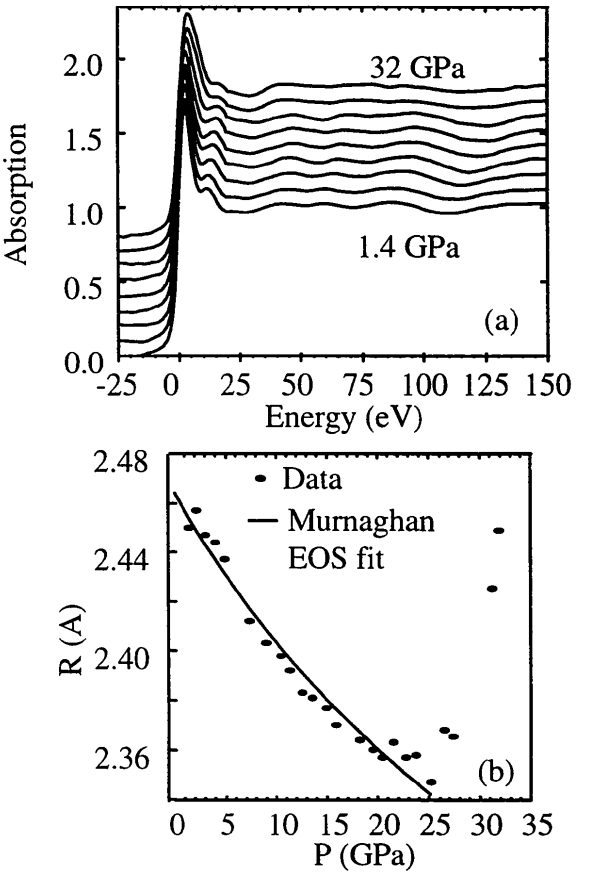

Figure 1
a) Ga K-edge absorption spectra and b) GaSe bond distance as a function of applied pressure. Below 25 GPa, the data is well reproduced by Murnaghan's equation of state, which relates volume variations V/V_0 (and therefore distance variations R/R_0) to the applied pressure P, using a first order expansion of the modulus of compressibility B as a function of P, $B = dP/dV = B_0 + B_1P$:

$$\frac{R}{R_0} = \left(1 + P\frac{B_1}{B_0}\right)^{-\frac{1}{3B_1}}$$

Above 25 GPa a rapid increase of this distance occurs, related to a transition to a six-fold coordination.

This experiment has also opened the field of new measurements taking advantage of the linear polarisation of the photons to evaluate the evolution of the structural anisotropy of single crystals under high pressure.

A large portion of the first experiments on ID24 dealt with X-ray Magnetic Circular Dichroism (XMCD), where quarter wave plate crystals are used to tune the helicity of the photons (Pizzini, 98). Here, the high stability of the dispersive set-up is exploited to obtain accurate small signals. Systems studied included highly correlated Ce based multilayers, magnetostrictive FeZrB amorphous alloys, amorphous GdCo thin films and two-phase NdFeB spring magnets.

Due to the parallel acquisition mode of the dispersive set-up it is possible to do time-dependent XMCD using the pump-probe scheme (Bonfim 98) to study the dynamics of magnetisation switching, which is an essential issue in recording technology. This experiment on ID24 takes advantage of the single-bunch filling of the ESRF, which opens up a tuneable delay (from 0 to 2.8 μsec) between pump and probe pulses. Fig. 2 illustrates the results obtained on GdCo amorphous thin films, used as model system before passing on to TbFeCo amorphous thin films, currently used as a magneto-optical recording media. Time-resolved XMCD selects the Gd magnetisation response of the films, which tells us about the dynamics of nucleation and wall propagation as a function of bias field.

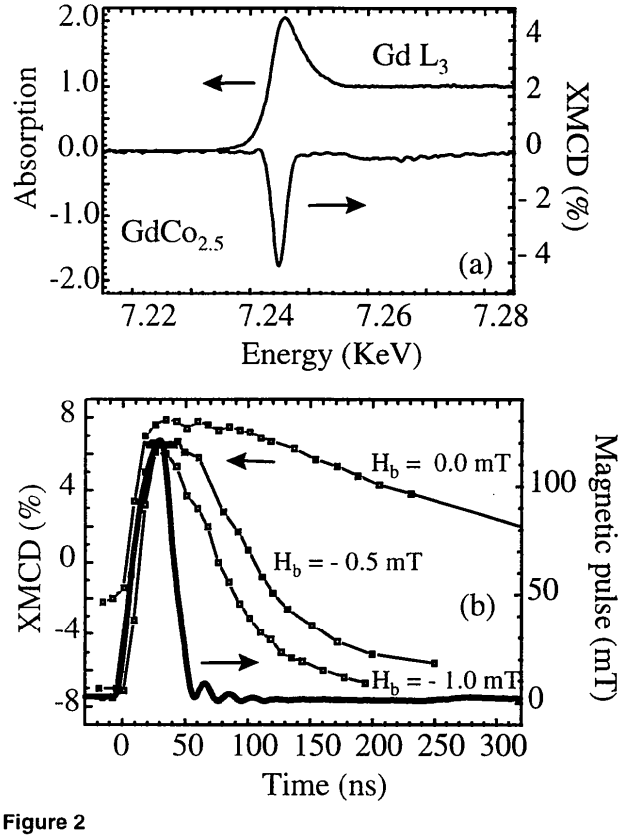

Figure 2

a) Gd L_3 absorption and XMCD on a-$GdCo_{2.5}$. b) Time response of the XMCD signal (dots) after applying a 100mT 50ns long magnetic pulse (bold line), with different bias fields.

These examples show that the advent of third generation sources has given a new perspective to the field of time-resolved x-ray absorption in the dispersive mode. However, the reduction of source size and the lengthening of beamlines have introduced new problems related to the much higher sensitivity to beam instabilities. The higher sensitivity arises mainly from the fact that since the spectra are obtained as 1-dimensional images, they suffer from distortions due to phase contrast phenomena (or "speckle") associated to imperfections in the optics, and which appear as irregular fringes on the image. The presence of such spatial intensity modulations on the image clearly amplifies the effect of beam instabilities. With respect to the conventional scanning mode, the dispersive set-up is intrinsically more sensitive to such instabilities due to the fact that the intensity before (I_0) and after (I_1) the sample are not measured simultaneously, leading to normalisation problems.

Time-resolved XAS investigations of dynamic processes are mostly affected by normalisation problems; notwithstanding such limitations, the identification of intermediate solution species in homogeneous alkene oligomerisation catalysts was possible (Corker 97).

To address these problems, the first step consisted in performing a detailed analysis of the amplitudes and frequencies of beam instabilities. The main sources of vibrations were pin-pointed as being characteristic of the electron beam in the undulator. This work was carried out in collaboration with the ESRF machine group and led to the implementation of a local feedback (Plouviez 96) on the horizontal electron beam position in the straight section of ID24. This achievement, together with the global feedback (Koch 98) on the vertical electron beam position, led to a damping of respectively a factor 5 and 3 in the horizontal and vertical beam instabilities on the sample.

Other solutions have been investigated on ID24. Tests using random phase plate systems (Cloetens 96), which artificially increase the source size in the attempt to reduce the coherence length of the beam, and therefore "average out" the spatial intensity modulations on the image, have also been performed. Phase contrast objects have been specifically designed in order not to perturb the energy-direction correlation established by the polychromator. Although the interference fringes are effectively smoothened, a certain degree of energy resolution degradation is also observed. This effect is attributed to scattering induced by the phase object in the horizontal plane, thereby destroying the energy-direction correlation established by the polychromator.

Among the other solutions investigated, the most ambitious one is that of developing detectors for a simultaneous parallel acquisition of I_0 and of I_1. A thin CVD diamond multi-strip detector will soon be tested as I_0 detector. This development however will not improve the quality of the data in cases where the sample itself modifies the energy-angular correlation of the impinging beam (i.e. SAXS). In this case, each ray of energy E impinging on the sample is elastically scattered into a cone centered around the initial direction, and will therefore impinge on a larger number of pixels on the position sensitive detector: this leads to a loss in energy resolution. A similar effect is obtained when speckle is produced by the sample, except that in this case, more than a loss in energy resolution, the spectra may be affected by distortions. This problem remains unsolved in the parallel data acquisition scheme.

In order to cope with "strong SAXS" producing samples, we have used a new technique (developed on ID24) of sequential acquisition of energy points using dispersive optics (Pascarelli 98), overcoming many of the problems encountered in the classical dispersive mode. In Turbo-XAS (T-XAS), absorption spectra are recorded using two gas detectors or photodiodes, positioned respectively before and after the focal point, which measure the signal generated by a monochromatic beam, selected by scanning a narrow slit through the energy-dispersed fan of radiation immediately after the polychromator. This technique is successful at the ESRF thanks to the small source size, allowing energy resolution to be controlled by the width of the slit.

In T-XAS, the cone of elastically scattered radiation is efficiently detected by the I_1 detector, which measures the spatial integral of the transmitted intensity as a function of energy: for this reason energy resolution is not affected.

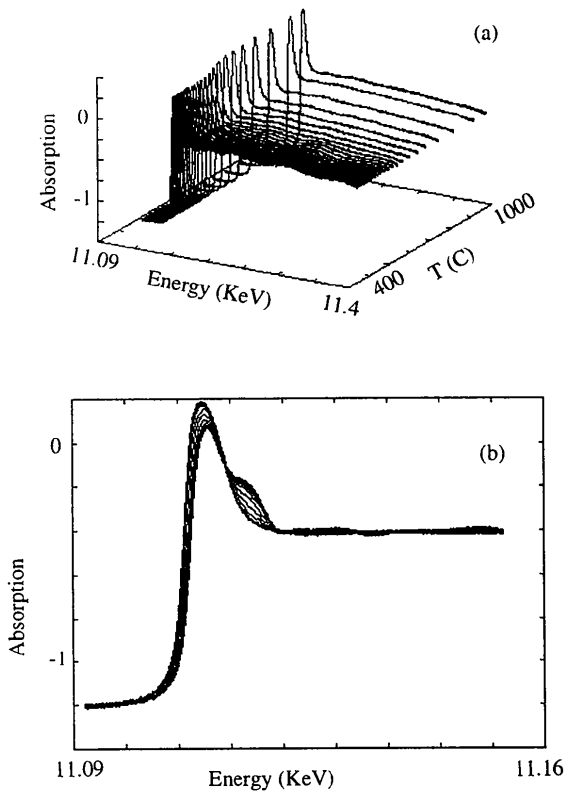

Figure 3
Sequence of Ge K-edge a) EXAFS (520 ms/spectrum) and b) XANES (120 ms/spectrum) during a rapid cooling (~ 40 Ks^{-1}) from the melt.

This new mode has been devoted to studying the evolution of undercooled Ge. Such an investigation is of fundamental interest due to the interplay between the covalent and metallic nature of the bonding which characterise the solid and liquid phases of Ge respectively. Fine Ge powder dispersed in a BN matrix produces strong SAXS which makes the experiment not feasible using the conventional parallel data acquisition mode. Fig. 3 shows the time evolution of Ge K-edge spectra: the absorption edge gradually shifts towards higher energies, mainly due to the formation of the gap, while the variations of the fine structure above the edge may give a new insight into the local structure in the metastable liquid. Besides the good time-resolution, T-XAS gives us the possibility to detect fluorescence/electron yield, and therefore opens the way to investigating samples otherwise inaccessible in the transmission mode.

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