ESRF	Experiment title: **DAFS experiments by using "Dispersive Diffraction"**	Experiment number: MI-213
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Background and scientific content :

Since the development of synchrotron facilities, anomalous diffraction has been a powerful tool for crystallographic studies. One of the first methods to emerge was MAD (Multiple Anomalous Diffraction), which uses the anomalous variations to determine the phase of the structure factor for each reflection, thus allowing the resolution of more complex structures, mainly for macromolecular studies [I], and also for modulated structures [2]. More recently, DAFS (Diffraction Anomalous Fine Structure) [3] was developped to allow the separation of f' and f" factors for the same anomalous atom in non-equivalent crystallographic sites, and therefore provides information about their valence and local environments.

Since these methods require diffracted intensities measurements at several wavelengths, they are beamtime-consuming. In order to reduce acquisition time, we are now developping the energy-dispersive diffraction setup [4] at the ESRF.

Report :

The analysis of the data collected during our first commissioning experiments (feb and dec 96) has shown (i) that the energy variations of the intensity of the incoming beam (IO) exhibits dips and time instabilities and (ii) that a good energy resolution was required in order to yield a better phasing power and a more precise fine structure spectra.

This has lead us to choose a somewhat different experimental method : we used a commercial MarResearch setup, which included an 30 cm diameter imaging plate with on-line reading, a fast one-axis goniometer and a fast shutter, all remotely controled and coordinated with MarResearch software. This allowed us to make many oscillations during the acquisition of each image, thus reducing the influence of the incident beam instabilities by a fair amount and ensuring that all reflections were measured with the same "averaged" incident beam. The monochromator configuration was also optimized in order to use a small energy range (**40** eV at the iron K-edge) around the absorption edges, thus yielding a much better energy resolution.

Samples studied :

(a) Study of valence in mixed oxides : Measurements have been carried out on magnetite (Fe304). This was the first material in which a charge-ordering transition was observed. It crystallizes in the inverted spine1 structure in which tetrahedral sites A contain Fe^{3+} ions while octahedral sites B contain an equal number of Fe^{3+} and Fe^{2+} in Bl and B2 sites respectively. The site selectivity of DAFS allows a separated measurement of the two different environments. The data was taken above and below the Verwey transition (Tv=120K) at the Fe K edge (7111eV). To improve the energy resolution, which is vital for fine structure studies, the IP detector was moved away from the sample, thus yielding a fair number of pixels for each reflection ; because of the small size of the unit cell (a=8.384Å) and the relatively large wavelength, only a few number of Bragg reflections have be measured on each image. Data are still under treatment.

Some measurements have also been made at 12284 eV (far from any absorption edge in the compound) on the magnetite sample : by comparing the integrated intensities I=f(E) with the IO reference spectra, we will be able to quantify the effect of mosaicity on the resulting energy resolution.

(b) Phasing studies : This part of the experiment was carried out on (TaSe4)2I at T=100K, well below the Charge-Density-Wave (CDW) transition (Tc=265K). We measured dispersive anomalous diffraction spectra for approximately 30 reflections with their satellites. In order to measure [H K L] reflections with high L indices (these are a more selective source of information about the tantalum displacements), we moved the detector in different orientations , thus collecting reflections with L=0 to L=8. Preliminary treatment show, as expected :

(i) a much better reproductibility of measurements, thanks to the averaging due to the many oscillations made for each image
(ii) a much better energy resolution, due to the small energy range

Reflections integration for both Bragg and satellites using the DAD program [5] is under way, and phase determination as well as the determination of the atomic displacements associated with the CDW will follow. To fully qualify the Dispersive Anomalous Diffraction method for phasing studies, we will also compare results obtained with those following the standard MAD method in the monochromatic mode.

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[3] H. Stragier *et al.*, Phys Rev. Lett. **21** (69), 3064 (1992)
[4] J-L. Hodeau et *al.*, Rev. Sci. Inst. 66, (2) (1995)
[5] V. Favre-Nicolin *et al.*, in preparation