Energy dispersive XAS and diffraction

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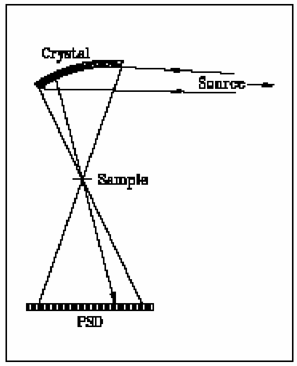
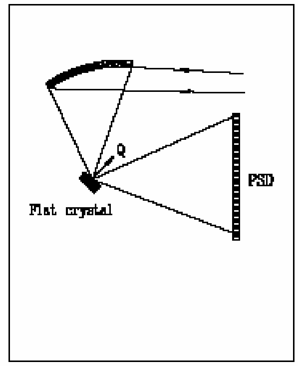
CHESS will soon provide users the opportunity to perform Energy Dispersive X-ray Absorption Spectroscopy (EDXAS) and Diffraction (EDXD) experiments utilizing a focusing crystal polychromator and position sensitive diode array detector (PSD). A preliminary series of measurements with this type of system has resulted in two papers; one on Circular Magnetic X-ray Dichroism (CMXD)[1] and a second on EDXD[2].

An energy dispersive optical system permits the simultaneous collection of data with good energy resolution over a wide energy range[3]. The data are collected using the geometry illustrated in Figure 1. A tightly bent silicon monochromator crystal collects and focuses a horizontal swath of bend magnet radiation. The focused beam has a broad energy width because of the asymmetric cut and large focal ratio. The sample is positioned at the focus and the beam is either transmitted through, or diffracted from this point. The PSD is placed a sufficient distance from the sample to permit the beam to spread out and be collected with good spatial resolution. The perfect crystal monochromator combined with a small source and detector pixel size afford high energy resolution.

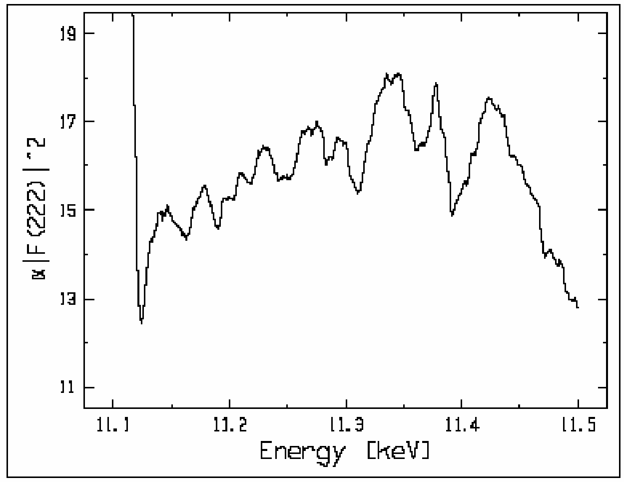
The monochromated intensity is the same as, for instance, a 2cm wide beam at C2 but the energy is spread out over a 100 - 1000 eV range. The PSD made by Princeton Instruments uses a 1024 pixel (25 μm pixel size) Redicon chip and 16-bit ADC where typically one count is one x-ray photon. It can be read out at a rate of 5 microseconds per pixel and has a minimum exposure time of 5 μsec. (or 10 mseconds between exposures). Thus the maximum count rate, about 10^{10} photons/second, is well matched to the intensity from the mono. In a typical experiment one signal averages by accumulating several seconds or more of exposure; in a high count rate situation this means thousands





(Figure 1, right) Schematic layout of an energy dispersive optical system. The monochromator is a bent perfect crystal (top). The transmission geometry at left is used for x-ray absorption studies. At right is illustrated the arrangement for dispersion-matched diffraction from a sample single crystal.

(Figure 2, right) The simultaneous collection of diffraction data from the (222) reflection in a germanium single crystal. A cusp at the K-edge (11.106KeV) and the so-called DAFS are visible in the diffracted intensity.



of exposure-readouts. Unlike the ion chambers we typically use for absorption spectroscopy, the PSD has readout noise (1-2 counts/readout) that will ultimately limit the maximum accumulated signal to noise ratio. This feature would most strongly affect experiments where a weak signal is to be measured in the presence of a large background intensity. It has not proven to be a significant deficiency. One strength of the arrangement is the possibility of time sampling the signal with a frequency range from 100 to 0.01Hz. For short time resolution processes, the best experiments are those for which the excitation can be repeated many times and the sequence of time slices averaged.

The scientific applications of this method can be illustrated by several examples. In the field of electrochemistry, EDXAS is used for the *in-situ* structural study of active sites on surface confined electrocatalysts. Standard electrochemistry has offered only indirect information on the structural nature of such sites. They are known to act as low energy pathways connecting reactants and products. The promise of this approach comes from combining element specificity with an ability to monitor in time (or as a function of electrode voltage) changes in short range order.

In a related area, workers at CHESS have used EXAFS to study the self-sustaining oscillatory oxidation of carbon monoxide over supported platinum catalysts[4]. The basic question is whether small metal clusters making up the catalyst display morphological change as their oxidation state changes. The most interesting part of this reaction is re-ignition which lasts less than one second. By repeated observation of the reaction cycle it should be possible to resolve this question using the sub-second time sensitivity available with dispersive optics.

An important application for which the energy dispersive CMXD offers significant advantage is the investigation of magnetic order using elliptically polarized x-rays. This spin dependent, near-edge absorption technique is sensitive to the electronic environment and magnetic state of the spin-polarized electrons in a solid. Measurements at CHESS have shown that compared to a double bounce arrangement, a single bounce side-diffracting monochromator can produce more intensity at a higher purity of circular polarization. Reference 1 will describe some results of dichroism studied as a function of angle using the energy dispersed beam.

Finally, a novel application for dispersive optics is being developed at CHESS. In the area of anomalous diffraction it is possible to simultaneously collect a diffraction pattern over a continuous energy range from a single set of Bragg planes in a crystal. This idea is illustrated in figure 2 which shows the integrated intensity of a germanium (222) reflection in a 400 eV range about the germanium K-edge. We have analyzed[2] these oscillations and obtained germanium near-neighbor distances in good agreement with the know values. By eliminating monochromator movement as the energy is changed and by taking advantage of the small focal spot size, this new method should facilitate anomalous diffraction studies on small crystals. In addition, the wide energy bandpass is ideal for measurement of diffraction anomalous fine structure (DAFS) in single crystals.

Results from our first energy dispersive run are very encouraging as is the interest it has generated in the user community. Since that time, Matt Borthwick, a Cornell COOP (undergraduate) student, has been developing software that permits the PSD to interface with the SPEC software used for data collection at our stations. A second run is being planned for early Spring 1994. Please contact CHESS to discuss other possible uses for dispersive optics.

1 J.C. Lang *et al.*, Submitted to Phys Rev B (1994).
2 K.D. Finkelstein and Mark Sutton, Nuc Instr. Meth. (1994) in press.
3 A. Fontaine, et.al, Rev. Sci. Instrum. 63 (1), 960 (1992).
4 H.J. Robota and Di-Jai Liu, submitted to J. Phys. Chem. (1993).