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DISPERSIVE X-RAY SYNCHROTRON STUDIES
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ABSTRACT

We demonstrate the simultaneous acquisition of high-resolution x-ray absorption spectra and scattering data, using a combination of energy-dispersive optics and a two-dimensional CCD detector. Results are presented on the optical constants of Pt and on the reflectivity of a platinum-carbon multilayer at the L_{III} absorption edge of Pt.

INTRODUCTION

Unique characteristics of synchrotron radiation, such as tunability and excellent vertical collimation, offer many advantages for the study of surfaces and interfaces¹. Two of the most powerful structural probes which exploit these characteristics are the EXAFS technique,^{2,3} and x-ray diffraction carried out close to the glancing angle for total external reflection.⁴ While the former methods address basically short-range structural correlations, the latter provide information principally on the long-range atomic ordering. The two types of measurement provide complementary information but they require quite different experimental conditions and are not usually performed together on the same sample.

In this paper we describe a new method which permits simultaneous recording of x-ray absorption spectra and x-ray scattering data. As a demonstration of the technique we measured the optical constants of Pt near its L_{III} edge (~ 11.564 keV) where the anomalous corrections become important.⁵ Using this information we compare the measured glancing-angle reflectivity with values calculated using an iterative Fresnel method.

The use of energy dispersive optics⁶ and a high-resolution charge coupled device (CCD) detector⁷ makes for fast, efficient, data acquisition. The methods thus have much to offer for a wide range of measurements including near-edge spectroscopy, EXAFS, and small-angle scattering. The parallel nature of data acquisition also presents some interesting possibilities for time-resolved measurements.⁸

EXPERIMENTAL DETAILS

The measurements were performed on the DCI storage ring at LURE. The heart of the dispersive optics is a triangular-shaped Si(311) bent crystal with an energy band-pass given by⁶ $\Delta E = E_0 L (R^{-1} - \sin \theta_B / p) \cot \theta_B$, where L is the length of the crystal

illuminated, p is the source to crystal distance and R is the radius of curvature. The nominal energy, E_0 , is determined by the choice of Bragg angle, θ_B .

Fig. 1 shows the experimental layout with a white beam incident on the bent crystal and an outgoing beam which is energy-resolved in space. The sample is placed at the polychromatic focus point and, if a position sensitive detector is located on the Rowland circle, the energy resolution is Darwin-width limited (typically $\sim 2\text{eV}$ for $E_0 \approx 11\text{keV}$). The dispersive method is discussed in more detail by Fontaine et al.⁹ in this Proceedings. The bent crystal was adjusted to have $\Delta E \approx 500\text{eV}$ centered on the L_{III} edge of platinum.

Fig. 1: Schematic arrangement for energy-dispersive measurements using a CCD position-sensitive detector.

One axis of the CCD detector (parallel to the pixel rows) is oriented accurately along the energy fan of the bent crystal so that the positional coordinate along this axis corresponds to a particular energy. In the perpendicular direction, the detector registers the scattering angle (momentum transfer). In this way we can obtain spectroscopic data and scattering information simultaneously.

The CCD detector has 390×584 pixels each of area $22 \times 22 \text{ (}\mu\text{m)}^2$. In order to maximize the effective collection area the detector chip is coupled to a Trimax phosphor¹⁰ screen 40 mm in diameter, using a pair of photographic lenses. This resulted in a 4:1 image reduction at the CCD chip. Dark current was suppressed by cooling the chip to -50°C with a thermoelectric element. The Pt-C multilayers were prepared by sputtering and consisted of ~ 20 bilayers, each layer (Pt or C) being $200\text{\AA}$ thick. The top layer of the sample is Pt.

RESULTS AND DISCUSSION

In order to investigate the near-edge reflectivity our first task was to measure the optical constants for Pt, these being the dominant factors compared to the values for carbon. The anomalous scattering corrections, $\Delta f'$ and $\Delta f''$, are related to the absorption cross section, $\sigma(\omega)$, in the usual way:⁵

$$\Delta f''(\sigma) = \frac{mcw\sigma(\omega)}{4\pi e^2} \quad (1)$$

and

$$\Delta f'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \Delta f''(\omega) d\omega'}{\omega^2 - \omega'^2} \quad (2)$$

The imaginary part of the anomalous structure factor, $\Delta f''$, was obtained directly from absorption cross-section measurements on a thin foil of Pt placed at the polychromatic focus (see Fig. 1); no self-absorption corrections were applied. The real part, $\Delta f'$, was then calculated using the Cauchy principal value of the Kramers-Kronig integral (Eq. 2) spanning $\hbar\omega_{LIII}$ to 100keV.

The energy dependences of $\Delta f'$ and $\Delta f''$ around the L_{III} edge obtained in this way are shown in Figs. 2(a) and 2(b), respectively. The data were averaged over 44 frames each with an exposure time of 100 msec.

Fig. 2: Anomalous corrections to the structure factor of Pt.
(a) real part; (b) imaginary part.

Reflectivity Measurements

The arrangement shown in Fig. 1 was used to measure the reflectivity of the multi-layer as a function of incidence angle. The two-dimensional CCD readout permits one to measure reflectivity values simultaneously over a range of photon energies (Fig. 3). For simplicity we present the behavior at just one energy (11.56 keV) slightly below the absorption edge. Data were accumulated over a range of glancing angles from 0.2 mrad to 7 mrad, the sample tilted with respect to the incoming beam in increments of 0.1 mrad.

Fig. 4 is an example of the data obtained in this way; the absorption edge is clearly visible on the specularly reflected beam. Note that at small angles a portion of the direct beam escapes over the top of the sample; this is useful for calculating values of the absolute reflectivity and as a reference " I_o " for absorption measurements.

Fig. 3 : Reflectivity of Pt-C multilayer around the L_{III} -edge of Pt measured using energy-dispersive techniques. The angle of incidence was fixed at 6 mrad.

Fig. 4 : Two-dimensional CCD readout of Pt-C multilayer glancing-angle reflectivity.

In Fig. 5(a) we show the measured reflectivity curve at 11.56 keV. The reflectivity decreases rapidly, as expected, towards the critical angle, θ_c , at ~ 6.6 mrad. This is in good agreement with the calculated value from $\theta_c = \sqrt{2\delta}$ ($= 6.56$ mrad) using the complex refractive index ($\tilde{n} = 1 - \delta$) determined from the optical constants of the multilayer. As a first approximation the contribution of the carbon layers can be neglected. More accurate calculations, as described below, include the carbon optical constants explicitly.

The fine structure on the reflectivity curve is a result of the multilayering geometry. In order to prove this, it is necessary to calculate the reflectivity allowing reflection and transmission at each interface. Note that well below θ_c the evanescent wave penetrates only the first ~ 50 Å below the surface.¹¹ At higher angles, the multiple scattering at the various interfaces will become important. The reflection coefficient at the interface between the j th and $(j+1)$ th layers given by:¹²

$$R_{j,j+1} = a_j^4 \left(\frac{R_{j+1,j+2} + T_{j,j+1}}{R_{j+1,j+2} T_{j,j+1} + 1} \right) \quad (3)$$

where

$$T_{j,j+1}^\sigma = \frac{g_j - g_{j+1}}{g_j + g_{j+1}} \quad (4)$$

and

$$g_j = (\tilde{n}_j^2 - \cos^2 \theta)^{1/2} \quad (5)$$

$T_{j,j+1}^\sigma$ is a transmission coefficient (for σ polarization) which depends on the complex refractive index, $\tilde{n}_j$, and the angle of incidence θ ; a_j is an absorption factor. The computational scheme starts at the substrate and works iteratively back to the surface. The resulting reflectivity is related to the intensity by $I(\theta)/I_o = (R_{12})^2$.

The calculated reflectivity is compared with the measured curve in Fig. 5. The feature at ~ 5.5 mrad is clearly reproduced in the calculated reflectivity curve. The other prominent feature, a dip at ~ 4 mrad is found to be very sensitive to the carbon optical constants. Better values for the latter are required in order to improve the agreement with the measured curve. Even so, the overall fit is reasonable indicating that the interfaces are abrupt and that there is very little intermixing of the constituents. This is also confirmed in our conventional diffraction measurements of the 00 ℓ profile.

Fig. 5 : Glancing-angle reflectivity curves for Pt-C multilayer at 11.56 KeV:
(a) measured; (b) calculated.

CONCLUSIONS

We have demonstrated that a two-dimensional CCD detector, in conjunction with energy dispersive optics, can be used to obtain simultaneous scattering data and photon energy dependence. The method is useful for studies of the complex optical constants and for reflectivity determination close to absorption edges. These techniques are also promising for time-resolved surface EXAFS and glancing angle diffraction measurements.

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