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DEPTH CONTROLLED EXAFS AND NEAR EDGE SPECTROSCOPY TO STUDY SURFACE LAYER STRUCTURE

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Abstract

Calculated and experimental intensity values are presented and compared for EXAFS spectrometry at grazing incidence with fluorescence or reflectivity detection, and samples in the form of single or double metal films evaporated onto flat glass substrates.

The limited and controllable penetration of X-rays incident at grazing angles onto flat samples provides scope for the investigation of surface regions. An EXAFS and near-edge X-ray spectrometer with grazing incidence and fluorescence or reflectivity detection has been developed at the SRS of the Daresbury Laboratory. The instrument has been used to study actinide behaviour during the water corrosion of borosilicate glasses for high-activity radioactive waste disposal [1]. The effect of the corrosion may be the formation of a layered structure on the surface of the glass; this possibility may introduce ambiguities into the interpretation of the results. There was therefore interest in looking at the behaviour of known layered structures. This paper describes some tests of the instrument with samples in the form of single or double films evaporated onto polished flat borosilicate substrates.

The angular scale of such measurements is set by the critical angle $\varphi_C$ for total external reflection, approximately given by the expression $\varphi_C \approx 1.64 \lambda \rho \text{ mrad}$, where $\lambda$ is the wavelength in Å and $\rho$ is the density in g cm$^{-3}$. For grazing angles $\varphi \ll \varphi_C$ the depth of penetration of the X-rays, $Z$, is approximately $48/\sqrt{\varphi}$ Å, independent of absorption or wavelength. This is what is meant by 'surface region' - perhaps 4 atom layers for dense materials, 20 atom layers for light materials. As $\varphi$ is increased, $Z$ increases, to a value of $(\lambda/4\pi \mu)^{1/2}$ for $\varphi = \varphi_C$, where $\mu$ is the X-ray absorption coefficient. Thus $Z$ is about 200 Å for $\mu = 200$ cm$^{-1}$. For $\varphi = \varphi_C$ and increasing, $Z$ increases rapidly and tends to the geometric value of $(\varphi^2 - \varphi_C^2)^{1/2}/\mu$.

How do these changes in $Z$ appear in the experimental measurements? For a homogeneous material, with fluorescence detection, the intensity is approximately proportional to $(1-R)$, where $R$ is the reflectivity [2,1]. The observed increase in fluorescence intensity as $\varphi$ is increased from zero arises because a greater proportion of the incident intensity is able to penetrate into the sample, rather than being reflected. The variation of the penetration depth of the radiation with $\varphi$ does not affect the intensity directly. How then can the depth effect be checked?
Consider a double film, where the lower film has a higher electron density than the upper film, for example Pt below Cu, on a flat glass substrate. How will the intensity of Pt fluorescence depend upon the grazing angle \( \phi \)? Fluorescence will be observable only if \( \phi \) is large enough for the penetration depth through the upper film to be greater than the film thickness. For film thicknesses of a few hundred A, this means \( \phi \) just greater than the critical angle for the upper film.

Thus it is necessary to consider the X-ray optics for a thin film of Cu with vacuum on one side and a more dense medium (e.g. Pt) on the other side. The thickness of the Pt layer will be assumed to be infinite. Suppose X-rays are incident at a grazing angle \( \phi \) on a Cu film of thickness \( h \), with refractive index \( n_1 \), on a Pt substrate with refractive index \( n_2 \). The quantities to be calculated are the reflectivity \( R = |r|^2 \) and \( T = |t|^2 \), where \( r \) and \( t \) are the reflection and transmission coefficients (i.e. amplitude ratios) for the film. Expressions for \( r \) and \( t \) are given, for example, in [3]. Some calculated values of \( R \) and \( T \) for a range of values of \( h \) and \( \phi \) are shown in Fig. 1. The material constants used were for \( \lambda = 1.05 \) A (just above Pt LIII edge). The critical angles for the pure materials are 5.1 mrad for Cu and 8.0 mrad for Pt.

The quantity \( T \) gives a measure of the penetration of the X-ray beam into the Pt, so it will be related to the magnitude of the Pt fluorescence signal. For \( \phi = 5 \) mrad - i.e. in the vicinity of the Cu critical angle - as the film thickness \( h \) is increased, \( T \) decreases. The Pt is being shielded by the Cu film. For larger values of \( \phi \), some structure starts to appear both in \( R \) and in \( T \). This behaviour of \( R(\phi) \) at fixed \( h \) is familiar. For relatively small \( h \), there is a dip near the Cu critical angle, then an increase as the X-rays penetrate the Cu and are reflected by the Pt followed by a second drop near the Pt critical angle. For larger values of \( h \) there are Kiessig oscillations representing multiple-beam interference. The present calculations show that these two effects blend into one another.

![Fig. 1 Calculated values of R and T for X-rays (\( \lambda=1.05A \)) incident at an angle \( \phi \) on a film of Cu of thickness \( h \) with a Pt substrate.](image-url)
Fig. 2 Observed variation of fluorescent (crosses) and reflected (squares) intensity with grazing angle. (a) X-ray energy 50 eV above Pt LIII absorption edge; (b) X-ray energy 50 eV below absorption edge.

Measurements were made with a sample consisting of 500A Pt then 200A Cu evaporated onto a polished (λ/10) flat borosilicate glass substrate. The instrument, described in [1], was used on experimental station 9.2 of the SRS at the Daresbury Laboratory. The X-ray energy was set to be above the absorption edge for Pt LIII radiation. Fig. 2(a) shows the variation of the reflected and the fluorescent intensity with grazing angle ϕ. The oscillatory structure appearing in Fig. 1 is present in both signals; the general resemblance to the theoretical values is good. Fig. 2(b) gives the corresponding 'fluorescence' measurement at an energy below the Pt LIII absorption edge. Thus it indicates the angular dependence of the background scattering and fluorescence. The oscillatory structure is absent; this effect has been found with other samples also. The probable reason is that the scattering comes mostly from the Cu film.

Fig. 3. Fluorescence intensity for different grazing angles ϕ from Pt film covered with 500 A Cu. The absorption edge observed is the Pt LIII edge at 11.56 keV. (a) ϕ/ϕ_C = 0.77; (b) ϕ/ϕ_C = 0.84; (c) ϕ/ϕ_C = 1.4, where ϕ_C is critical angle for Pt.
Fig. 4 Variation of the increase in fluorescence intensity at the Pt LIII absorption edge with grazing angle for Pt (squares) and for Pt covered with Cu (crosses). The intensities are scaled to be equal for $\varphi/\varphi_{C, Pt} = 1.4$. The vertical dashed lines indicate the critical angles for Cu and Pt.

Fig. 2(a) was used to choose angles for energy scans where the intensity of the fluorescence from Pt was varying rapidly. Some measurements are shown in Fig. 3. The variation of the height of the observed Pt LIII absorption edge with $\varphi$ is shown in Fig. 4. For comparison, the same quantity has been measured for a 500Å film of Pt alone; this is also shown in Fig. 4. The shielding effect of the Cu film is shown clearly. The Pt fluorescence intensity varies more rapidly with $\varphi$ when shielded by Cu, and is suppressed completely in the vicinity of the critical angle for Cu.

What is the significance of these results? There is useful information contained in angular scans at fixed energy, if the sample is suspected to be non-homogeneous. Because $\varphi_C$ is so small, measurement of the $R(\varphi)$ curve is not easy. However, to obtain reliable and known control of the penetration depth by varying $\varphi$, it is necessary. The fluorescence signal for the present samples had to come from the Pt film. However, the same element could be distributed within a layered structure. This is a possibility for the glasses described in [1]; a surface layer of different density may be formed. Both the surface layer and the substrate will contain U, the element of interest. If the form of the layering can be established, then suitable values of $\varphi$ may be chosen for the measurement required. Even for non-homogeneous samples it would then be possible confidently to assert that a particular value of $\varphi$ corresponded to a certain penetration into the material.

References

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