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THE SURFACE SENSITIVITY OF FLUORESCENCE EXAFS AT REFLECTION CONDITIONS

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ABSTRACT

The development of reflection EXAFS methods has led to the technique becoming a potentially important tool for the study of solid surfaces. Here we present the results for thin films of silver supported on quartz substrates. Two experimental measurements can be used to collect reflection EXAFS data, i.e. detection of 1) the emitted fluorescence or 2) the reflected X-ray beam. Both detection methods have been employed in this work and, of the two, the latter method has been shown to be more surface sensitive. Fluorescence is less so because of contributions from deeply penetrating X-rays which are not involved in the reflection process. These effects can be understood by considering the dynamical theory of X-ray scattering which is consistent with our experimental data. The results from Ag films indicate that, under atmospheric conditions, the metal surface is covered with a thin layer of oxide. Additional data suggests that the surface coating is 2 monolayers of oxide, the reflection EXAFS data suggests that this coating has a structure similar to AgO.

INTRODUCTION

Extended X-ray absorption Fine Structure (EXAFS) has been very frequently shown to be a most useful technique in material science [1]. There has been an ever increasing interest in the surfaces of materials although the techniques applicable to their study are greatly limited. In 1976 it was pointed out [2] that the technique of EXAFS could be applied to the study of...
surfaces. This led to the development of the surface analogue technique, SEXAFS. Measurements are taken by collecting the 'by products' of the process of absorption (i.e. the electron or fluorescence yields) and surface sensitivity introduced by monitoring the 'adsorbate' edge. Generally speaking this 'conventional' application of the technique to surfaces is limited to studies of the gas/solid interface. An alternative to this has been developed where advantage is taken of the surface sensitivity of 'totally externally reflected' X-rays [3]. This offers enormous advantages insofar as it can be applied to liquid/solid and solid/solid interfaces, in addition to the gas/solid interface [4].

EXPERIMENTAL

The experiments were performed on wiggler beam line at SERC Daresbury Laboratory. A schematic of the experimental set-up is shown in figure 1. Using slits $S_1$ and $S_2$ to define a collimated beam (30$\mu$m width) incident at the sample, the totally reflected X-ray beam was detected. The critical angle at the silver K-edge was found to be $0.125^\circ$. Both the reflected beam (measured at ion chamber $I_2$) and the fluorescent wave (measured at ion chamber $I_1$) carry EXAFS information.

RESULTS AND DISCUSSION

A typical reflection EXAFS (REFLEXAFS) spectrum is shown in figure 2. This was recorded at $\theta/\theta_c = 0.7$, where $\theta$ is the incident angle and $\theta_c$ the critical angle. All data were taken in atmosphere from evaporated silver films. X-ray Photoelectron Spectroscopy (XPS) revealed an oxide covering of about 2 monolayers at the surface. Figure 3 shows a Fourier transform of this spectrum, together with those of data taken in fluorescence geometries with various photon incidence angles. All three transforms are very similar. Above the critical angle, $\theta/\theta_c = 2$, penetration of the sample is large and the thin oxide covering is not detected. The expected increase in surface sensitivity as the critical angle is approached is still not enough to allow significant oxide contribution; the data shows little difference. However, when compared with figure 3 a), differences can be observed, the most striking feature being the appearance of a shoulder at around $3.1^\circ$. This peak corresponds closely with the 'non-phasesshift corrected' Ag-Ag distance in AgO and thus indicates the greater surface sensitivity on decreasing the incident angle below the critical angle. The theoretical Fourier transform is shown with that of the experiment in figure 4.
Using an argument stemming from dynamical theory and the analysis of diffraction, interference is allowed between penetrating incident photon waves and diffracted (in this case reflected) waves, resulting in a standing wave of very low penetration depths. Thus both fluorescence and reflected signals should contain surface information (theoretical models are currently being developed at Strathclyde University). For real samples, where perfect reflectivities are not observed, fluorescence is also generated by deeply penetrating incident X-rays. For the incident wave, surface sensitivity can be estimated from, \( \frac{I}{I_0} = \exp(-\alpha t / \sin \theta) \) where \( \frac{t}{\sin \theta} \) is the effective escape depth in the sample (\( \theta \) being the angle of incidence with the surface plane) and \( \alpha \) is the linear absorption coefficient. Because of the interference between reflected and incident radiation at angles close to the critical angle, \( \alpha \) is around twice the value normally recorded. Because of the \( 1/e \) attenuation of signal, \( t \) can be calculated from \( t = \sin \theta / \alpha \). Using \( \alpha = 238.5 \), we obtain an effective penetration depth of about 900\( \AA \). Because attenuation of the evanescent wave also occurs, the actual penetration depth is somewhat less than this; a 10\( \AA \) oxide film would thus produce negligible contribution to the signal, although some may be expected from fluorescence created at reflection. For the reflected wave the attenuation depth at \( \theta/\theta_0 = 0.7 \) is predicted by dynamical theory [5] and given by the extinction factor \( \xi \),

\[
\xi = \exp \left\{ -\pi k \Gamma \frac{E}{\sin \theta} \right\}
\]

where \( \xi \) is the distance in the sample, \( \Gamma = r_e \lambda^2 V \), \( k \) is the incident wave vector and \( \Gamma \) a scattering term. The terms for \( \Gamma \) are \( V \), the unit cell volume and \( r_e \) the classical electron radius. At the Ag edge \( \lambda = 0.568 \). The attenuation of the \( 1/e \) signal then results in an escape depth of around 10\( \AA \). We might then suspect a large contribution from the oxide layer.

CONCLUSIONS AND SUMMARY

Use of EXAFS under reflection conditions has been shown to be surface sensitive. By recording intensities of reflected X-rays, there is considerable enhancement of depth sensitivity when compared to fluorescence X-ray measurements. For Ag films, a two monolayer covering of the silver oxide can be observed at the surface. The structure of this film appears to be very similar to that of AgO, as can be seen from the Fourier transform shown in figure 4.

We have shown that this technique is applicable to the direct observation of the solid/gas interface. Not only does the technique avoid the experiment complications of the SEXAFS technique but it also surmounts the so-called
"pressure-gap" between Ultra-High-Vacuum surface analysis and the true reaction conditions of a catalytic process.

REFERENCES


4. This is discussed by the authors in a paper to be presented at the 8th International Conference of Crystal Growth (York, July 1986).


Fig. 1 Experimental arrangement for reflexafs experiments. C is the sample and J1 and J2 to present collection of the straight through beam. Not shown is an ion chamber immediately after S2 to measure incident radiation intensity.

Fig 2
Typical reflexafs spectrum (reflection geometry). The vertical scale is an arbitrary linear intensity scale, the horizontal scale in electron volts.
Fourier transforms of reflexafs data (a) in reflection at $\theta/\theta_c = 0.7$
(b) (c) (d) in fluorescence at $\theta/\theta_c = .7, 1, 2$ respectively. The horizontal scale is in A.

Theoretical fit of the data in Figure 2........ is the experimental data and the theoretical fit.

Fig. 3

Fig. 4