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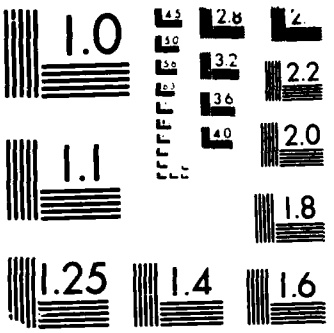

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In-Plane Structure of Underpotentially Deposited Copper on Gold (111) Determined by Surface EXAFS

by

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In-Plane Structure of Underpotentially Deposited Copper on Gold (111) determined by Surface EXAFS

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Abstract

The Surface Extended X-Ray Absorption Fine Structure (SEXAFS) spectrum of an electrochemically deposited ad-layer of copper on a gold (111) electrode immersed in solution and under potential control was obtained by employing fluorescence detection and grazing incidence geometry. The x-rays were polarized parallel to the plane of the gold surface. Two peaks were observed in the radial distribution function, indicating two different near neighbors for copper. The near neighbors were determined to be gold at 2.58 ± 0.03Å and copper at 2.92 ± 0.03Å. The copper-copper distance is identical to the gold-gold lattice spacing showing that at full coverage, the copper ad-layer forms a 1 x 1 commensurate layer on the gold (111) substrate. The intensity of the gold-copper scattering relative to the copper-copper suggests the copper atoms sit in 3 fold hollow sites.

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Introduction

We have previously reported SEXAFS of both underpotentially deposited metal monolayers and polymer films.[1,2] Underpotentially deposited layers are good model systems to study at the metal/solution interface both because stable monolayer (and submonolayer) coverages can be obtained and because they form well ordered layers.[3] ***In-situ*** studies of such systems are relevant because they can provide the structural details necessary for an understanding of the properties of solid/liquid interfaces.

In a recent study,[1] we demonstrated the feasibility of employing SEXAFS as an ***in-situ*** tool for the structural study of copper monolayers electrodeposited onto gold (111) electrodes. One of the more unexpected and significant findings was the observation of strong scattering from oxygen which meant that either water or electrolyte ions (sulfate) were adsorbed on the ad-layer. It is not surprising that water and/or electrolyte is adsorbed at the interface. Both radiotracer[4] and ***ex-situ*** experiments[5] have shown that sulfate is adsorbed on the copper ad-layer. The observation of EXAFS from an adsorbed layer is, however, surprising. EXAFS oscillations of aqueous solutions of metal ions are strongly damped because of their large thermal motions (so called Debly Waller factor).[6] The observation of well defined metal-oxygen EXAFS not only suggests that the electrolyte (or water) is adsorbed on the surface, but that it is adsorbed at well defined distances.[1,2]

SEXAFS differs from EXAFS of polycrystalline or amorphous materials[6] in that the sample is orientated, and hence, the polarization of the incident beam strongly influences the amplitude of the EXAFS oscillations. Bonds whose vector lies in the plane of polarization contribute significantly to the observed oscillations whereas bonds whose vector is normal to

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the polarization will not. For K edge spectra of an oriented sample, the effective coordination number for a particular shell, N_{eff} is approximately related to the true coordination number N by:[7]

$$N_{eff} = 3 \sum_{i=1}^{N} \cos^2\theta_i \qquad (1)$$

where θ_i is the angle between the vector connecting the absorber and its neighbor and the E-vector of the incident beam. Thus, if the polarization of the incident beam is perpendicular to the surface, the absorber's neighbors which lie parallel to the surface will not contribute to the EXAFS signal. In the previous SEXAFS experiments on copper underpotentially deposited on gold (111),[1] the E-vector of the incident x-rays were polarized perpendicular to the plane of the electrode surface. As a result, only atom pairs which had a substantial component of their atom-atom vector perpendicular to the plane of the surface (parallel to the plane of polarization) were observed. Thus, copper-gold and copper-oxygen distances were observed whereas the copper-copper distances were not.

In this paper, we report the ***in-situ*** grazing incidence SEXAFS of a monolayer of copper underpotentially deposited on a gold (111) electrode with the polarization of the incident beam parallel to the surface. Comparison of these results with those obtained with the polarization perpendicular to the surface allow the geometry of the adsorbed sulfate ion to be probed and also provides the additional information required to make a complete structural determination at an electrochemical interface.

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Experimental

Gold (111) electrodes were prepared by epitaxially depositing 2500 Å of Au onto cleaved (in air) mica (ASTM V-2) surfaces which were maintained at 300 C during the deposition. Epitaxy was confirmed by Laue x-ray diffraction backscattering. The underpotential deposition of copper on these film electrodes was identical to that reported on bulk gold (111) single crystals.[9] The films were stored in an inert atmosphere prior to use in the electrochemical cell.

The electrochemical cell and x-ray geometry are illustrated in figure 1. The cell was fabricated from polycarbonate and was approximately 1.5 x 3.5 x 1 in. To improve collection efficiency, the cell was tilted 15° with respect to the horizontal. Although in this geometry the polarization of the E-vector is not exactly parallel to the surface of the electrode, from equation (1), one calculates that species with their atom-atom vector perpendicular to the surface will contribute less than 7% of the EXAFS signal. The gold electrodes (A) were 1 x 3 in. and held in place by small polycarbonate clamps under which electrical contact to a gold wire (F) was made. When placed in the cell, the gold surface extended slightly above the outer lip of the cell which allowed grazing incidence geometry to be used. The reference electrode (B) was a Ag/AgCl (3 M KCl) microelectrode, against which all potentials are reported. A Pt coil (C) was used as the counter electrode. Solutions were deoxygenated with nitrogen and added (and removed) from the cell through ports (G and H) which were sealed when not in use. These ports also allowed the cell to be flushed with nitrogen before the addition of solution. The electrolyte was contained between a thin (0.5 mil) polypropylene film (D) and the electrode. This film was attached to the cell with an O-ring. The chamber containing the electrochemical cell was continuously flushed with nitrogen to eliminate any problems from diffusion of oxygen through the polypropylene film.

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The electrolyte was 0.5 M sulfuric acid (Baker Ultrex) containing 5 x10^{-5} M copper sulfate (Aldrich Gold label) and was prepared using pyrolytically distilled water.[10] Prior to deposition, solution was added to the cell so that the polypropylene film distended somewhat, allowing the UPD layer to be deposited from bulk electrolyte. The monolayer was deposited from bulk electrolyte because of the low copper concentration. At this concentration approximately 10 minutes were required to form the monolayer, which was deposited at +0.13 V. All measurements were made at full monolayer coverage. After deposition, solution was removed, leaving only a thin layer of electrolyte, whose thickness we estimate to be of the order of 20 μ, between the electrode and polypropylene window. In the thin layer configuration (at full monolayer coverage), we calculate less than 5% of the absorbing copper atoms are present as ions in the electrolyte. As a result, the interference from copper in solution can be ignored. The absorption edge for Cu^{2+} is also markedly different from that of Cu^{0} (vida infra) so interference from Cu^{2+} is easily detected in the absorption edge if present. All experiments were conducted at room temperature.

Experiments were preformed at the Cornell High Energy Synchrotron Source (CHESS) on beam line C2. A Si (111) double crystal monochromator was used to select the incident wavelength. The incident beam was typically detuned 50% to eliminate higher order harmonics. The absorption spectrum was measured about the Cu K edge, at 8979 eV, by monitoring the the Cu K_{α} fluorescence line at 8040 eV. This was isolated by a 36 mm diameter high purity germanium solid state detector (E) (Ortec GLP-36360/13-S) coupled to a Tennelec TC 224 spectroscopy amplifier and an Ortec 551 single channel analyzer. To operate this detector in its linear regime, it was necessary to limit the total intensity of x-rays

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impinging on it. Two things were done. First, the x-ray beam was incident on the sample at grazing incidence, i.e., angle of incidence greater than 89°, though the actual angle was not measured. Since the penetration depth of x-rays in the sample is small, this greatly reduces the scattered radiation (Compton and elastic). Furthermore, the signal from the copper is enhanced as the incident x-ray beam undergoes total external reflection[11] increasing the intensity of x-rays at the surface at least by a factor of 2. The angle of the sample was adjusted experimentally to minimize scattering while maximizing the fluorescence signal. Second, a nickel filter (approximately 25 microns thick) was used to preferentially absorb the elastic and Compton scattered radiation. Nickel has its K edge at 8333 eV and thus has a substantially lower absorptivity for the Cu fluorescence at 8040 eV than for the the elastic and Compton scattering which lie at energies higher than 8500 eV. Soller slits (I) were used to reduce the Ni fluorescence from the filter incident on the detector. The incoming beam was collimated by slits (J) and its intensity was measured by an ionization chamber.

Data were collected in scans of 20 to 30 minutes and approximately 50 scans were averaged to obtain reasonable signal to noise ratio. These data were analyzed by well established procedures.[12] The major inflection point in the edge jump was taken to be the position of the edge. Bond distances were obtained by fitting the oscillatory part of the EXAFS equation[12] to the experimental oscillations with the phase shift for the pair of interest being obtained experimentally from copper foil, $CuAu_3$ and Cu_3Au.

Secondary ion mass spectra (SIMS) were obtained on a Cameca IMF-35 Ion Microscope using O_2^+ as the primary ion beam.

Results and Discussion

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The x-ray absorption spectrum from the monolayer of copper is shown in figure 2. The electrode was held at 0.13V. This potential is between that at which full monolayer coverage is obtained and the onset of bulk deposition. That this signal arises from the monolayer of copper on the surface can be shown by changing the potential to a value (0.50V) where the monolayer is oxidized to Cu^{2+} which dissolves into the thin layer of electrolyte. The oxidation of the copper monolayer raises the concentration of Cu^{2+} in the thin layer to approximately 10^{-3} M. The near edge spectra under these conditions are compared to that of the UPD layer in the inset in figure 2. There are two key differences. First, the Cu(II) has an absorption edge approximately 4 eV higher in energy than the copper monolayer. The position of the absorption edge is sensitive to the oxidation state of the element much as in XPS. This shift to a higher energy is consistent with the larger binding energy for the higher oxidation state of Cu^{2+}. Second, there is a strong, characteristic absorption (white line) in Cu^{2+} just above the edge which is absent in the spectrum of the copper monolayer. The position and shape of the edge of the copper monolayer is identical to that of copper foil (which also does not have the distinctive white line). The lack of a characteristic Cu^{2+} absorption edge in the spectrum of the monolayer verifies that interference from Cu^{2+} in the thin layer of electrolyte is insignificant.

Some studies have suggested that the deposition of copper on gold results in alloy formation[13] and that not all of the copper is stripped upon oxidation. Our previous experiments with the polarization perpendicular to the surface, however, showed strong scattering from adsorbed solvent or electrolyte which could only have arisen from copper atoms on the surface. In addition, we performed depth profiling studies on the gold electrodes

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after stripping underpotentially deposited copper using SIMS. Copper is observed near the surface (less that 10Å) but the amount present was less than 5% of a monolayer. Thus, we conclude that the EXAFS signal is from an adsorbed copper layer.

The EXAFS function $\chi(k)$ obtained for the monolayer of copper is shown in figure 3. The insert shows the radial structure function (RSF), which represents the magnitude of the Fourier transform obtained from the k weighted data in the range from k=4 to 11Å.$^{-1}$ No significant changes were observed in the RSF using k^2 or k^3 weighted data. Two peaks are clearly present, one at approximately 2.17Å and one at 2.71Å. The dashed line superimposed on the raw EXAFS is the inverse transform of the two peaks in the RSF using a filtering function to isolate the range between 1 and 4Å.[12] Both the frequency and amplitude of the filtered transform fit the raw EXAFS over the entire spectrum showing that even at k = 11 noise does not yet dominate the EXAFS spectrum. As usual, the data is not analyzed for values of $k < 4$ (approximately 60 ev above the absorption edge) to avoid complications from multiple scattering effects.[12]

Before accurate bond distances can be extracted from the EXAFS data, it is necessary to know which backscattering element is responsible for each peak in the RSF. For copper underpotentially deposited on gold, only copper, gold and oxygen atoms should surround each copper atom. The distances in the RSF are much too long to correspond to scattering from oxygen leaving only copper and gold as the only possible backscatters. (The copper-oxygen distance measured in the earlier work was 2.08Å[1]). Although EXAFS is not particularly sensitive to the atomic number of the backscattering atom, it is possible to distinguish between two atoms with large differences in atomic number.

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EXAFS oscillations result from the interference between the ejected photoelectron wave and the wave backscattered off a near neighbor. For a particular shell, the EXAFS function $\chi(k)$[12] is:

$$\chi(k) = \frac{N}{k\ R^2}\ A(k,z)\ \sin(2kR + \phi_z)\ e^{(-2\sigma^2k^2)}\ e^{\left(\frac{-2R}{\lambda}\right)} \qquad (2)$$

N is the coordination number of the shell, k is the photoelectron wave vector, R is the interatomic distance, A(k,z) is the backscattering amplitude, ϕ_z is the phase shift, σ is the Debye Waller factor for EXAFS and λ is the mean free path of the photoelectron. The total EXAFS signal is the sum of the individual shells. Both the shape and the magnitude of the backscattering amplitude A(k,z) depend weakly on the atomic number (z).[14] The backscattering amplitude envelop corresponding to each peak in the RSF can be determined using a fourier filter and inverse transforming individual peaks in the RSF. The net result of this procedure is to isolate the EXAFS resulting from the backscattering of different neighbors. This inverse transform contains only one frequency and its envelope of intensity is the backscattering amplitude function. The results of this operation are shown in figures 4a and 4b for the peaks in the RSF at 2.17 and 2.71Å respectively. The most prominent difference between the two envelopes is the dip in the EXAFS amplitude at k = 6 in figure 4a. This feature is characteristic of high z elements,[14] and thus we feel confident in ascribing this peak to scattering from gold. The absence of this feature in figure 4b is consistent with this frequency being associated with backscattering from copper near neighbors.

The photoelectron does not scatter from the nucleus of the near neighbor, but rather from its electron cloud.[12] Thus, the peaks in the RSF appear at a slightly shorter distance than the

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inter-atomic distance and must be corrected for the phase shift of both the absorbing and the backscattering atoms. These phase shifts depend both on the atomic number and to an extent on the chemical environment. Teo and Lee[14] have carried out ab-initio calculations to obtain theoretical phase shifts and backscattering amplitudes, but because of the slight inadequacies in the theory, it is preferable to experimentally determine the phase shifts from model compounds. Using the phase shifts evaluated from the model compounds and fitting equation (2) to the measured EXAFS yields copper-gold and copper-copper distances of 2.58 $\pm$0.03Å and 2.92$\pm$0.03Å respectively.

The copper-copper distance is identical, within experimental error, to that for the known gold-gold spacing in the (111) plane of 2.89Å. This agreement shows that the copper forms a (1 x 1) commensurate ad-layer on the underlying gold (111) surface. The electrochemical data reported by others also support a commensurate structure. The coverage calculated from the charge passed during deposition of the monolayer is equal to the number of gold surface atoms suggesting the formation of a (1 x 1) ad-layer[9]. The copper-gold distance in in good agreement with that measured in the earlier experiment in which the polarization of the incident beam was perpendicular to the surface. It is also close to the value of 2.56Å reported by Palmberg and Rodin[15] for copper adsorbed on gold (001) in vacuum. The observation of gold backscattering and its intensity relative to the copper-copper signal suggests the copper atoms sit in the gold 3-fold hollow sites. This determination is based on the dependance of the copper-gold signal on the polarization of the incident x-rays. If each copper atom were associated with only one gold atom (ie. an "atop" site), then, the polarization of the E-vector would be perpendicular to the copper-gold atomic vector and no copper-gold scattering would be expected. Copper atoms bound in "bridge sites" would be expected to have significant scattering, although since the EXAFS intensity is proportional to the number of scatters (eq.

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2) and the angle between the E-vector and the Cu-Au atomic vector, less intensity would be expected than for copper in three fold hollow sites.

Perhaps as significant as the structural determination above is the absence of any scattering from oxygen adsorbed on the copper. The absence of a copper-oxygen peak in the RSF in figure 2 strongly suggests that the oxygen occupies atop sites on the copper ad-layer. If the oxygen occupied 3-fold hollow or bridge sites, some EXAFS intensity would have been expected. Thus, we propose the structure shown in figure 5 for copper underpotentially deposited on gold (111) from sulfate containing electrolytes. Water has been shown adsorbed on the copper for convenience.

Conclusion

Using grazing incidence geometry and fluorescence detected SEXAFS, unambiguous structural determinations for monoatomic ad-layers at a metal/liquid interface can be made ***in-situ***. For copper underpotentially deposited on gold (111) at full coverage, copper-copper and copper-gold distances were found to be 2.92 ± 0.03Å and 2.58 ± 0.03Å respectively. This, coupled with the EXAFS intensity, shows that the ad-layer has a (1 x 1) structure with the copper atoms occupying 3 fold hollow sites. Both the position and shape of the absorption edge show that the adsorbed copper atoms are fully reduced. Unlike measurements where the polarization of the incident beam was perpendicular to the electrode surface, no scattering from adsorbed oxygen was observed. This shows that the sulfate ions or water molecules are adsorbed on "atop" sites. The ability to make structural determinations ***in-situ*** should significantly advance our understanding of the metal/electrolyte interface.

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Figure Captions

Figure 1: Electrochemical cell: Gold (111) film on mica (A); Ag/AgCl reference electrode (B); Pt reference electrode (C); 0.5 mil polypropylene film (D); Solid state detector (E); Gold wire working electrode contact (F); Solution inlet and outlet (G,H); Soller slits (I); Collimating slits (J).

Inset: X-ray geometry and appropriate angles. The beam is incident on the sample at grazing incidence ($\theta > 89°$) and the polarization of the E-vector is 15° off parallel with the surface.

Figure 2: X-ray absorption spectra around the Cu K_α edge for UPD Cu on Au(111) at 0.13V.

Insert:Comparison between the x-ray absorption spectra at 0.13V where the monolayer is stable (***Dashed line***) and at 0.50V where the layer is oxidized to Cu^{2+} (***Solid line***)

Figure 3: The EXAFS function for UPD Cu on Au (111) with the potential controlled at 0.13V (***Dashed line***:) and the inverse transform of the RSF using a fourier filter between 1 and 4Å (***Solid line***).

Insert: Radial Structure Function (RSF) analyzed between k=4 and k=11.

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Figure 4: Inverse transform and backscattering envelops of the individual peaks in the RSF in figure 2.

a) Peak at 2.17Å.

b) Peak at 2.71Å.

Figure 5: Schematic diagram of the structure of the underpotentially deposited copper ad-layer on gold (111) at full monolayer coverage. Water has been shown adsorbed on the copper although sulfate ions could equally well occupy these sites. The orientation of the hydrogen atoms has been assumed to be random.

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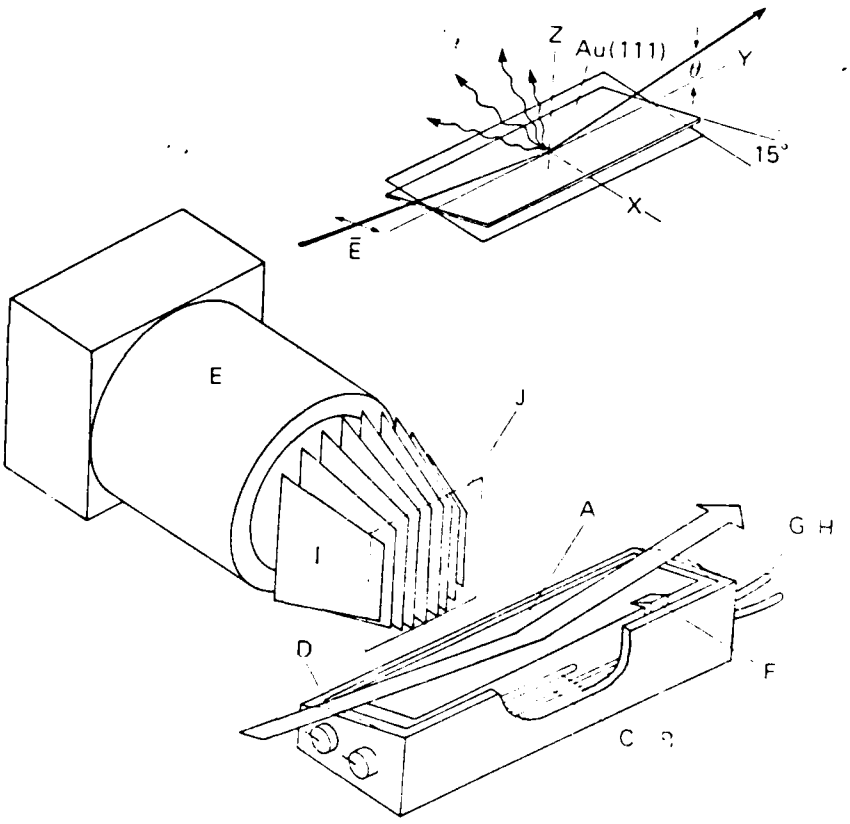

Fig 1

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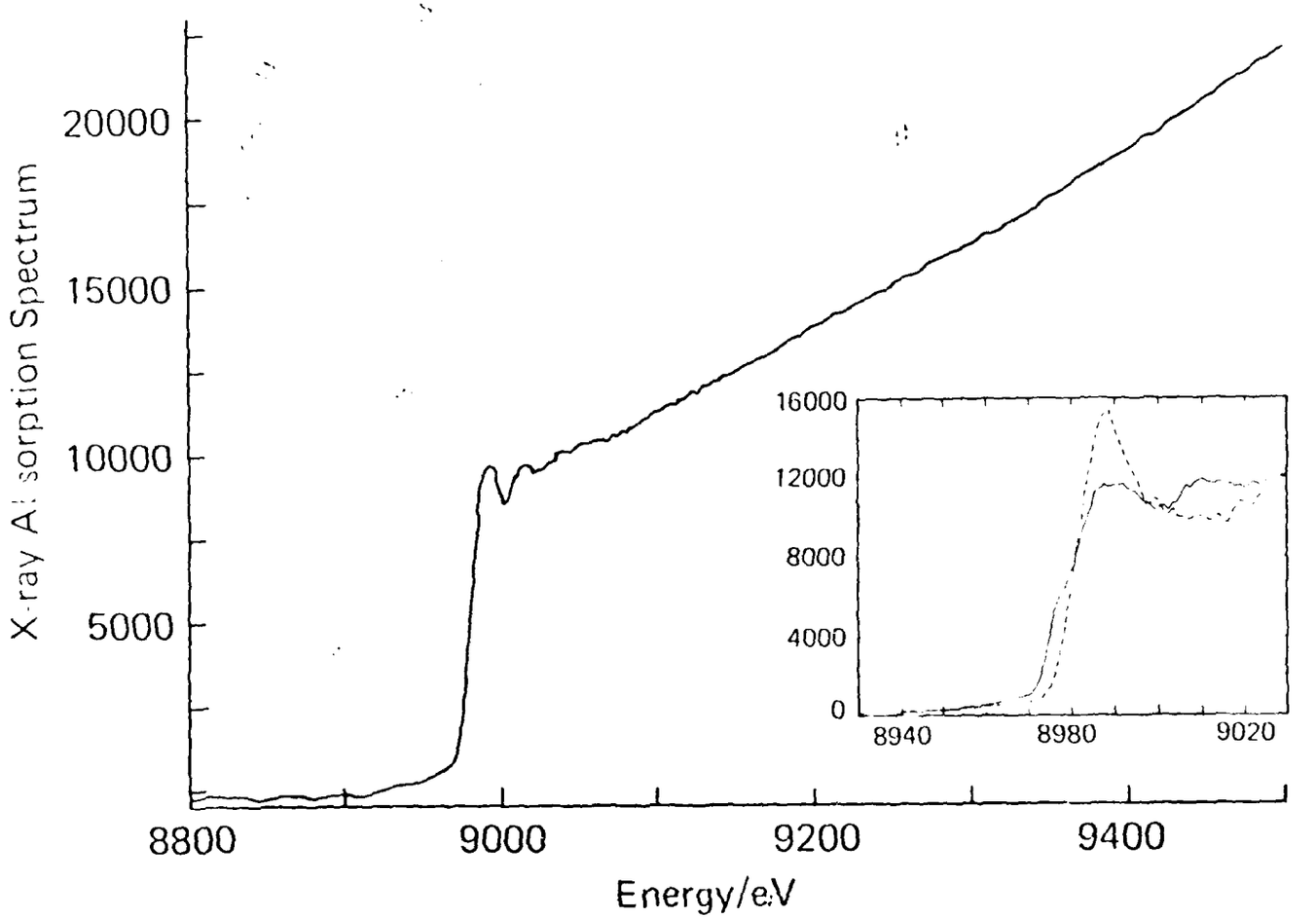

Fig. 2

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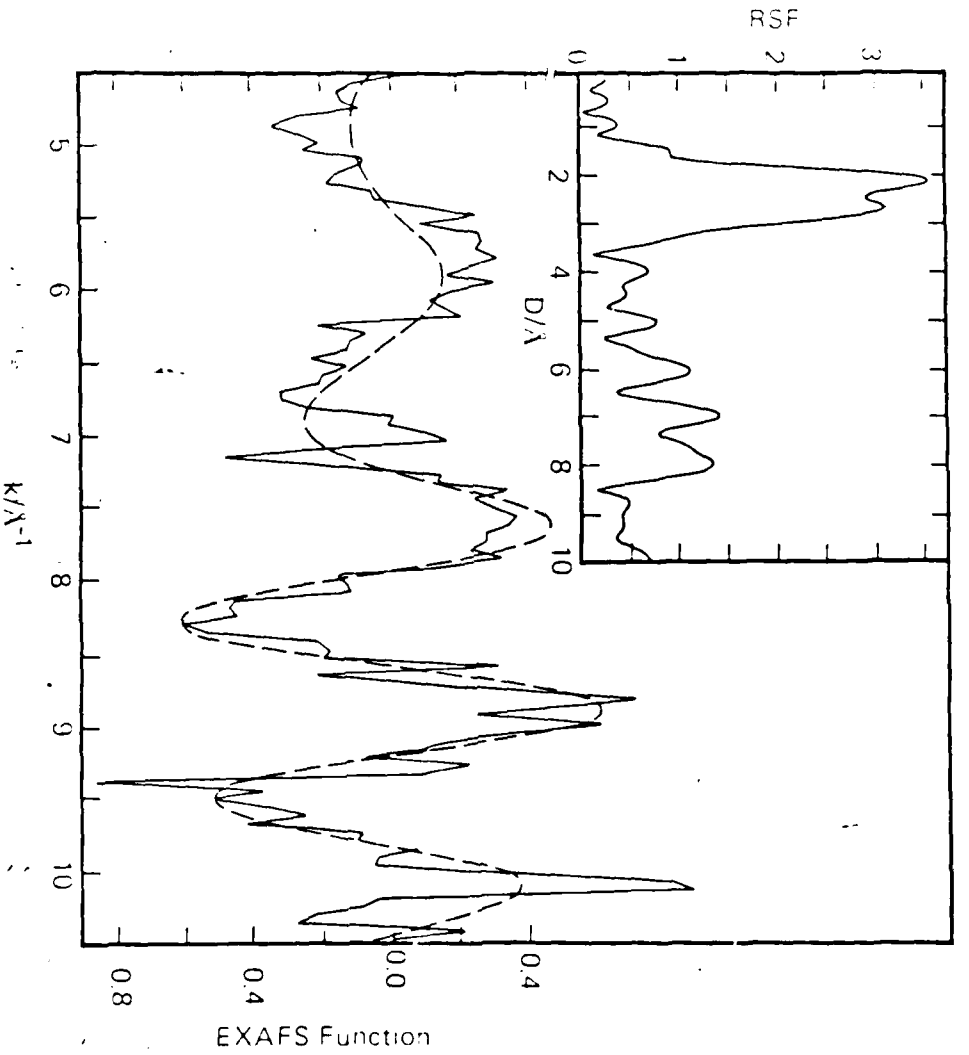

Fig 3

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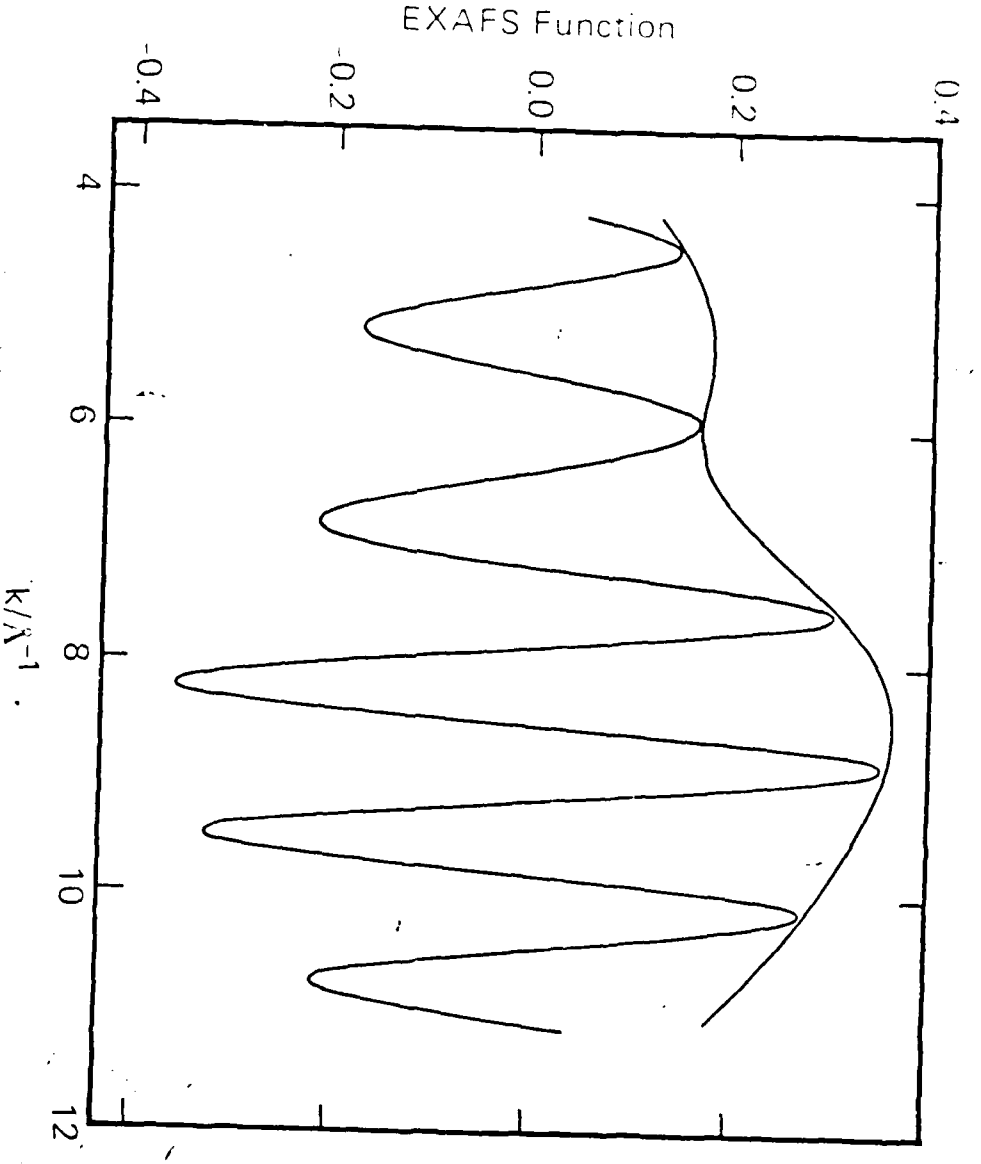

Fig 4a

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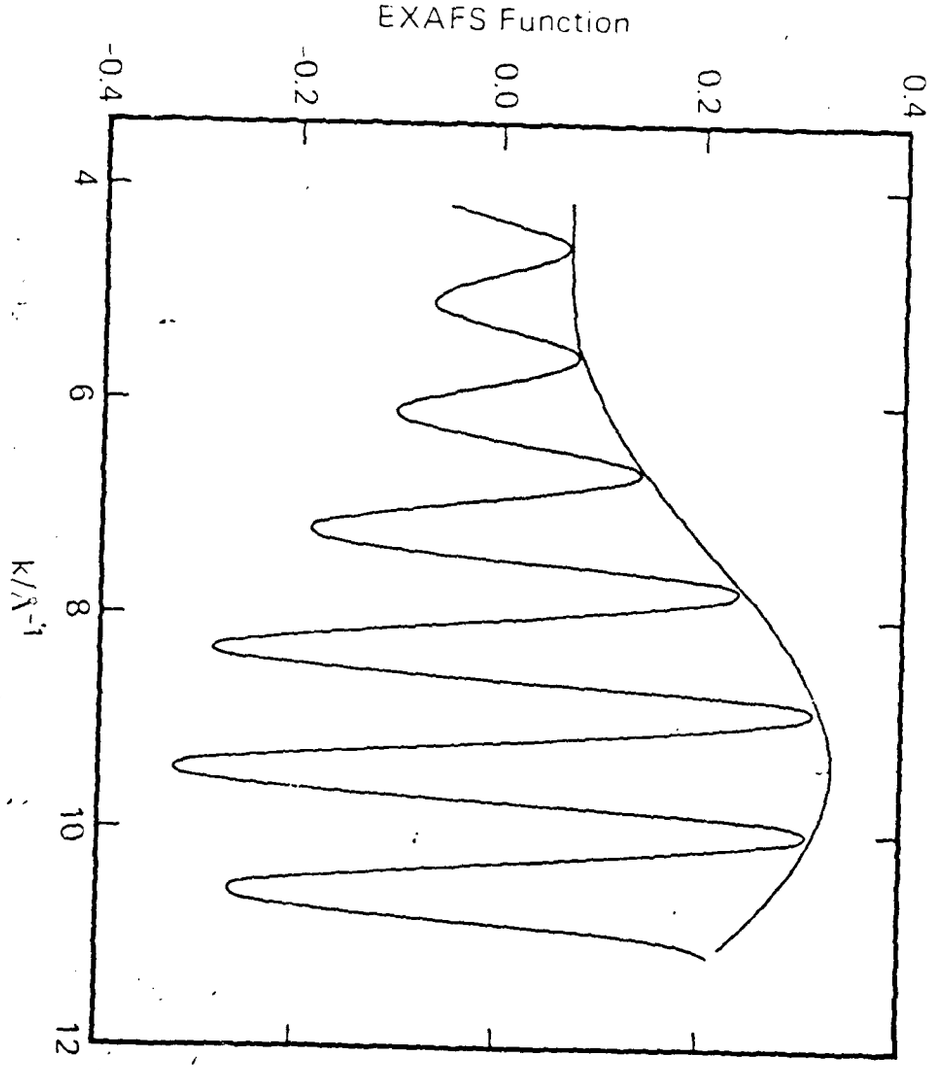

Fig 45

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Fig 5

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