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# Study of underpotentially deposited copper on gold by fluorescence detected surface EXAFS

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Using grazing incidence geometry and fluorescence detection, surface EXAFS of a monolayer of underpotentially deposited copper on epitaxially deposited gold (111) on mica was observed. Both Cu–Au and Cu–O scattering are observed. The results are interpreted in terms of models in which the Cu–O distance is  $2.08 \pm 0.03$  Å and the Cu–Au distance is  $2.5 \pm 0.06$  Å. The copper and three gold atoms at the metallic surface form an elongated tetrahedron, with the oxygen on top of the copper. Two plausible models for the oxygen arrangement are proposed, one involving only one oxygen, the other with a sulfate ion adsorbed. This second model yields a slightly better fit of the data.

## INTRODUCTION

Our knowledge of the structure of the polarized interface between a conducting electrode and an ionic solution has been, up to recent times, based on indirect evidence provided by measurements of capacitance, surface excess concentration, surface tension, or other macroscopic electrical or thermodynamic measurements, which depend mostly on averages over large portions of the interface. The electro-optical measurements are also of the same nature, since the wavelength of the light is of the order of 1000 Å. These measurements can be interpreted in terms of simple and reasonable models and have given us our best microscopic picture of the interface. The problem is that there are many models that will fit the data of a given electrothermodynamic experiment. There is no substitute for a direct structure determination, but because the surface to volume ratio is so small, these experiments have to be carried out in ultrahigh vacuum. The information obtained from these experiments show, that indeed, the adsorbate on a metallic surface is very complex,<sup>1</sup> and that it can undergo a rich variety of phase transitions. For example, it can be ordered and commensurate with the metal lattice, or it can be incommensurate and still ordered, and finally, it can be amorphous or mobile on the surface.

*Ex situ* experiments on interfaces of interest to electrochemists have provided a wealth of very interesting and revealing information. The work of Yeager,<sup>2</sup> Hubbard,<sup>3</sup> Ross,<sup>4</sup> and Sass<sup>5</sup> have shown that in many cases, the adsorbed layers on Cu, Pt, Ag, Au, and other metals of electrochemical interest form mostly ordered phases commensurate with the metallic underlayer. It is an open question to see whether the removal of the interface from the electrolytic cell changes the structure. Indeed, in the case of a polarized electrode the fields can be large. Furthermore, much of the interesting properties of the electrodes are due to the solvent effects, and the theory predicts that the thermodynamic and kinetic properties should depend strongly on the nature of the solvent. It is therefore important to have techniques that can

probe the surface *in situ*. Such are the techniques of optical spectroscopy. The work on the surface enhanced Raman effect (Fleischmann<sup>6</sup> and Van Duyne<sup>7</sup>), surface infrared spectroscopy (Pons<sup>8</sup> and Bewick<sup>9</sup>), surface plasmons (Gordon<sup>10</sup>), and second harmonic generation (Shen<sup>11</sup> and Philpott<sup>12</sup>) have shed light on important questions regarding the structure and state of adsorbates at the charged interface. However, these spectroscopic measurements probe the bond polarizability and do not yield structural information directly. In actual fact, if the structure were known, then one could infer from these experiments local fields and field gradients, which are extremely interesting quantities.

Among the surface sensitive structure determination techniques, fluorescence detected surface EXAFS (SEXAFS) seems to be one that has the unique characteristics needed to provide information about the environment of an adsorbate at the electrode interface.<sup>13,14</sup> The EXAFS modulation are produced by interference between the photoelectron wave emitted by the central absorbing atom and the wave backscattered by the neighboring atoms. One can selectively probe the local environment of a given element by exciting its *K* or *L* shell electron. Since it is essentially an electron scattering process, it is not only dependent on the electron scattering cross sections of the individual atoms, but also on the chemical environment and bonding. Even backscattering from light elements such as oxygen can be detected without major difficulties. This is different from the x-ray diffraction technique, in which the x-ray scattering cross section is a function of the square of the atomic number and therefore, heavy elements tend to obscure the signal from the lighter ones. Another advantage of SEXAFS is that the analysis of the x-ray absorption near edge structure (XANES<sup>15</sup>) yields information about the state of oxidation of the central atom.

Using a transmission technique, Kordesch and Hoffman<sup>16(a)</sup> monitored the EXAFS spectrum from passivated iron films in an electrolyte. To obtain a good signal to noise ratio these authors used multiple layers of the films. A simi-

lar experiment for passivated nickel films was recently reported by Bosio, Cortes, and Froment,<sup>16(b)</sup> who used a reflection geometry. In the present communication we report observations of fluorescence detected SEXAFS from an underpotentially deposited (UPD) monolayer of copper on gold [111].

## EXPERIMENTAL

The sample was prepared by epitaxially depositing gold on a cleaved mica substrate.<sup>17</sup> The gold film has a [111]

surface, of about  $25 \times 100$  mm in size. Epitaxy was confirmed by Laue x-ray diffraction backscattering. It was mounted at the end of a Lexan<sup>®</sup> holder, suspended inside a rectangular Lexan<sup>®</sup> cell with mylar windows which can be filled with electrolyte. The holder was attached to a rotating stage permitting a full  $360^\circ$  rotation with about  $2^\circ$  setting accuracy, and with a finer control of  $0.02^\circ$  accuracy over a  $5^\circ$  range. Soller slits and a nickel filter were used to enhance the Cu  $K_\alpha$  fluorescence (8.03 KeV) relative to the elastic and Compton scattering. The detector was a high purity germanium solid state detector (EG&G ORTEC) with an energy

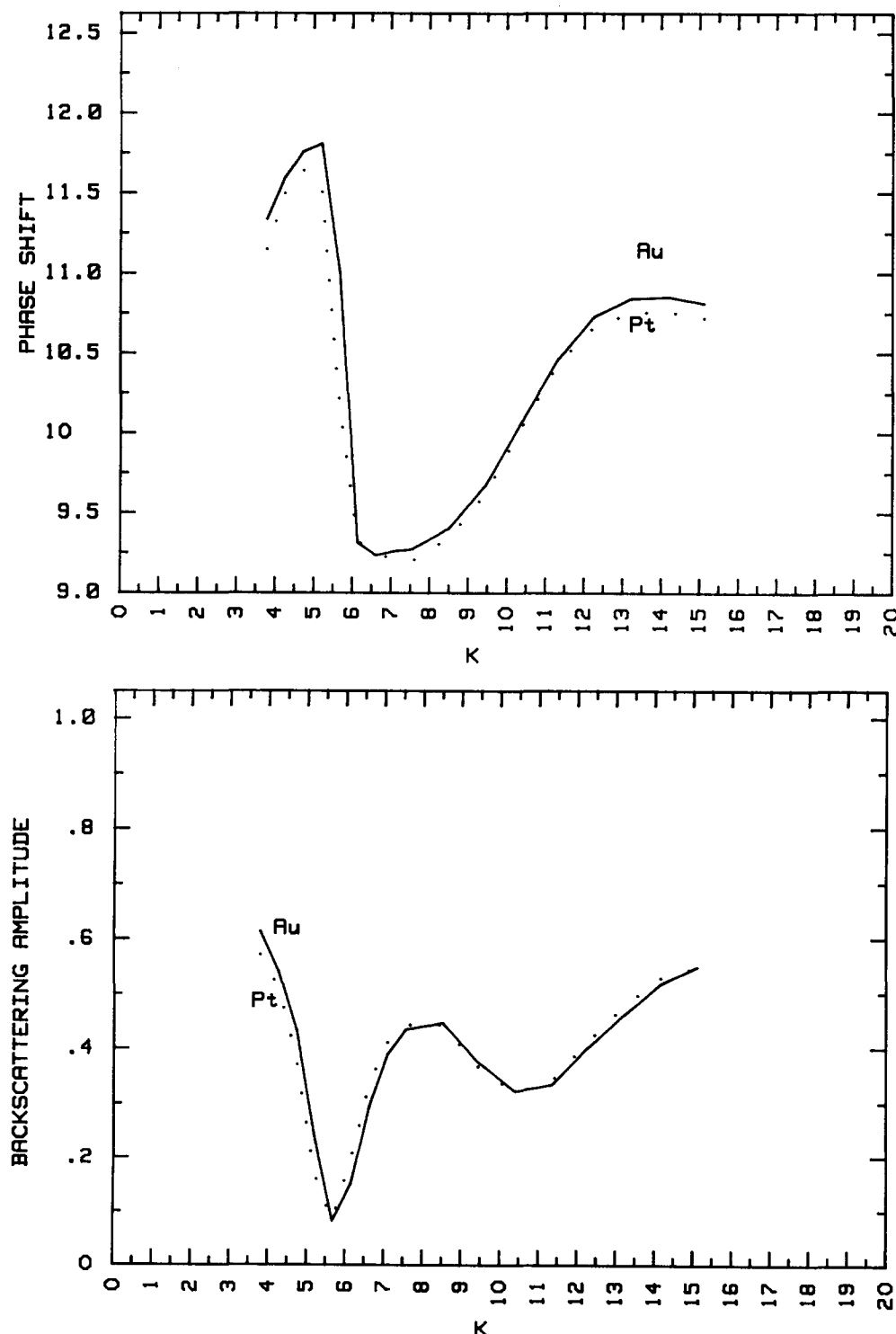


FIG. 1. Phase shifts and amplitudes for Au and Pt. Data taken from Ref. 21. Units for  $k$  are  $\text{\AA}^{-1}$ . The values for Pt, shown as an illustration that the resonance is not strongly dependent on chemical environment, are the dots.

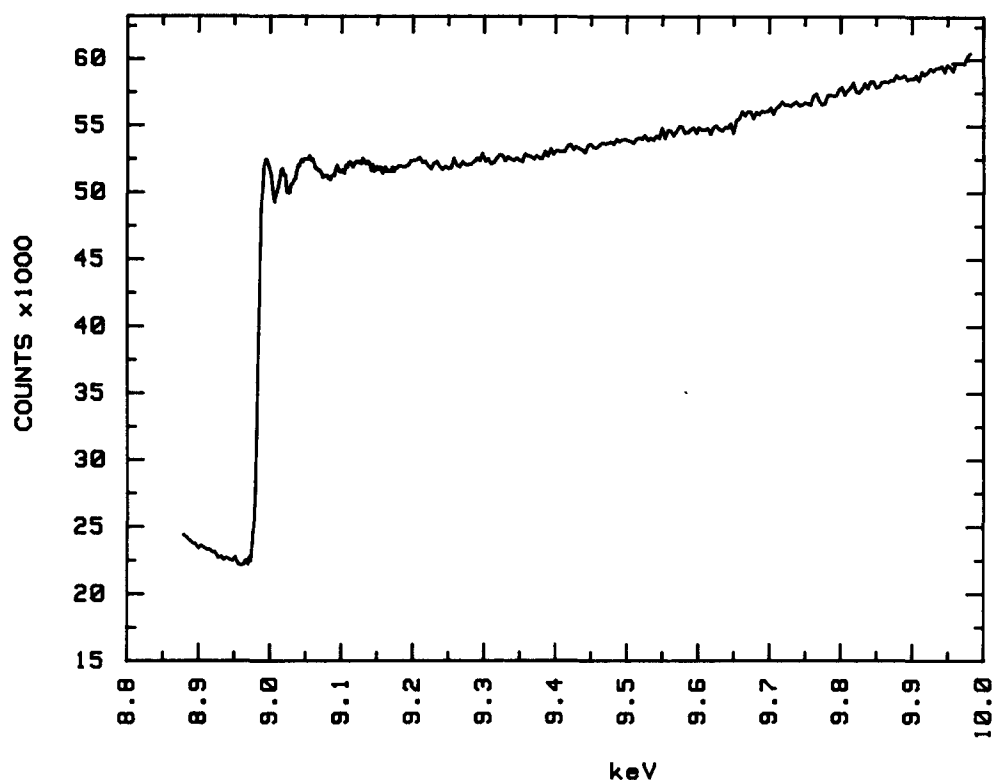


FIG. 2. Raw spectra of UPD Cu monolayer on Au [111].

resolution of 600 eV at our count rates. This was sufficient to isolate the signal from the Compton and elastic background and the fluorescence from the filter, as well. The copper was deposited from a  $2 \times 10^{-5}$  M solution of  $\text{CuSO}_4$  in 1 M

$\text{H}_2\text{SO}_4$ . During the electrodeposition of the copper, the level of electrolyte was raised to cover the active area of the electrode. After deposition the level was lowered. The electrode was covered, at all times, by a 0.005 in. thick mylar film,

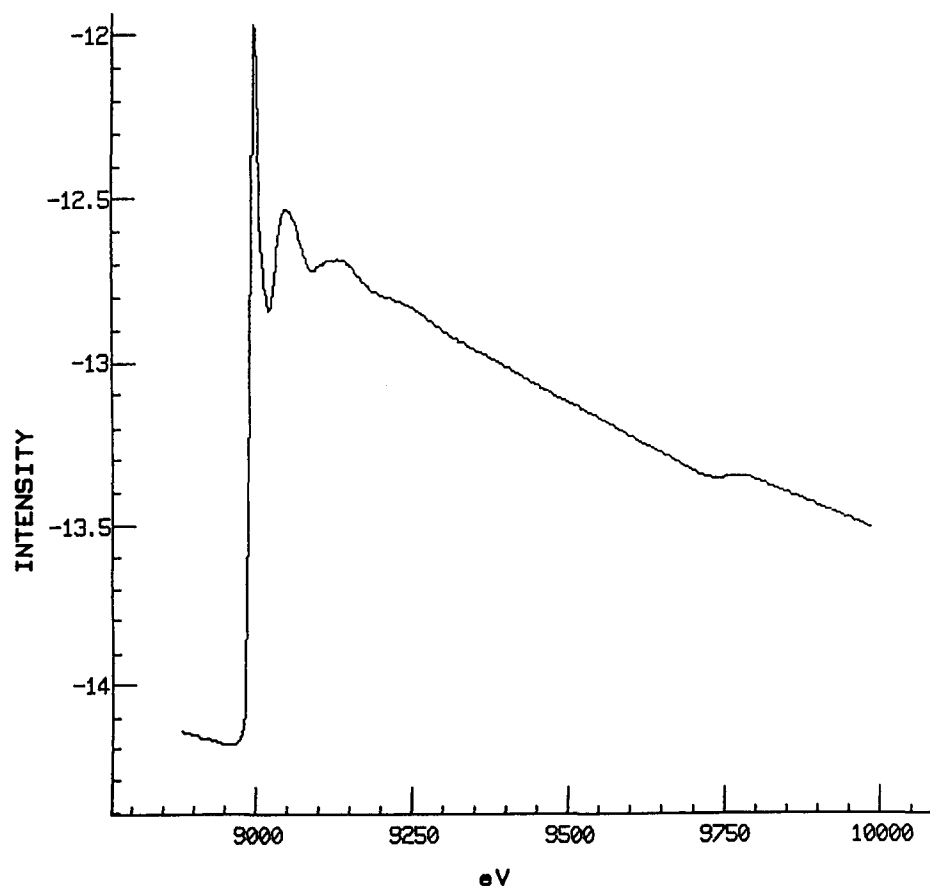


FIG. 3. Raw spectra of  $\text{CuSO}_4$ .

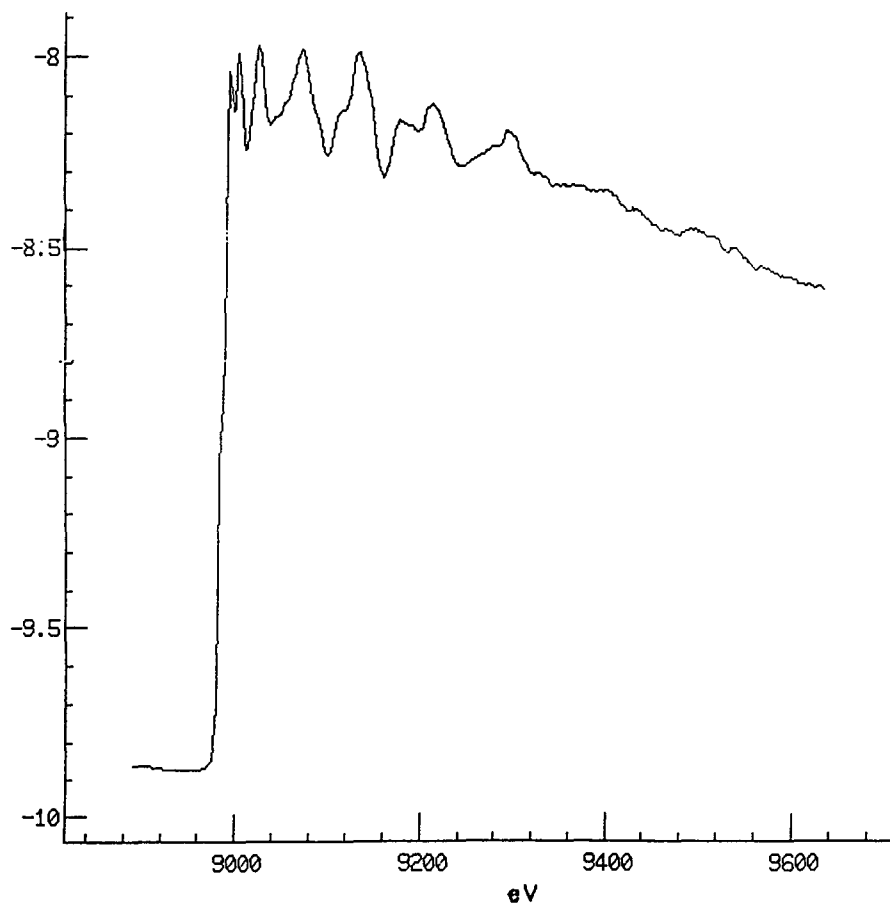


FIG. 4. Raw spectra of 2% Cu-Au alloy.

which held the electrolyte by capillary action. The deposition potential was 0.13 V vs a 3 M KCl/Ag/AgCl reference electrode. As a result of the low Cu concentration in the electrolyte, deposition of the monolayer required 10 min.

Monolayer coverage was confirmed by measuring the stripping charge. The cell and the electrolyte were continuously purged with He. The potential control was verified by monitoring of the Cu absorption edge position. Oxidation of cop-

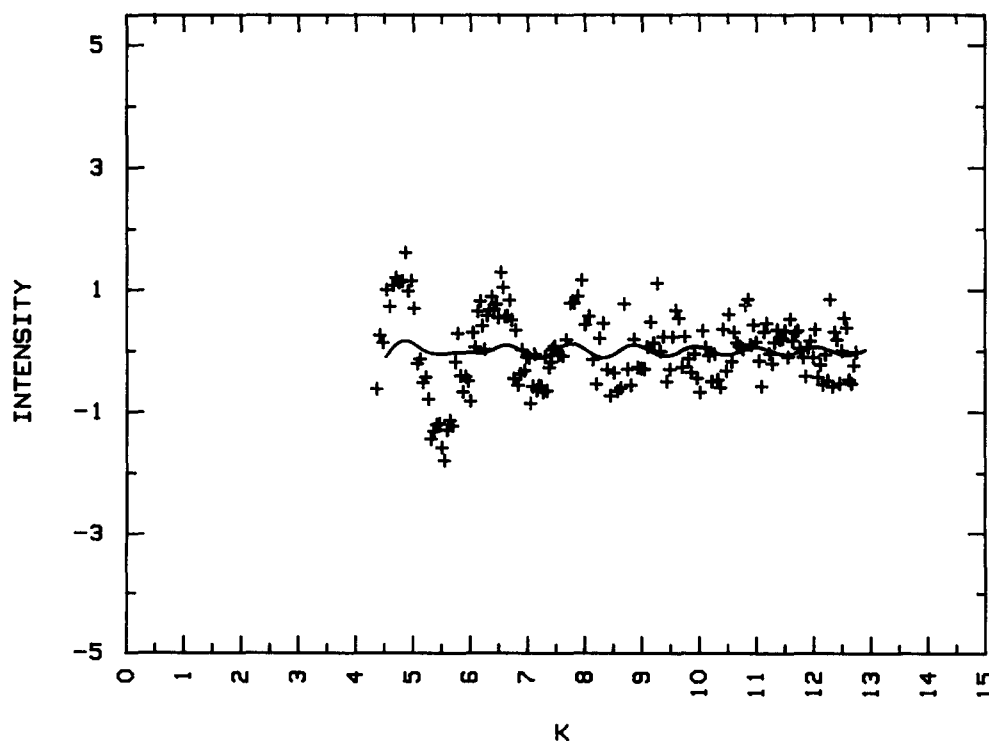


FIG. 5. Data after background removal (+). The curve is the theoretical fluorescence from Eq. (1) using only Au backscattering. The distance is 3 Å. Units for  $k$  are Å<sup>-1</sup>.

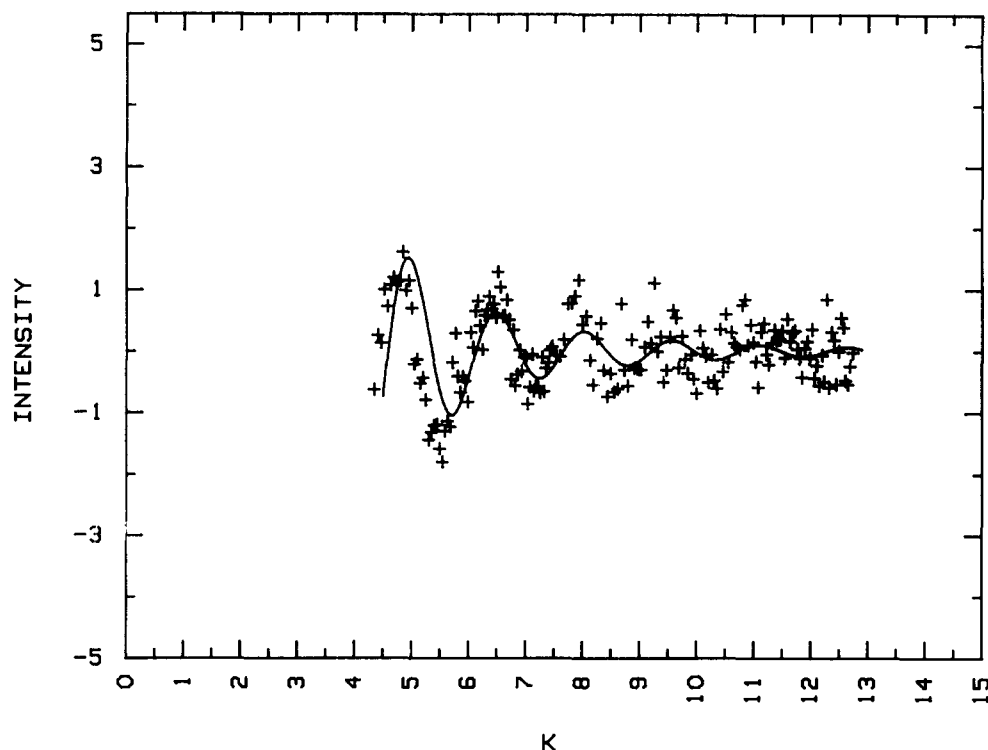


FIG. 6. Same as Fig. 5 but fitted to oxygen as the sole backscatterer.

per results in a 4 eV shift in the edge position. The data was collected using the CHESX XOPLUS program.

## RESULTS AND DISCUSSIONS

To obtain spectra of sufficient quality it was necessary to use the grazing angle technique of Heald and Stern,<sup>18</sup> in which the x rays are incident almost parallel to the surface of the metal. This produces both an enhancement in the inten-

sity and because the penetration depth is small, a decrease in the background scattering. This technique was used recently by Lairson *et al.*<sup>19</sup> to study bromine adsorbed on a nickel [001] surface. In all experimental runs, the gold surface was kept vertical, so that, since the polarization of the synchrotron beam is horizontal, it was parallel to the bonds perpendicular to the surface. As will be shown, bonds in the plane of the surface do not contribute to the SEXAFS in this geometry.

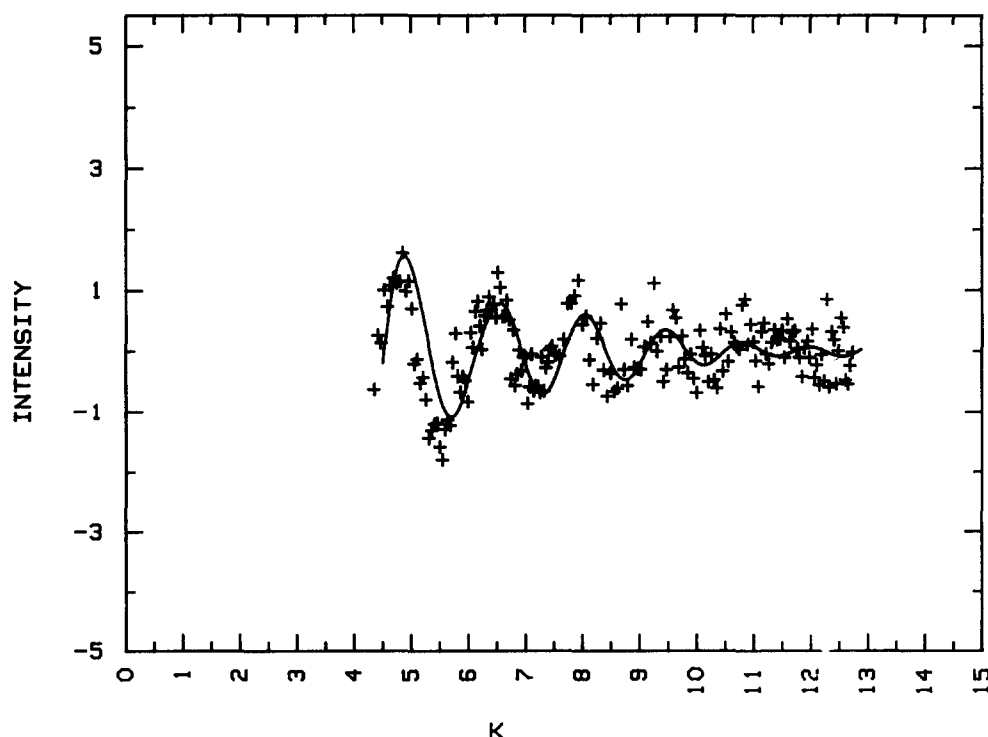


FIG. 7. Same as Fig. 5, fitted to the model of Fig. 8(b).

For the excitation of a  $s$  level electron (the K edge),<sup>20</sup> the EXAFS function  $\chi$  is given by

$$\begin{aligned}\chi(k) &= (\mu - \mu_0)/\mu_0 \\ &= \sum_j 3 \cos^2 \Theta_j N_j F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j} \\ &\quad \times \sin[kr_j + \phi_{ab}(k)]/kr_j^2,\end{aligned}\quad (1)$$

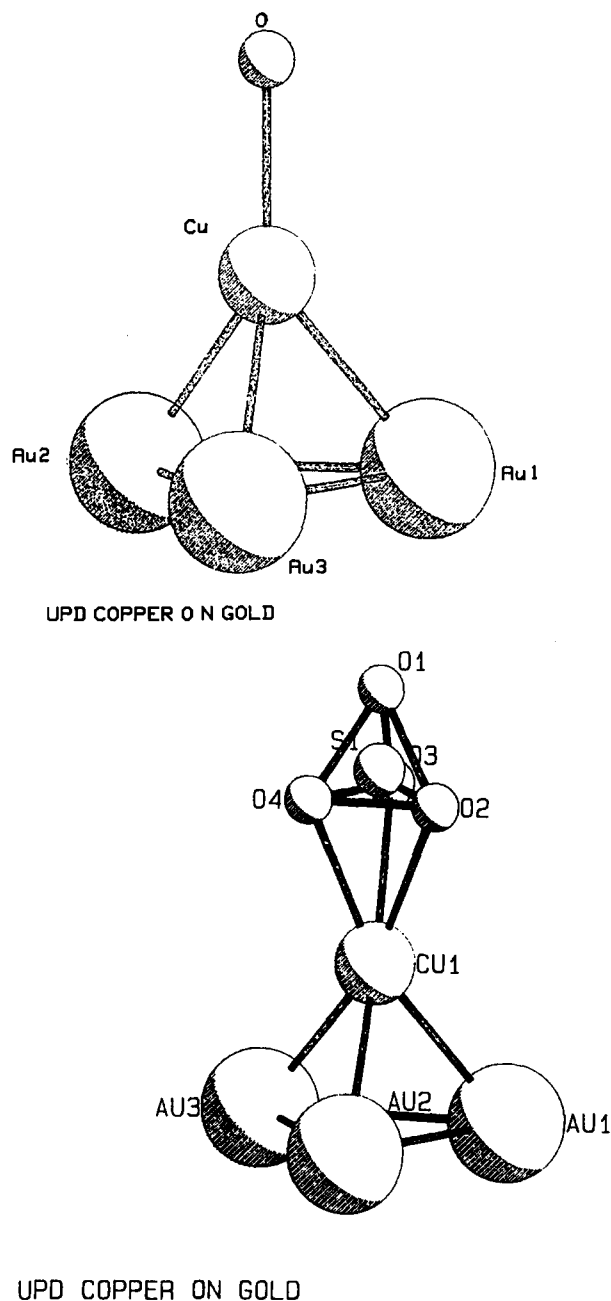
where  $F_j(k)$  is the backscattering amplitude from each of the  $N_j$  neighboring atoms of type  $j$ , with a Debye–Waller-type factor  $\sigma_j$  (to account for the thermal motion of the atom), and  $r_j$  which is the distance to the central atom.  $\Theta_j$  is the angle between the polarization vector of the x rays and the direction of the bond to the  $j$  atom. The parameter  $\lambda_j$  takes into account the inelastic scattering losses of the photoelectron. To a reasonable approximation the phase shift of the backscattered electron is given by

$$\phi_{ab}(k) = \phi_a(k) + \phi_b(k) - \pi, \quad (2)$$

where  $\phi_a(k)$  is the phase shift due to the absorbing atom, and  $\phi_b(k)$  is that of the backscattering atom. When the backscatterer is a heavy element, there is a strong resonance at about  $k = 6 \text{ \AA}^{-1}$ , which corresponds to an absorption peak for the electron [and a dip in the scattering amplitude  $F_j(k)$ ]. This feature is illustrated in Fig. 1, where we display results of Teo and Lee<sup>21</sup> for Au and for its next neighbor element Pt. These strong features produce a very characteristic signature at  $k = 6 \text{ \AA}^{-1}$  in the spectra. Our present analysis of the experimental data is based on this feature.

The spectra obtained for Cu UPD monolayer on Au (111) by signal averaging is shown in Fig. 2. For comparison, we show also the raw spectra of aqueous  $\text{CuSO}_4$  (Fig. 3), and that of a Cu–Au alloy (Fig. 4). The Cu in solution shows a very sharp near edge peak (previously observed in similar  $\text{Cu}^{++}$  solutions<sup>22</sup>, while the EXAFS is strongly damped, which is an indication of large Debye–Waller-type factor, or a loosely bound hydration shell. It should be noted that the x ray absorption edge is 4 eV higher than that for the UPD Cu. For the Cu in the alloy the near edge structure is very different, since it shows a small double peak, and then a number of well defined oscillations in the EXAFS region.

For data analysis, the background was removed by fitting a second degree polynomial to a preselected portion of the spectra. The base line was insensitive to the size of this region, as long as it was of reasonable size ( $> 500 \text{ eV}$ ). The patterns obtained after background removal are shown in Figs. 5, 6, and 7. For analysis we have considered the region between 4 and  $13 \text{ \AA}^{-1}$ . If one assumes that the backscattering is due only to gold, then the best fit is obtained for the unreasonable Cu–Au distance of  $3 \text{ \AA}$ . But more importantly, the feature due to the resonance at  $k = 6 \text{ \AA}^{-1}$  is missing altogether as shown in Fig. 5. If the only backscatterer is oxygen, then the fit is much better, as is shown in Fig. 6. A Cu–O distance of  $2.1\text{--}2.12 \text{ \AA}$  is obtained. Clearly, this model is saying that the Cu is coordinated to solution species (water or sulfate ions) via oxygen atoms only, which is inconsistent with the near edge structure, which corresponds more closely to Cu metal. And indeed the pattern has a series of well defined oscillations, which is different from aqueous copper sulfate. The answer to this puzzle is obtained by as-



UPD COPPER ON GOLD

FIG. 8. (a) Plausible geometrical arrangement of the Cu and O atoms on the Au [111] surface. (b) Plausible geometrical arrangement of the Cu and  $\text{SO}_4^{2-}$  on the Au [111] surface.

suming that the signal comes from reduced copper bound to the gold atoms of the surface with strongly bound oxygen atoms right on top. The fit to this kind of model is shown in Fig. 7. There are a number of models that are consistent with the data. In Fig. 8(a) we have drawn a model that assumes only one oxygen on top of the copper presumably from water. The best fit of the data to this model yields a distance of  $2.05 \text{ \AA}$  for the Cu–O bond and  $2.5 \text{ \AA}$  for the Cu–Au bond. The error in the assignment of the latter distance is necessarily much larger than for the distance to the oxygen. A second plausible model has a sulfate ion sitting on top of the copper as shown in Fig. 8(b). Since in this case the weight of the oxygen backscattering is about three times that of the former model, the oxygen part clearly dominates. In this case the

best fit corresponds to a distance of 2.08 Å, for the same Cu–Au arrangement. We must insist, however, that these may not be the only models consistent with the data.

A distance of 2.5 Å for the Cu–Au bond is not too different from that reported by Palmberg and Rodin<sup>23</sup> for the distance between copper and gold on an [001] surface (2.56 Å). The Cu–O distance is well within the accepted values for crystalline compounds (which however are Cu<sup>++</sup>)<sup>24</sup> and very close to that reported for solutions.<sup>25</sup>

## CONCLUSIONS

Reliable SEXAFS data were obtained from Cu monolayer present on Au (111) at electrode/electrolyte interface. The data can not be interpreted in terms of backscattering from Au atoms alone. The backscattering from light element such as oxygen must be included to fit the experimental data. A geometrical model of the surface in agreement with SEXAFS data is the one in which Cu and three Au atoms at the metallic surface form an elongated tetrahedron, with O on top of the Cu atom.

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<sup>3</sup>A. Hubbard, *Acc. Chem. Res.* **13**, 177 (1980).

<sup>4</sup>P. N. Ross, *Surf. Sci.* **102**, 463 (1981).

<sup>5</sup>K. Bange, D. E. Grider, T. E. Madey, and J. K. Sass, *Surf. Sci.* **136**, 381 (1984).

<sup>6</sup>M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 173 (1974); *J. Electroanal. Chem.* **65**, 933 (1975).

<sup>7</sup>D. J. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.* **84**, 1 (1977).

<sup>8</sup>S. Pons, *J. Electroanal. Chem.* **150**, 495 (1983).

<sup>9</sup>A. Bewick, *J. Electroanal. Chem.* **150**, 481 (1983).

<sup>10</sup>J. G. Gordon and S. Ernst, *Surf. Sci.* **101**, 499 (1980).

<sup>11</sup>C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 1010 (1981).

<sup>12</sup>R. M. Corn and M. Philpott, *J. Chem. Phys.* **81**, 4138 (1984).

<sup>13</sup>D. E. Sayers, F. W. Lytle, and E. A. Stern, *Adv. X-Ray Anal.* **13**, 248 (1970).

<sup>14</sup>P. Eisenberger and B. M. Kincaid, *Science* **200**, 1441 (1978).

<sup>15</sup>R. G. Shulman, Y. Yafet, P. Eisenberger, and W. E. Blumberg, *Proc. Natl. Acad. Sci. U.S.A.* **73**, 1384 (1976).

<sup>16</sup>(a) M. E. Kordes and R. W. Hoffman, *Nucl. Instrum. Methods Phys. Res.* **222**, 347 (1984); (b) L. Bosio, R. Cortes, and M. Froment in *EXAFS and Near Edge Structure*, edited by K. Hodgson, B. Hedman, and J. E. Penner-Hahn (Springer, Berlin, 1984).

<sup>17</sup>K. Reichelt and H. O. Lutz, *J. Cryst. Growth* **10**, 103 (1971).

<sup>18</sup>E. A. Stern and S. M. Heald, *Rev. Sci. Instrum.* **50**, 1579 (1979); S. M. Heald, E. Keller, and E. A. Stern, *Phys. Lett. A* **103**, 155 (1984).

<sup>19</sup>B. Lairson, T. N. Rodin, and W. Ho, *Solid State Commun.* **55**, 925 (1985).

<sup>20</sup>P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, *Rev. Mod. Phys.* **53**, 769 (1981).

<sup>21</sup>B. K. Teo and P. A. Lee, *J. Am. Chem. Soc.* **101**, 2815 (1979).

<sup>22</sup>P. Eisenberger and B. M. Kincaid, *Chem. Phys. Lett.* **36**, 134 (1975); R. H. Sandstrom and F. H. Lytle, *Annu. Rev. Phys. Chem.* **30**, 215 (1979); P. Lagarde, A. Fontaine, D. Raoux, A. Sadoc, and P. Migliardo, *J. Chem. Phys.* **72**, 3061 (1980).

<sup>23</sup>P. W. Palmberg and T. N. Rodin, *J. Chem. Phys.* **49**, 134 (1968); J. E. Muir and R. W. Vook, *Ann. Proc. Electron Microsc. Soc. (1974)*, as cited by G. Somorjai, *Chemistry in Two-Dimensional Surfaces* (Cornell University, Ithaca, N. Y., 1981).

<sup>24</sup>L. Pauling, *The Nature of the Chemical Bond* (Cornell University, Ithaca, N. Y., 1960); O. Kenard *et al.*, *Molecular Structure and Dimensions* (Crystallographic Data Center, Cambridge, 1965); G. M. Brown and R. Chidambaram, *Acta Crystallogr. Sect. B* **29**, 2393 (1973), **25**, 676 (1969).

<sup>25</sup>G. W. Neilson, *J. Phys. C* **15**, L233 (1982); Y. Marcus, *J. Solid Chem.* **12**, 271 (1983).

<sup>1</sup>G. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell University, Ithaca, NY, 1981).

<sup>2</sup>E. Yeager, *J. Electroanal. Chem.* **128**, 1600 (1981).