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THE CHEMISORPTION OF OXYGEN, WATER, AND SELECTED HYDROCARBONS ON THE (111) AND STEPPED GOLD SURFACES

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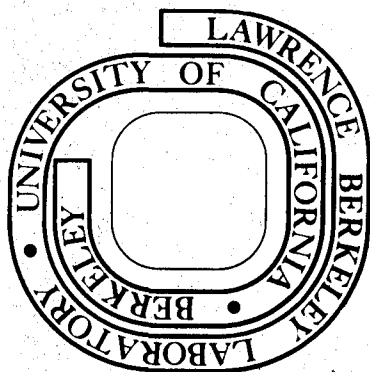
M. A. Chesters and G. A. Somorjai

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THE CHEMISORPTION OF OXYGEN, WATER,  
AND SELECTED HYDROCARBONS ON THE (111) AND  
STEPPED GOLD SURFACES

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Abstract

The dissociative chemisorption of oxygen and water is reported on both (111) and  $[6(111) \times (100)]$  crystal faces of gold. The oxide formation becomes rapid above  $500^{\circ}\text{C}$  at pressures of about  $10^{-6}$  torr. The resulting gold oxide is bound strongly. It is similar in structure to the corresponding sulphide and is stable on both surfaces to  $800^{\circ}\text{C}$  in vacuum.

Ethylene, cyclohexane, n-heptane, benzene did not chemisorb on gold under low pressure conditions on either the (111) or on the stepped gold surface while naphthalene exhibited dissociative chemisorption on both types of surfaces. Hydrocarbon fragments are bound strongly to the gold surface but the activation energy for dissociative adsorption of light hydrocarbon molecules appears to be high.

Introduction

Gold is one of the least active metals in chemisorption; none of the common adsorbates, including oxygen, have been found to chemisorb at room temperature. Early work by Trapnell<sup>1</sup>, on polycrystalline gold films, showed that reversible molecular

adsorption of  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  etc. occurred with a low heat of adsorption ( $10\text{-}20 \text{ kcal mole}^{-1}$ ) similar to that on copper.

Dissociative adsorption is generally not observed but atomic hydrogen and oxygen will chemisorb, the latter rather strongly.<sup>2</sup>

This work is part of a broad programme aimed at understanding the catalytic properties of platinum and its neighbours in the periodic table. Pure gold is of interest since, although relatively inert, it is one of the few materials known to catalyse skeletal isomerization reactions of hydrocarbons.<sup>3</sup> Also, systems of gold alloyed with more active metals, e.g., Pt, Ir, continue to provide valuable information on mechanisms of metal catalysis.

We have investigated more fully the activity of a low index, Au (111), and a high index, Au(S)- [6(111)x(100)] , gold surface in chemisorption of oxygen and water and of hydrocarbons at room temperature and above. Recent studies on high index (stepped) crystal surfaces of platinum,<sup>4,5,6</sup> copper, and palladium<sup>4,5,6</sup> have shown that dissociative adsorption occurs more readily than on low index planes and the important role of ordered monatomic steps in selective catalysis has been discussed extensively in connection with the isomerization and dehydrocyclization of hydrocarbons on platinum.<sup>7</sup> Since the adsorption of all of these molecules have already been studied on both the Pt (111) and Pt(S)- [6(111)x(100)] crystal faces, direct comparison can be made of the chemisorption characteristics of gold and platinum surfaces of the same atomic surface structure.

### Experimental

The gold crystals were cut to within  $1^\circ$  of the desired orientation and their surfaces polished and etched as described

previously for platinum.<sup>8</sup>

Cleaning was first attempted by oxidation in  $10^{-5}$  torr of oxygen at temperatures up to  $800^{\circ}\text{C}$ . This technique was partially successful in removing carbon but produced a stable oxygen covered surface, as will be discussed below. Calcium was also found to segregate at the gold surface on heating in oxygen. The more conventional technique of ion bombardment was successful in cleaning both gold surfaces.

The Auger spectrum of Figure (1a) shows the clean gold surface produced by several cycles of Argon ion bombardment followed by annealing at  $700^{\circ}\text{C}$ .

The LEED pattern of Figure (2b) shows that the stable form of the Au(S) -  $[6(111) \times (100)]$  surface is one of 6 atom width terraces and one atom depth steps. Similar stable stepped surface structures have been found for high index planes of Pt,<sup>8</sup> Pd,<sup>6</sup> and Cu.<sup>5</sup> The doublet diffraction features are rather diffuse, which suggests that the stepped surface is not very well ordered. Annealing at up to  $800^{\circ}\text{C}$  produced no noticeable improvement or deterioration in this pattern.

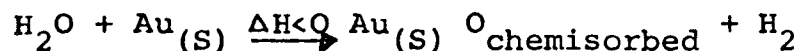
## Results and Discussion

### 1. Oxygen and Water Adsorption

During our attempts to chemically clean the gold surfaces some difficulty was experienced in removing oxygen after oxidation treatment to remove carbon. It was initially thought that the stability of the chemisorbed oxygen might be due to the presence of calcium. The reactivity of gold towards oxygen was investigated further on the clean surfaces on which calcium was no longer detectable.

Treatment in  $6 \times 10^{-7}$  torr of oxygen at increasing temperatures produced no detectable change in the Auger spectrum until, at  $500^{\circ}\text{C}$ , a small oxygen signal appeared after 30 mins exposure. Adsorption was accelerated on heating to  $700^{\circ}\text{C}$  where the Auger spectrum of Figure (4) was obtained after 30 mins at  $6 \times 10^{-7}$  torr. The LEED pattern of the oxidized surface was complex, (Figure 3a&b), but the structure was essentially the same on both the Au(111) and the stepped surfaces of gold. This structure may be analysed in terms of an overlayer with a square unit mesh of dimension  $3.4 \text{ \AA}$ , which exists in three domains rotated at  $30^{\circ}$ , Figure (4). The oxide layer proved to be very stable; heating to  $800^{\circ}\text{C}$  for 12 hrs in vacuum produced no reduction in the oxygen Auger peak height. No difference was detected between the rate of oxidation of the Au(111) and the stepped gold surfaces.

It was also found that the oxide layer could be produced by treatment in water vapour under identical conditions as for oxygen. This is somewhat surprising since it suggests a large binding energy for an oxygen atom on gold assuming that this surface reaction is exothermic, i.e.,



The bulk gold oxide  $\text{Au}_2\text{O}_3$  cannot be formed by reaction of the metal with oxygen gas<sup>9</sup> but is formed by precipitation of  $\text{Au}(\text{OH})_3$  followed by gentle heating. The oxide decomposes above  $140^{\circ}\text{C}$ . However oxygen chemisorbed on gold has been shown to be stable to high temperatures. It would appear that the 'surface oxide' owes its stability to the unique chemistry of the surface - in particular to the readily changing valency of surface atoms.

The structure of the oxide layer is similar to that reported for two dimensional sulphide layers on gold,<sup>10</sup> i.e., a square mesh. By analogy with the interpretation of Oudar et al.<sup>10</sup> a possible structure for the gold 'oxide' layer is given in Figure (5). Taking the oxygen anion diameter as 2.6 Å this puts the gold ion diameter at 2.2 Å which is between that of Au<sup>+</sup> (2.7 Å) and Au<sup>3+</sup> (1.7 Å). // The oxide forming characteristics of the (111) and stepped crystal faced of gold were found to be identical. In contrast, it has been shown that the reactivity of platinum surfaces towards oxygen and other diatomic molecules is very dependent on the presence of steps<sup>11</sup>)

(The Pt(111) surface does not chemisorb oxygen at room temperature or form a surface oxide under the conditions described here for gold but the Pt(S) - [6(111)x(100)] surface does chemisorb oxygen readily at room temperature and above.<sup>11</sup> Subsequent to the experiments on gold, a study of the interaction of water-vapour with platinum surfaces was undertaken. No chemisorption was detected by Auger spectroscopy, either at room temperature or at 800°C, on both the Pt(111) and the Pt(S) - [6(111)x(100)] surfaces. // Thus the chemisorption of oxygen appears to be structure insensitive on gold while very sensitive to surface structure on platinum.

## 2. Hydrocarbon Adsorption

The crystals were exposed to a series of hydrocarbon molecules (ethylene, cyclohexene, n-heptane, benzene and naphthalene) at room temperature and above, and adsorption was monitored using the carbon Auger peak.



The difference in the adsorption characteristics of hydrocarbons on gold surfaces on the one hand and on platinum surfaces on the other is striking. The various light hydrocarbons studies (ethylene, cyclohexene, n-heptane and benzene) chemisorb readily on the Pt(111) surface and form ordered surface structures<sup>12,13,14</sup>. These molecules do not adsorb on the Au(111) crystal face under identical experimental conditions as far as it can be judged by changes that occur in the Auger spectra. Naphthalene forms an ordered (6x6) surface structure on Pt(111)<sup>13</sup> while it forms a disordered layer on adsorption on the gold (111) surface. // The stepped [6(111)x(100)] face of platinum unlike the Pt(111) face reacts readily with all of the adsorbed hydrocarbons<sup>8</sup>. The partially dehydrogenated carbonaceous layers that form as a result of dissociative hydrocarbon chemisorption are largely disordered. In contrast, the stepped gold surface of the same atomic structure remains inert to adsorption of the light hydrocarbon molecules just as the Au(111) crystal face, and the chemisorption behaviour of the two types of gold surfaces are indistinguishable. Naphthalene however, adsorbs on both gold surfaces and the adsorption behaviour (lack of ordering, absence of naphthalene in the mass spectrum on flash desorption) indicates dissociative chemisorption. The hydrocarbon fragments that form are strongly bound.

These results indicate that while chemisorption of hydrocarbons on platinum surfaces requires little or no activation energy, chemisorption on gold has large enough activation energy to prevent adsorption at the studied low pressures ( $\sim 10^{-6}$  torr) and temperatures ( $\leq 550^{\circ}\text{C}$ ). The activation energy for surface

reactions, such as the rupture of C-H and C-C bonds, is greatly reduced at atomic steps on the platinum surface. This effect is not apparent on gold surfaces.

Recent calculations by Kesmodel and Falicov<sup>15</sup> indicate a marked variation of charge density of atoms at a step as compared to atoms in the low index crystal face. This effect is only significant however, if there is a large density of states near the Fermi level. Thus, large variation of charge density at surface irregularities is expected for most transition metals. On the other hand, gold has only a small density of states near the Fermi level and therefore large fluctuations in the charge density along the heterogeneous surface is unlikely. Our observations are certainly in support of this theory.

### Conclusion

It has been known for some time that oxygen atoms chemisorb strongly on gold surfaces and consequently that resistance to molecular oxygen must result from a high activation energy for dissociative adsorption.

We have shown that chemisorption of molecular oxygen on gold is highly exothermic but occurs rapidly only above 500°C; this suggests an activation energy of the order of 30-50 kcal mole<sup>-1</sup>.

The absence of chemisorption of light hydrocarbons under our experimental conditions is perhaps not too surprising. One might expect extensive hydrocarbon chemisorption at much higher pressures, judging from Trapnell's values for heats of adsorption and from the behaviour of naphthalene in this work.

Surface steps do not play a critical role in chemisorption on gold, in contrast with the chemisorption behaviour of stepped

platinum surfaces. The activation energy for dissociative adsorption on gold may well be reduced at a step but the overall value remains high. One may conclude that the existence of steps is most important on surfaces where such activation energies are finite but small. It is precisely these surfaces which make the most versatile heterogeneous catalysts.

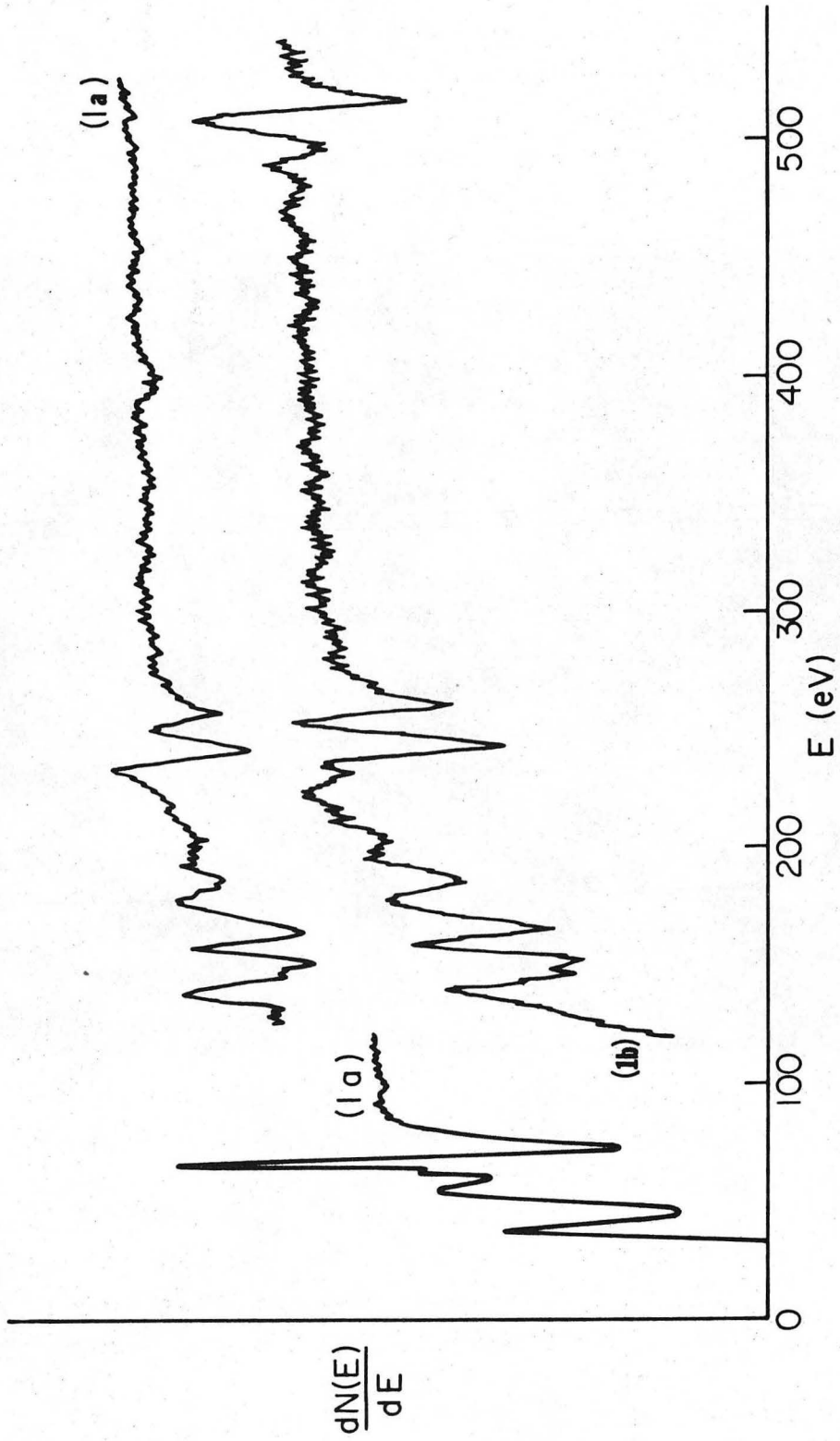
#### Acknowledgements

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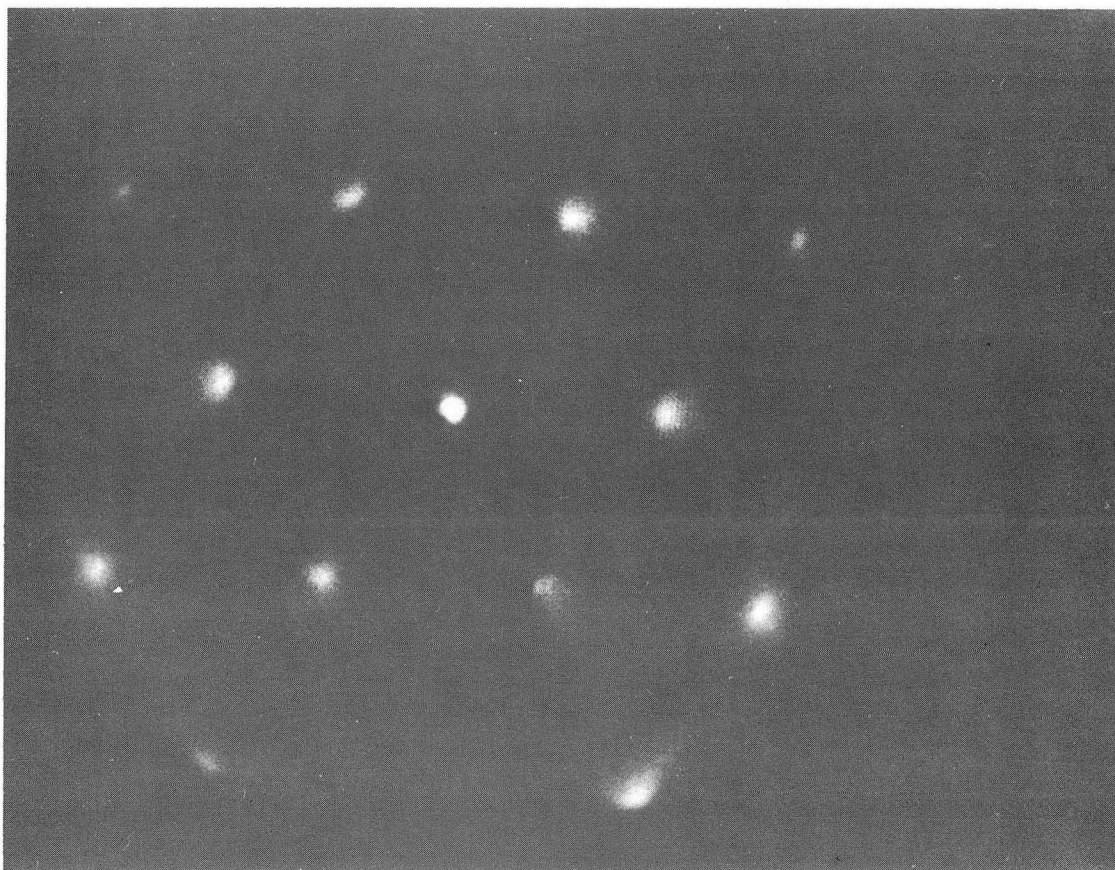
FIGURES

- 1(a) Auger Spectrum of clean gold.
- (b) " " of the gold oxide.
  
- 2(a) Au(111) LEED Pattern.
- (b) Au(S) - [6(111)x(100)] LEED Pattern.
  
3. LEED Patterns of Oxide Surfaces.
  - (a) Au(111) 'oxide'.
  - (b) Au(S) - [6(111)x(100)] 'oxide'.
  
4. Oxide Reciprocal Mesh.
  
5. Possible Oxide Structure.



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Fig. 1

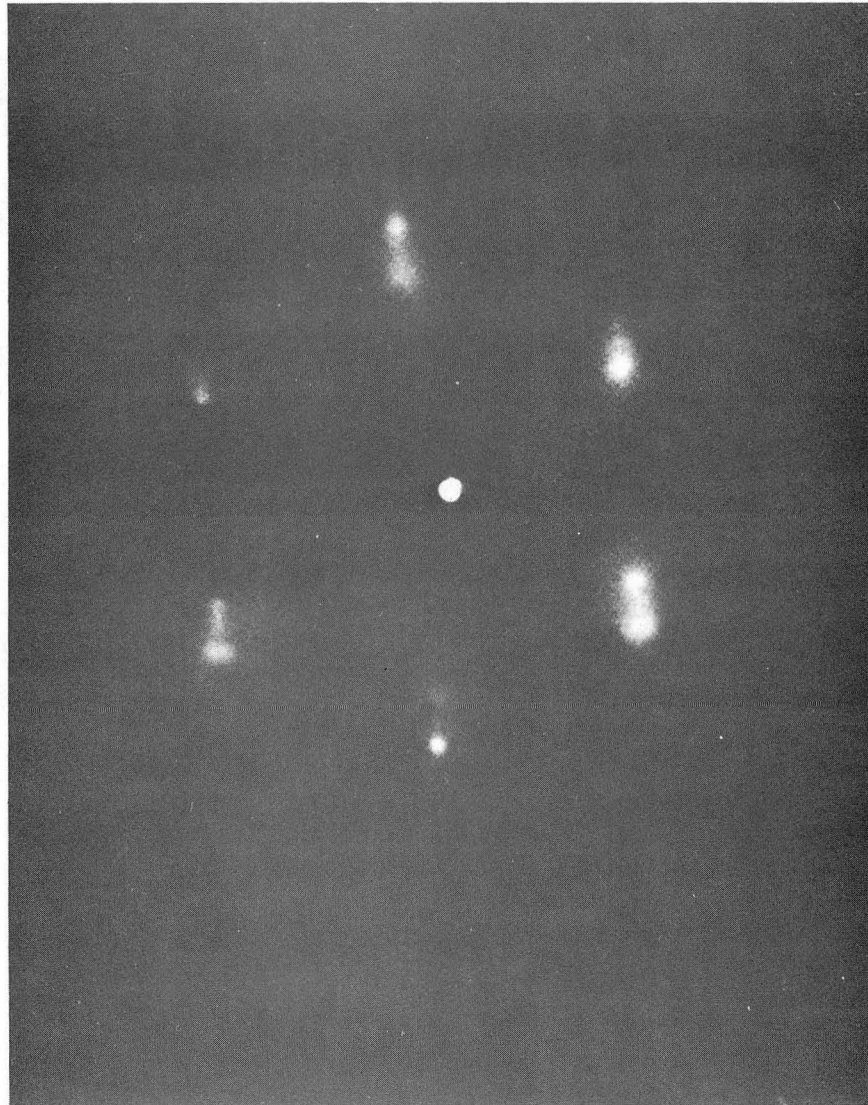


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Fig. 2a

0 0 0 0 4 3 0 2 7 0 3

-13-



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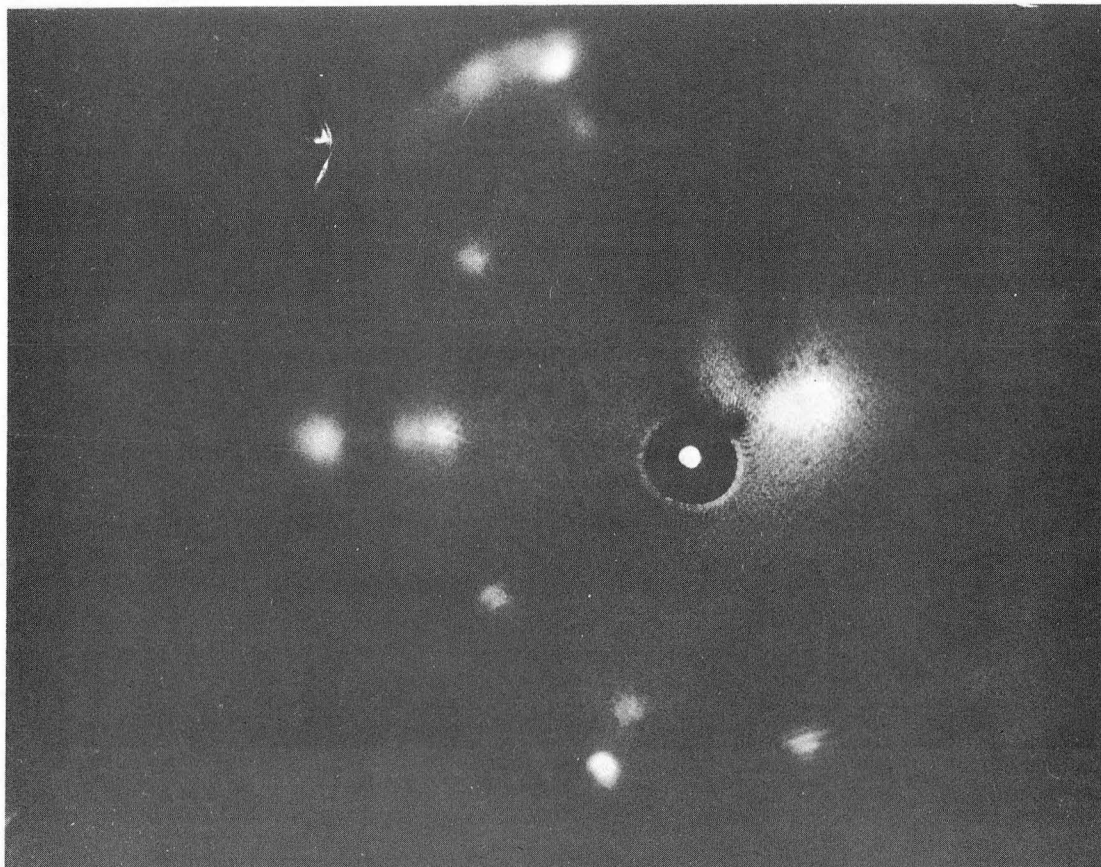
Fig. 2b





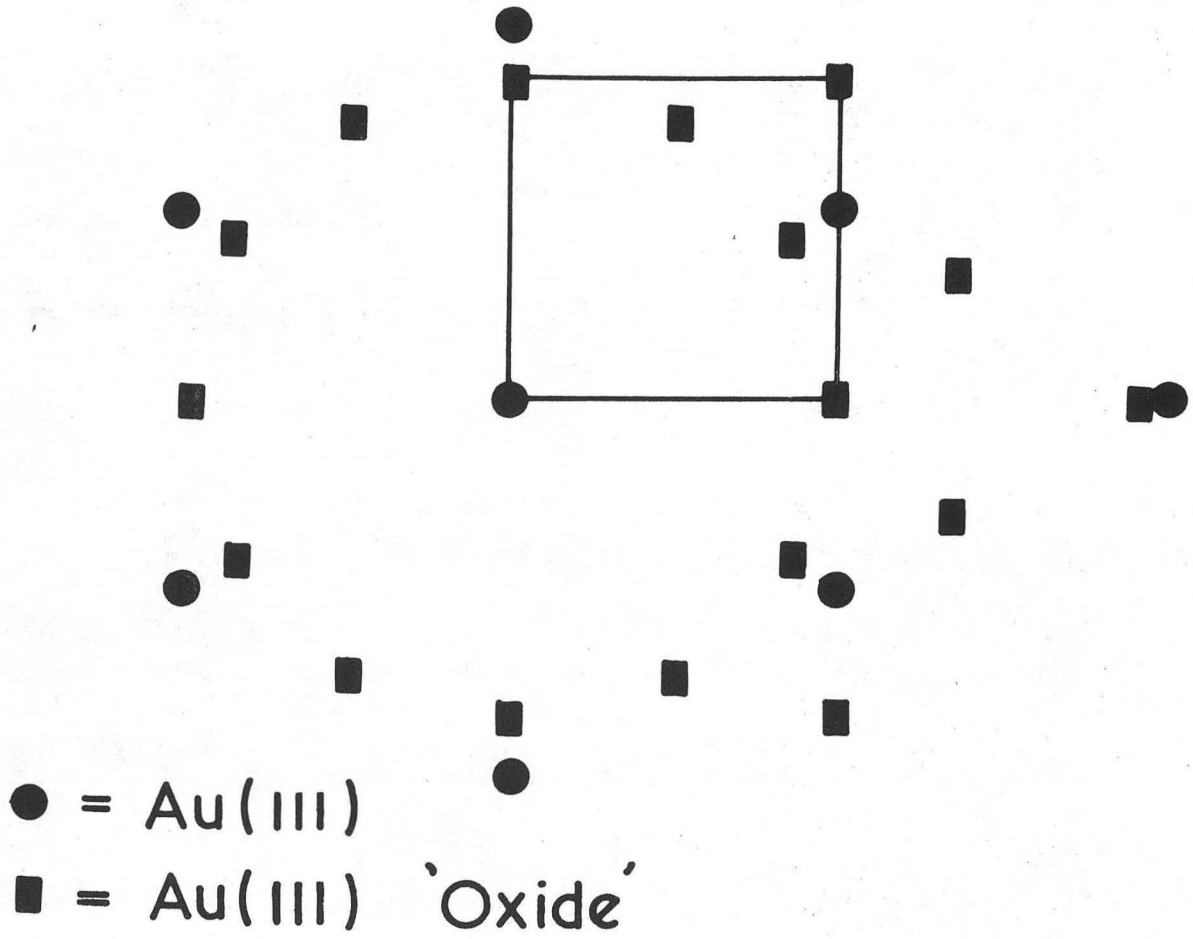
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Fig. 3a



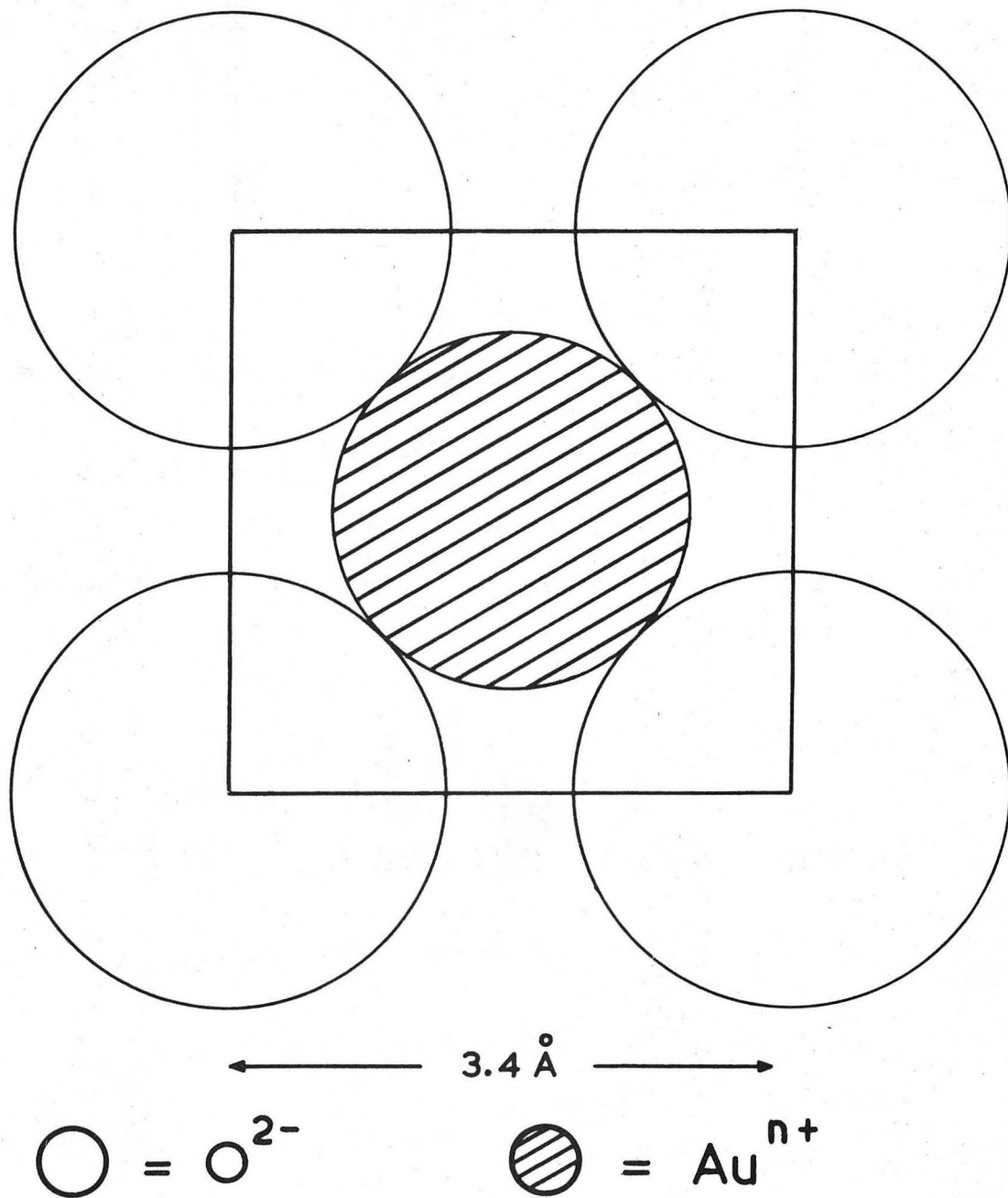
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Fig. 3b



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Fig. 4 'Oxide' reciprocal mesh



XBL 753-505

Fig.5 Possible 'oxide' mesh

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