

A Contribution to the Analysis of the Effects Observed on Heating Gold in Air. II

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The possibility of employing electron diffraction to determine the structure of surface compounds, when little or no subsidiary evidence is available, has been investigated in the particular case of a gold system. The basic framework of the structure has been determined and a model for one of the possible complete structures has been tested. The model is based on the disposition of gas atoms in the tetrahedral holes of the gold lattice.

Introduction

The practicability of employing single-crystal electron-diffraction data for the determination of crystal structures was demonstrated by Cowley, Rees & Spink (1951) in the course of a study on secondary elastic scattering.

The main considerations relevant to the technique were subsequently discussed by Cowley (1953*a*), who also demonstrated its applicability to compounds which crystallize only in the form of a very fine powder (Cowley, 1953*b*). Cowley (1953*c*) further showed that the method has application to problems of hydrogen bonding.

Examples of the use of polycrystalline electron-diffraction data in the determination of crystal structures have been given by Pinsker and Vainshtein (for instance, Vainshtein & Pinsker, 1950). It is the purpose of the present communication to show that at least the main features of the structure of surface compounds, so far inaccessible to other techniques, may be displayed by the use of single-crystal electron-diffraction data.

This particular crystal structure appeared to offer a variety of advantages in a first attempt at this type of work.

First, an authentic surface reaction seems to be involved in that no method of preparation is described in the literature which will yield a specimen of more than a few hundred Ångström units in thickness. Electron-diffraction techniques therefore offer the only means at present available for a direct attack on the structural problem.

Secondly, subsidiary evidence is very meagre. No chemical evidence as to a structural or even an empirical formula is available, the density is unknown, and no information relating to bond angles and bond lengths is available from structures of related systems. It might be considered that the absence of information usually considered a prerequisite in the determination of structures by X-ray methods imposes conditions which are unduly stringent, or even prohibitive, but until very substantial advances are made in a number

of techniques the greater part of this information will not be available in most structural investigations of surface reactions, and this must be accepted in a realistic test.

Thirdly, it was considered that this system might be structurally simpler than most.

Experimental procedure

Specimens were prepared by heating thinned foil and evaporated films in air for periods of the order of 1 hr. at temperatures of approximately 300° C. The various diffraction patterns which were observed are described in Part I (Moodie, 1956), only one of these being analysed in detail.

The camera used throughout was the high-resolution instrument designed by Cowley & Rees (1953). Single-crystal diffraction patterns were obtained with the beam focused both on the specimen and on the plate. The specimen-to-plate distance was varied between 50 cm. and 20 cm. in order to record the maximum number of reflexions. A wave-length of approximately 0.05 Å was employed, patterns being calibrated against zinc oxide.

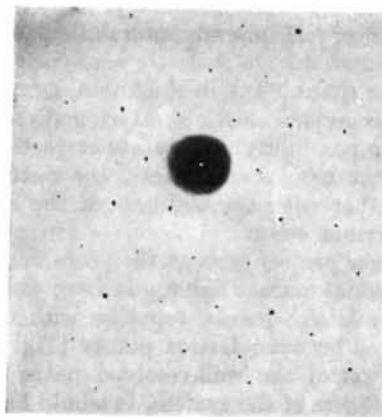


Fig. 1. Single crystal pattern obtained from gold foil heated in air for one hour at 280° C. As reproduced, $\lambda L = 3.34$ Å cm.

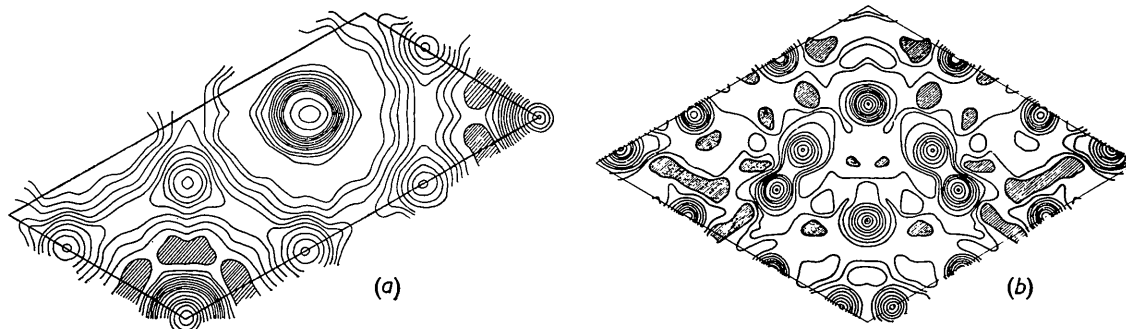


Fig. 2. (a) The $(hk0)$ Patterson projection. (b) The $(hk0)$ Fourier projection.

Analysis of the pattern

Single-crystal patterns in the form of a hexagonal net were obtained (Fig. 1). The basal parameter was found to be $5.32 \text{ \AA} \pm 0.01 \text{ \AA}$, in agreement with Trillat (Trillat & Oketani, 1936). As far as can be judged from the published data, the intensity distribution is also very similar.

Patterns obtained from tilted specimens showed marked variations in the intensities of the various reflexions, indicating the existence of a definite unit cell. Unfortunately, the morphology of the specimen, together with the inherent difficulties associated with the manipulation of crystals of the order of 5μ in linear dimension, made accurate determination of the parameters of the unit cell difficult. By a method described in Part I the unit cell was found to be hexagonal with $c = 11.0 \pm 0.1 \text{ \AA}$.

The intensities of the diffraction spots were estimated by eye. Diffraction patterns obtained at different camera lengths and with different times of exposure were compared with each other and also with a calibrated scale. Here another difficulty in the technique is encountered in that it is very rarely possible to set a small crystal with high accuracy in a predetermined orientation with respect to the beam. It was, however, possible to estimate to a reasonable approximation that the patterns under consideration possessed a sixfold symmetry.

No correction for dynamic interaction was applied, since, as estimated from inelastic scattering, the crystals were less than 200 \AA in thickness. Error can also arise from secondary elastic scattering (Cowley *et al.*, 1951), but no possibility of accurate correction existed in the present case. Fortunately, the nature of the lattice, together with the thinness of the specimens, precluded serious error.

A Patterson projection was therefore computed in the conventional manner, giving strong, well-resolved peaks on the lattice points, together with ill-defined, weaker ridges between lattice points (Fig. 2(a)).

Examination of the well-resolved peaks explained a puzzling feature of the system. It would be expected that the structure would bear a close relationship to that of the gold lattice. Nevertheless, on purely geo-

metrical grounds no such relationship had hitherto been discovered. The Patterson map however, made it clear that in projection the framework of the structure consisted of nine units cells of the gold lattice viewed in the $[111]$ direction and with the positions $(0, 0)$; $(\frac{1}{3}, \frac{2}{3})$; $(\frac{2}{3}, \frac{1}{3})$ vacant (Fig. 3), the geometric relationship being masked by a 4% increase in cell dimension.

Since the system might be expected to be particularly simple, it had been hoped that when the framework of the structure had been definitely established it would be a straightforward matter to fit a model to it. The first attempts were not, however, successful, being based on the more obvious methods of stacking spheres. The lowest value for the discrepancy factor obtained from any of these configurations was 0.35.

Image-seeking methods were therefore used to define approximately the possible scattering areas. It was assumed that the scattering was due to gold atoms displaced from their equilibrium positions, and on this basis a series of models was tested by the usual Fourier methods.

Since the positions of the displaced atoms are largely determined by a limited number of weak reflexions, the intensities of which are difficult to estimate with accuracy, the results of this part of the work are somewhat tentative. Nevertheless the configuration of Fig. 3 gave a discrepancy factor of 0.26. The calculated

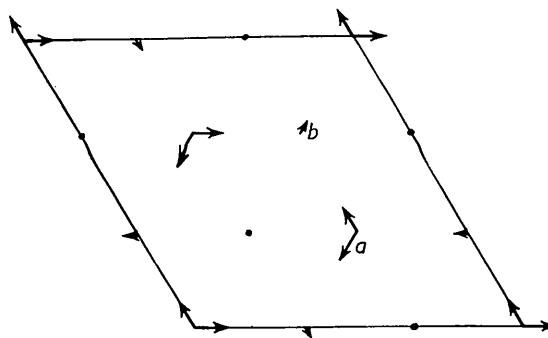


Fig. 3. Final atomic arrangement showing relationship to the gold lattice. $a = 0.09$. $b = 0.02$. a and b are the displacements of the gold atoms from their normal positions in fractions of the unit-cell edge.

and observed structure amplitudes are listed in Table 1. It will be noted that three of the atoms in the main framework have been shifted slightly.

Table 1

hk	F_o	F_c	hk	F_o	F_c
10	50	24	22	63	50
20	25	39	32	20	7
30	100	120	42	17	22
40	18	20	52	28	44
50	15	12			
60	35	26	33	50	47
			43	14	12
11	40	34	53	14	11
21	35	36	63	14	21
31	29	38			
41	39	47	44	28	38
51	14	12	54	10	7
61	10	11			
71	17	14	55	17	26

The Fourier projection calculated on the basis of this model is shown in Fig. 2(b). Series-termination effects are evident, but, in view of the limited accuracy of the data available, it was not considered realistic to attempt correction.

Discussion of the structure

The Fourier map (Fig. 2(b)) is interpreted as the projection of a four-layer structure with stacking AB_1CB_2 , the layers A and C forming the main framework, while the main displacements occur in layers B_1 and B_2 . Interest centres on the agency responsible for these displacements. There would appear to be three possibilities: that some unsuspected impurity is present, that this structure is an intrinsic property of gold under certain conditions of growth, or that gas has diffused into the lattice.

The various patterns observed when copper is present in traces have been analysed in some detail in Part I, and there can be little doubt that the pattern is not due to this most common impurity. The various experiments performed by Trillat and his collaborators had already left little doubt on this point (Trillat & Oketani, 1937*a, b*). Of the remaining likely impurities, mercury might be expected to be the most difficult to detect. Aylmer, Finch & Fordham (1936) have treated this point in some detail. The similarity of the scattering powers of the two elements, together with the multiplicity of the amalgam structures and the tendency for mercury to concentrate in thin films under heat, make it difficult to eliminate this possibility completely. However, in the present series of experiments, as well as in those of Trillat, the concentration of mercury must have been extremely low, even for this type of work.

Finch has suggested that the phenomenon might arise from the intrusion of gas into the lattice (Finch, Quarrell & Wilman, 1935). Trillat prepared samples

in vacuo and hence concluded that the pattern represented a stage of crystal growth. In view of the small quantities involved, however, and the pressures attained, some doubt must attach to this conclusion. Further, while the structure deduced does not appear to be directly related to any of the known defects, Dr A. L. G. Rees has pointed out that a simple interpretation is possible on the basis of an interstitial model. Thus gas atoms lying below the gold atom $(0, \frac{2}{3})$ and above the gold atom $(\frac{2}{3}, 0)$ would tend to give the displacements observed. Further, there is ample space for either an oxygen or a nitrogen atom exhibiting its covalent radius to fit into the tetrahedral hole.

Behaviour of this type has been observed in investigations on iron-nitrogen (Jack, 1950) and related structures. This point has been discussed by Pauling (1945) and also by Rees (1953).

Thus, while it is probable that only a micro-analysis *in situ*, for which no technique has yet been devised, would establish the point beyond all doubt, it is concluded that the evidence obtained from the structure indicates the presence of a gas-metal phase of composition Au_6X .

Finally it might be remarked that many variations on the proposed structure, modifying the intensity distribution only slightly, are possible, and it is considered that one of these has been observed. It is hoped to attempt an analysis of this at a later date.

It is a pleasure to acknowledge the continuous help, criticism and encouragement of Dr A. L. G. Rees and Dr J. M. Cowley, who initiated the positive steps in this work.

References

- AYLMER, A. E., FINCH, G. I. & FORDHAM, S. (1936). *Trans. Faraday Soc.* **32**, 864.
 COWLEY, J. M. (1953*a*). *Acta Cryst.* **6**, 516.
 COWLEY, J. M. (1953*b*). *Acta Cryst.* **6**, 846.
 COWLEY, J. M. (1953*c*). *Acta Cryst.* **6**, 522.
 COWLEY, J. M. & REES, A. L. G. (1953). *J. Sci. Instrum.* **30**, 33.
 COWLEY, J. M., REES, A. L. G. & SPINK, J. A. (1951). *Proc. Phys. Soc. A*, **64**, 609.
 FINCH, G. I., QUARRELL, A. G. & WILMAN, H. (1935). *Trans. Faraday Soc.* **31**, 1051.
 JACK, K. H. (1950). *Acta Cryst.* **3**, 392.
 MOODIE, A. F. (1956). *Acta Cryst.* **9**, 995.
 PAULING, L. (1945). *The Nature of the Chemical Bond*, 2nd ed., chap. 2. Ithaca: Cornell University Press.
 REES, A. L. G. (1953). *J. Proc. Roy. Soc. N. S. W.* **86**, 38.
 TRILLAT, J. J. & OKETANI, S. (1936). *C. R. Acad. Sci., Paris*, **203**, 1064.
 TRILLAT, J. J. & OKETANI, S. (1937*a*). *J. Phys. Radium*, **8**, 59.
 TRILLAT, J. J. & OKETANI, S. (1937*b*). *J. Phys. Radium*, **8**, 93.
 VAINSHTEIN, B. K. & PINSKER, Z. G. (1950). *J. Phys. Chem. U.S.S.R.* **24**, 432.