

Superstructures on Spherical Gold Crystals

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Spherically shaped crystals of gold were grown by solidification of a drop of melt in UHV. Their surfaces were investigated in situ by RHEED. The superstructures (001) (5×20) and (110) (1×2) were observed again. Further superstructures were found: on (001) vicinal planes, (227) (1×1), (111) (23×1) and $(551)c(1 \times 1)$. Several of the new structures are related to structures already known.

1. Introduction

Many fcc metals (Cu, Ag, Ni, Al etc.) have shown nets of surface atoms corresponding to the lattice of the bulk. On gold [1, 2], Pt and Ir deviations from these bulk nets were observed mostly on (001) planes by LEED and also by RHEED. Other rearrangements at the surface were found earlier on Si and Ge [3]. On gold the so called (001) (5×1) (later on and better (5×20)) structure was attributed to the clean gold [2], or it was supposed to be stabilized by impurities [1, 4]. Later investigations did not solve the problem completely, but at least two hexagonal nets of Au atoms were supposed with a mutual twist of 90° . Anomalous structures were also observed on other crystallographic surfaces of gold. Double diffraction between surface and bulk complicates the discussion. Most of these experiments were performed after cleaning the surface by ion bombardement and annealing or using epitactically grown thin films.

For our studies, gold crystals were grown by solidification of a drop of melt in a gradient of temperature [5]. Such crystals have surface areas and vicinal planes of all crystallographic orientations which can be investigated by scanning a single specimen.

2. Preparation and Surface Shape

Gold from three sources was used: Heraeus, Hanau "Au 5N4, 4ppm of impurities were detected by analysis". Johnson, Matthey, London "Au specpure, 10 ppm impurities". IMANCO (Metals Research, England) "Au 6N".

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For each specimen a charge of gold sufficient for a crystal with a diameter of 4 mm was etched in boiling aqua regia and rinsed in water. An electrolytic etch in KCN gave similar results. A UHV RHEED apparatus (Vacuum Generators, base pressure 1×10^{-10} torr) was used for crystal growth. The crystal support, formed by a sheet of spectral graphite (Ringsdorff RW III) in contact with an other one, was clamped on the specimen manipulator. The gold was melted by heating the graphite with stabilized direct current. The electric contact provides the main source of heat and in consequence a gradient of temperature on the graphite builds up. Therefore solidification starts from one point and advances in one direction if the heating current is lowered. The phase boundary between melted and solid gold can be clearly seen by the difference in thermal luminosity which is a consequence of the discontinuity of the optical constants of liquid and solid gold [6]. Solidification occurred mostly at 10^{-9} torr or before baking out at 10^{-7} torr. Often several cycles of melting and solidification were performed. First experiments were done in an older apparatus for RHEED at 10^{-5} torr. The results did not deviate systematically from those received in UHV.

The gold crystals, having nearly the shape of the sitting drop of melt, have nearly flat areas around their (111) and (001) poles as a consequence of minima of the free surface energy [7]. In contrast to copper [8], the gold flats are wavy and surrounded by terraces. Figure 1, photographed with a special technique supplying multiple concentric rings of illuminating light [9], shows a spherical gold crystal with four flat areas. This topography and the behaviour during solidification was characteristic for Au from Heraeus. The other two sorts of gold did not show smooth but zigzag shaped boundaries during solidification. The crystals from these



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Fig. 1. Micrograph of a spherical gold crystal with (111) areas (larger systems) and (001) areas (smaller) systems [9].

samples had on their whole surface additional grooves parallel to the direction of solidification. This behaviour may be caused by unknown impurities. Experiments with slightly alloyed copper crystals have shown similar effects, and earlier experiments with gold have demonstrated the extreme sensitivity of Au surfaces to impurities. When Au from IMANCO was melted, the quadrupole gas analyzer showed four Zn isotopes in the same peak ratios as known for natural zinc; these signals decreased if melting was continued. Therefore Au from Heraeus was used mostly in the following experiments.

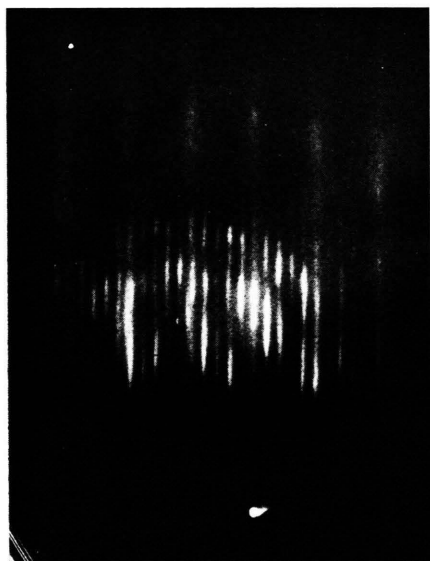


Fig. 2. RHEED diagram of Au(001) (5×20). Primary beam nearly parallel Au[110].

Diffraction was performed with 40 kV electrons immediately after the crystals had cooled down from solidification, or later. The finite diameter (0.3 mm) of the primary electron beam averages about $\pm 4^\circ$ with respect to the crystallographic orientation of the investigated surface on spherical crystals with diameters of 4 mm.

3. Au(001) (5×20)

From Au(001) diffraction patterns were observed as shown in Figure 2. Near the primary beam Laue patterns from the bulk were as weak on (001) as the Kikuchi patterns. If the primary beam was parallel to [100], patterns consistent with Figure 2 were received. Patterns taken from different crystals were not perfectly congruent as to length and intensity; these variations occurred also if the direction of incidence was changed slightly, which influenced the situation for double diffraction. Au from Johnson and Matthey and also from IMANCO often failed to show all the patterns of Figure 2. Figure 3 shows a sketched diffraction diagram corresponding to Figure 2. It is nearly consistent with other results and with the diagram of Au(001) sketched by Rhead [10] on the basis of LEED observations with highest resolution. So our observation made on crystals solidified from a drop of melt confirm the model of the Au(001) (5×20) structure: On Au(001) there are two nearly hexagonal nets of scattering centers. They are mutually perpendicular in order to satisfy the fourfold symmetry of (001). The hexagonal net is compressed by 4.4% relative to the surface of the bulk. In some details there are differences from the

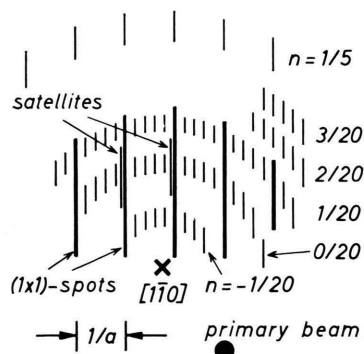


Fig. 3. Sketch for the diagram in Fig. 2 for Au(001) (5×20).

results with LEED. For instance some groups of spots may not lie exactly on Laue circles as required by the mentioned structure. The $(001)(5 \times 20)$ structure was the most stable one: There was no evidence that this structure could depend on impurities. Between but outside the poles (001) and (110) the vicinal planes on the $[100]$ zone circle did not show anomalous structures but only patterns from the bulk lattice.

4. Vicinal Planes Near (001) on the $[1\bar{1}0]$ Zone Circle

Vicinals near $\text{Au}(001)$ have never been investigated before. If an electron beam nearly parallel to $[100]$ did meet places on the spherical crystal in angular distances of a few degrees from (001) , the diffraction diagram did not show all details of the (5×20) structure but only of the (5×1) one. Only one net of both (5×1) nets could be observed, namely that with the period of five perpendicular to the ledges parallel to $[1\bar{1}0]$ which bound the (001) terraces forming the vicinal planes. The spots indicating the period of five got more blurred with increasing angular distance from (001) . If the primary beam was nearly parallel to $[100]$, the spots related to the period of five lay on different Laue circles; they joined and formed slightly curved streaks between the spots from the bulk (see Chapter 9). In this way planes perpendicular to the ledges are indicated in the reciprocal lattice corresponding to the period of one along the ledges parallel to $[1\bar{1}0]$. In this direction the fcc lattice has the highest density of atoms. The period of five becomes inefficient for producing sharp diffraction spots, because the terrace planes in higher angular distance from (001) become too narrow to contain sufficient periods of five.

If the primary beam was parallel to $[1\bar{1}0]$, diagrams like Fig. 4 were observed. Two systems of Laue circles are interpreted as resulting from two rows of scattering centers. These lie in the (001) terraces as the $[1\bar{1}0]$ direction does. The rows form angles of $\varepsilon = \pm(4.0 \pm 0.2)^\circ$ with $[1\bar{1}0]$. The radii of the Laue circles indicate $c = (41 \pm 2) \text{ \AA}$ as the distance between the scattering centers in these rows. These angles and this period did not change systematically if surface planes under investigation changed their angular distances from (001) up to 22° . On different crystals these spots on Laue circles have shown a high contrast if the

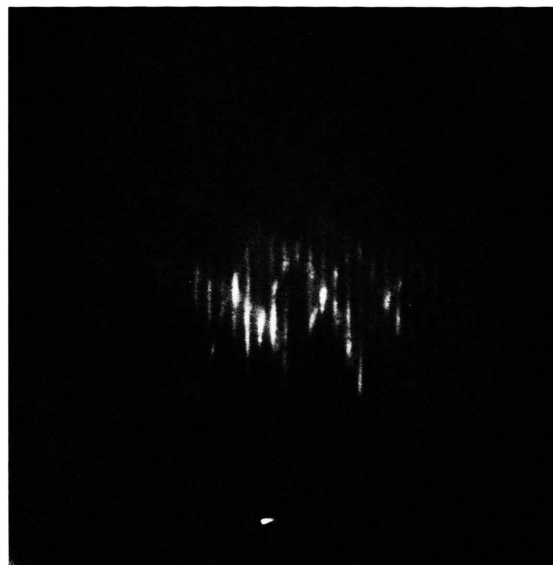


Fig. 4. RHEED diagram of a vicinal plane near to $\text{Au}(001)$. Primary beam nearly parallel to $\text{Au}[1\bar{1}0]$.

(5×20) spots from (001) and also the $(227)(1 \times 1)$ structure (see Chapt. 5) were shown clearly.

Whilst the position of the Laue circles was independent of the vicinal, the individual spots on the circles depend on the angular distance of the vicinal from (001) . At small angles most of the spots were near to the (5×1) spots. With increasing angle more spots appeared, became blurred and joined. That may be influenced by the finite diameter of the primary beam which averages the structures on different vicinals on the spherical crystal. Therefore the distances between these spots on Laue circles cannot be used for structure analysis.

The measured distance of $c \approx 41 \text{ \AA}$ between the scattering centers on the mentioned rows looks like the 14 fold of the distance $a = 2.88 \text{ \AA}$ between Au atoms in the bulk. This multiple of 14 may be compared with the multiple of 20 in the (5×20) structure. The observed angle $\varepsilon = 4^\circ$ does not show such a relationship.

In the following section we try to give a model for the net of scattering centers on the (001) terraces forming the (001) vicinals. We start from our observations in the near angular neighbourhood of (001) where the (5×1) structure was observed completely. We assume that a slightly modified structure is present also on the farther vicinals. This structure is a hexagonal net with a period of

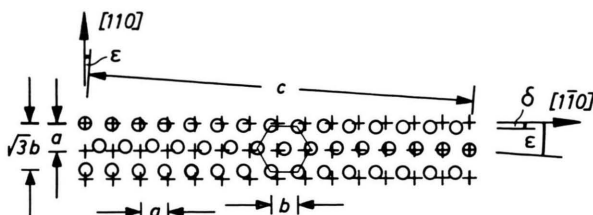


Fig. 5. One of the two hexagonal nets of centers (circles) on a (001) terrace of a vicinal plane near to (001). Crosses: Au atoms corresponding to the bulk lattice. The coincidences of centers with Au atoms are related to the supernets observed by RHEED.

$b = 0.964a = 2.78 \text{ \AA}$. Two hexagonal nets are presented. They have a twist towards the $[1\bar{1}0]$ direction of $\delta \approx \pm 0.7^\circ$. One hexagonal net is depicted in Figure 5. Two adjacent rows in this net cut two adjacent Au $[1\bar{1}0]$ atom rows. Areas of coincidence are formed — as a moiré — with distances of 40.5 \AA . These areas represent the observed scattering centers. They lie on rows with a twist of $\varepsilon = 4^\circ$ towards the bulk $[1\bar{1}0]$ direction. The net of centers is compressed by 3.6% relative to the surface net of the bulk. This compression is a bit smaller than the compression on (001).

5. Au(227) (1×1)

On places 22° from (001) a new diffraction diagram appeared (Figure 6). No other author has described a similar observation. Sometimes the

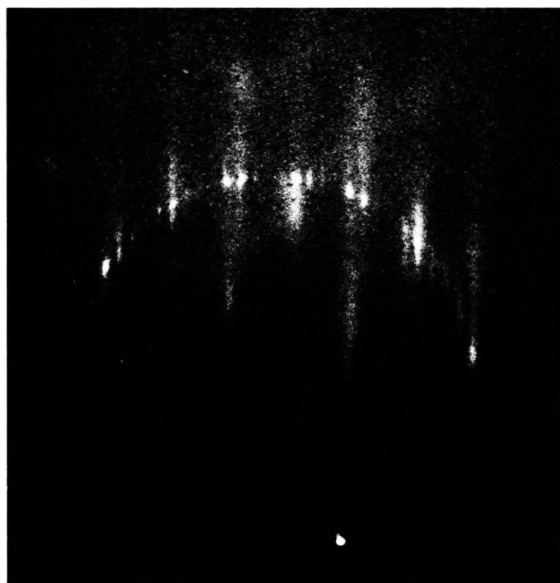


Fig. 6. RHEED diagram of Au(227)(1×1). Primary beam parallel $[1\bar{1}0]$.

same spherical crystal has shown this structure from one (227) pole but without any reason not from another one. The distances between the spots on the zero Laue circle indicate diffraction centers with distance of $(21.6 \pm 0.3) \text{ \AA}$ in the direction perpendicular to $[1\bar{1}0]$, that means in $[77\bar{4}]$. Diagrams with other directions of the primary beam show only the bulk period of $a = 2.88 \text{ \AA}$ in $[1\bar{1}0]$. The bulk Au(227) surface has distances of 2.88 \AA in $[1\bar{1}0]$ atom rows and $\sqrt{57}a = 21.7 \text{ \AA}$ between two $[1\bar{1}0]$ rows.

The Au(227)(1×1) surface structure is congruent with the net of that surface of the bulk crystal. In spite of that, the reported structure must be regarded as a speciality because it has very long rods in the reciprocal lattice, therefore it is related to a twodimensional net of diffraction centers. Other surfaces on spherical crystals also of copper and silver produce diffraction spots related to the threedimensional crystal, because their rods are elongated only a little corresponding to the finite depth the diffracted electrons come from.

6. Au(111) (23×1)

On (111) a structure deviating from the bulk (Figure 7) was observed in high contrast more frequently on crystals solidified from the melt without baking out the apparatus. From patterns like in Fig. 7 — consistent with other ones with the primary beam parallel to $\langle 110 \rangle$ — the reciprocal lattice of Fig. 8 was derived. Satellites exist only near the spots of the bulk. They form rows along the $\langle 110 \rangle$ directions indicating that the supernet of scattering centers is distorted against the bulk

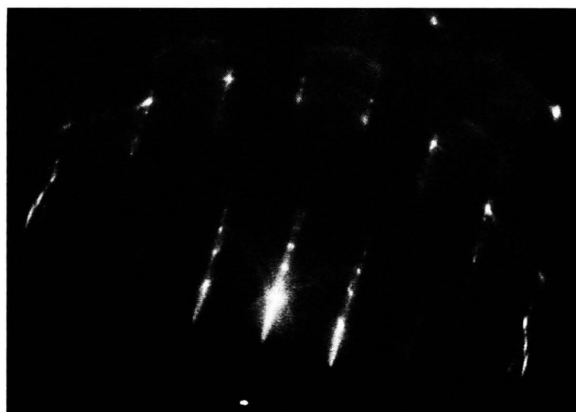


Fig. 7. RHEED diagram of Au(111)(23×1). Primary beam parallel $[1\bar{1}2]$.

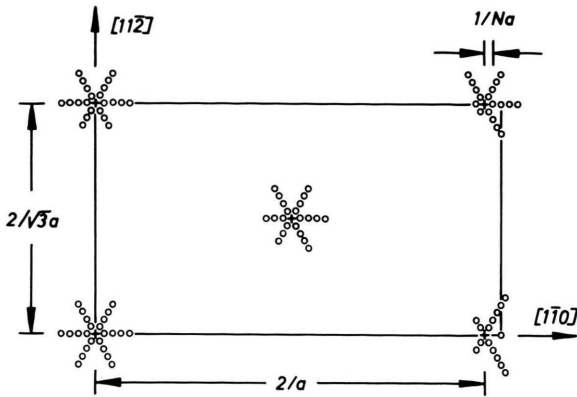


Fig. 8. (111) base of the reciprocal lattice for three supernets of Au(111)(23 × 1) extracted from patterns like in Figure 7. Crosses: foot points of rods corresponding to the ideal surface of bulk gold. Circles: the same corresponding to the beat frequencies.

net only in these directions and not in the $\langle 112 \rangle$ ones. Therefore the supernet cannot have a sixfold symmetry but only a twofold one. Three equivalent supernets with a mutual twist of 60° , satisfying the threefold symmetry of Au(111), must exist. The distances of spots in the reciprocal lattice for one of these supernets correspond to the distances in the bulk only along $[11\bar{2}]$. The distance between satellite spots along $[1\bar{1}0]$ is nearly $1/46$ of the distance between the spots of the bulk net. It is reasonable that the net of scattering centers is centered as the bulk net is a centered one. So the measured distance of $1/46$ can be understood by double diffraction giving $1/23$ as the beat frequency between the reciprocal period for the scattering centers and the reciprocal period for the bulk atoms. This superstructure can be called Au(111)(23 × 1). Along $[1\bar{1}0]$ it is compressed by 4.2% relative to the bulk.

A superstructure on Au(111) was also observed by Perdereau et al. [11] with LEED. It was described as $p(\approx 20 \times \approx 20)R 30^\circ$, i.e. hexagonal, and it was indicated to be compressed by nearly 5%. No other informations were given.

7. Au(110) (1 × 2)

The (110) net of the bulk gold is a primitive rectangular one with atomic distances of $a = 2.88 \text{ \AA}$ parallel to $[1\bar{1}0]$ and $a/\sqrt{2}$ parallel to $[001]$. The Au(110)(1 × 2) supernet has been reported by different authors [12, 13]. It was observed clearly on spherical gold crystals solidified from the melt

under different conditions. In $[1\bar{1}0]$ the distance between diffraction centers is equal to the distance between bulk atoms, in $[001]$ that ratio is 2:1. Several new features were observed:

a) If the primary beam was nearly parallel to $[1\bar{1}0]$, the spots from the supernet were pointlike. They lie on the zero Laue circle. For other directions of the primary beam — especially parallel to $[001]$ — an additional Laue circle is generated by the supernet.

b) With the primary beam parallel to $[001]$ the shape of spots on this Laue circle depended sensitively on the angle of incidence to the crystal surface. The spots from the supernet were pointlike if near spots from the bulk showed maximum intensity. That may indicate double diffraction. It seems possible that the ratio of distances is not exactly 2:1.

c) Few crystals showed a splitting of spots from the supernet if the primary beam was nearly parallel to $[1\bar{1}0]$. That split was measured relative to spot distances from the bulk. The split was

$$1/d = \sqrt{2}/[(17 \pm 1)a].$$

This can be understood assuming the normal Au(110)(1 × 2) structure on (110) terraces building an Au(17, 17, 1) vicinal plane. This vicinale has an angle of tilt $\delta = 2.38^\circ$ with the (110) plane. As shown previously [14], the reciprocal lattice for vicinal planes is given by a product $F_1 \cdot F_2 \cdot F_3$ of three structure amplitudes. F_3 can be sketched as straight rods perpendicular to the vicinal plane. Their distances are reciprocal to the atomic periods in this plane. $F_1 \cdot F_2$ is related to the diffraction from one terrace which builds the vicinale as a relief. $F_1 \cdot F_2$ is sketched in the reciprocal lattice as a sequence of bands standing perpendicular to the terrace. Their distances are given by the atomic period in the terrace. The width of the bands is given by the number of meshes along the width of the terrace. The product $F_1 \cdot F_2 \cdot F_3$ defines a finite length for the rods. Figure 9 depicts the reciprocal lattice derived from this concept. The measured split $1/d = 2\delta/a$ results from this model. As mentioned earlier the diameter of the primary beam averages structures over an area of $\pm 4^\circ$ on the spherical crystal. It is not clear why the superstructure on the Au(17, 17, 1) plane is so prominent.

d) On few crystals of gold from IMANCO a (110)(1 × ≈ 3) structure was observed.

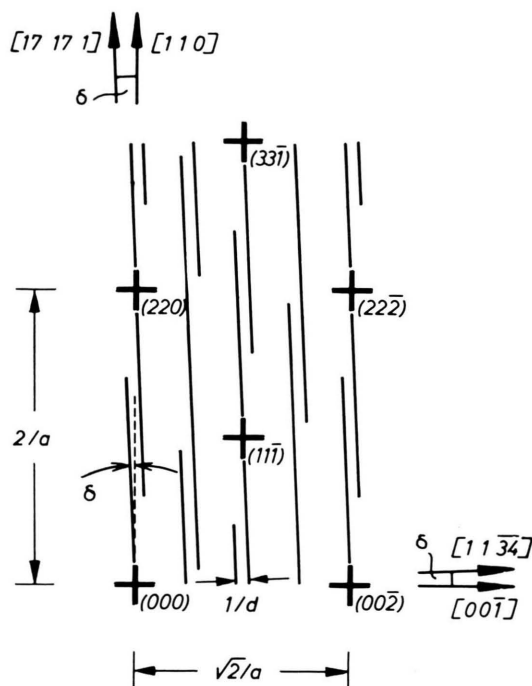


Fig. 9. Reciprocal lattice parallel $(1\bar{1}0)$ for the supernet on the Au(17, 17, 1) vicinal plane containing the $[1, 1, 34]$ direction.

8. Au(551)c(1 × 1)

The (551) pole has an angular distance of 8.0° from (110). Also on this plane a two-dimensional structure which has not been reported before, was observed frequently. Figure 10 depicts a diffraction pattern. Beside the elongated spots from the bulk the zero Laue circle shows spots with distances corresponding to diffraction centers in a two-dimensional net with a period of $\sqrt{51} \cdot a/2$ in the $[1, 1, \bar{1}0]$ direction which is perpendicular to $[1\bar{1}0]$. If the primary beam is tilted with $[1, 1, \bar{1}0]$ as the axis of tilt, the diffraction diagrams scan the rods in the reciprocal lattice. They stand perpendicular to the (551) surface. Diagrams with other directions of the primary beam show the period $a = 2.88 \text{ \AA}$ in $[1\bar{1}0]$. Both periods are equal to periods in the (551) surface net of the bulk. That net is a centered one, but a centering of the supernet cannot be affirmed by the diffraction diagrams.

The (551) plane may be regarded as built by (110)- and (111)-terraces. If the surface is atomically smooth, the width of one (110)-terrace is equal to one period of two in the (110)(1 × 2) structure. But this period of two — if present — does not clearly

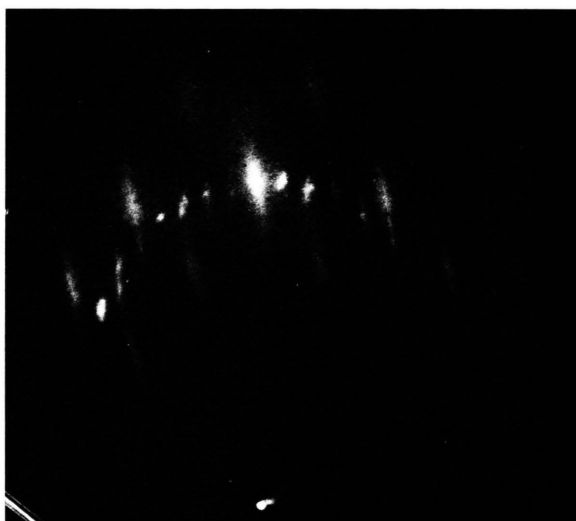


Fig. 10. RHEED diagram of Au(551)c(1 × 1). Primary beam parallel to $[1\bar{1}0]$.

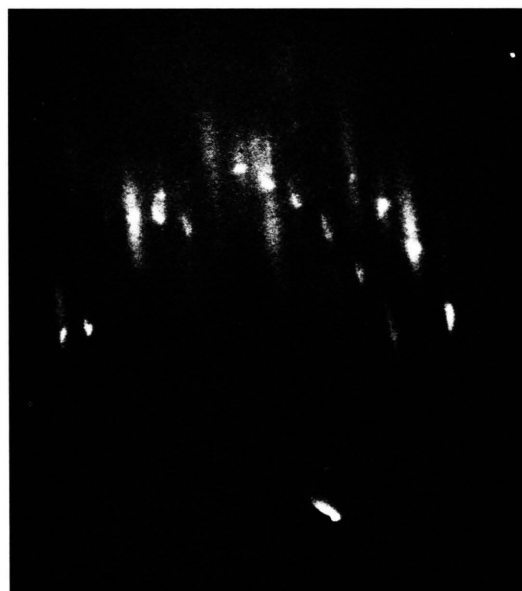


Fig. 11. RHEED diagram of a plane near Au(551) with an unusual supernet. Primary beam parallel to $[1\bar{1}0]$.

influence the observed (551)c(1 × 1) patterns, perhaps because only one period is not sufficient. If a crystal showed a clear diagram from (110)(1 × 2), its diagram from (551)c(1 × 1) was also a very clear one. Few crystals have shown an other diffraction diagram from one (551) surface (Figure 11), its discussion is not yet clear.

9. Other Au(hhl) Surfaces

As mentioned before, on other planes no two-dimensional supernets were found explicitly. But a characteristic feature was observed if poles of type (hhl) were investigated. All these surfaces contain the $[1\bar{1}0]$ direction with the shortest distance $a = 2.88 \text{ \AA}$ between Au atoms. If the primary beam was oblique to $[1\bar{1}0]$, the spots from the bulk lattice were connected by slightly curved lines. As discussed in Chap. 4, this can be understood in the reciprocal lattice by planes perpendicular to $[1\bar{1}0]$. The lines are curves of intersection between these planes and the Ewald sphere. These planes show that the atomic order in $[1\bar{1}0]$ is better than in other directions in the surface, i.e. the order between different atomic rows $[1\bar{1}0]$ is disturbed.

10. Graphite

Diffraction diagrams preferentially from Au(111) and (001) have shown special streaks perpendicular to the surfaces. Their distances correspond to the net of carbon atoms in the basis plane of graphite as observed already on Pt [15]. The distances between these streaks do not change if the azimuth of the primary beam is changed. Therefore the basis planes lie parallel to the Au surfaces. They have no preferential azimuths. Graphite appeared as clearly on Au crystals supported on graphite as supported on tungsten. The streaks of graphite appeared preferentially if the crystals were annealed in residual gases containing carbon arbitrarily. These streaks did not correlate to the diffraction diagrams of most of the supernets, but they anticorrelate probably with the diagrams from Au(111)(23×1) and Au(001)(5×20).

11. Diffraction Experiments at Higher Temperatures

Experimental problems inhibit temperature measurements on the spherical crystals by a thermocouple. Temperatures must be derived from the heating current related to the current for melting and from the colour of thermal radiation. Experiments were performed at 10^{-7} and 10^{-9} torr with crystals showing the supernets clearly. At increasing temperature the diffraction spots from the supernets disappeared into the background in the following sequence: first (111)(23×1) and (227)(1×1), then (551)c(1×1) and (110)(1×2)

at last the mentioned structure on the (001) vicinal planes. The (001)(5×20) structure was the most persistent one. During cooling down after annealing all structures reappeared in the reversed sequence. For (001)(5×20) and (110)(1×2) that influence of temperature was already observed in [1].

12. Influence of the Environment

The clearness of diffraction diagrams from the bulk lattice was satisfying mostly. But diagrams from the supernets were correlated with the regularity of the appearance of the specimen in thermal light during solidification and of its surface relief (Chapt. 2). Gold from Heraeus behaved best together with an etch in aqua regia before melting.

The observed supernets were the same if graphite or tungsten was used as support of an Au crystal.

Controlled by the quadrupole gas analyzer, the chemical composition of the residual gas could be influenced by different programs of pumping together with an artificial leak. 17 crystals solidified at 10^{-7} torr in different residual atmospheres (H_2 , N_2 , CH_4) did not show systematic differences concerning the supernets. This insensitivity with respect to residual gases in the surrounding space was confirmed by foregoing experiments with crystals grown in an older RHEED apparatus at 10^{-5} torr and in the UHV apparatus before the bake out at 10^{-7} torr. Storing the crystals at 10^{-8} or 10^{-10} torr for several days was without any influence on the diffraction diagrams.

If a crystal grown at 10^{-7} torr was baked out together with the apparatus, the diagrams of the supernets taken after cooling down of the apparatus were very poor: additionally to the spots from the bulk only spots from (001)(5×20) persisted. After the bake out several of the superstructures reappeared if the crystal was annealed at 10^{-9} torr and 800°C or higher for half an hour. But in order to reproduce the disappeared diagrams from all supernets the specimen had to be melted and solidified again at 10^{-9} torr. Superheating the melt gave the best results. The diagrams from the supernets were blurred also if a crystal was exposed at room temperature to purified nitrogen at atmosphere pressure for one hour.

13. The Frequency of Observing Supernets

The described supernets were observed with different frequencies on gold of different sources.

Table 1. Relative frequency of finding superstructures on different gold specimens. (Numbers of finds/Numbers of observations.)

Provenance of Au	Heraeus		Johnson & M.	IMANCO		Heraeus	
Support	Graphite		Graphite	Graphite		Tungsten	
Vacuum during solidification in torr	10 ⁻⁷	10 ⁻⁹	10 ⁻⁹	10 ⁻⁷	10 ⁻⁹	10 ⁻⁷	10 ⁻⁹
(001) (5 × 20)	3/3	44/44	2/6	1/3	5/9	2/2	9/9
(001) vicinal plane	2/2	14/27	0/2	1/1	1/8	2/2	6/7
(227) (1 × 1)	2/2	17/27	0/1	1/3	2/9	2/2	5/7
(111) (23 × 1)	3/3	12/34	4/6	1/3	2/8	2/2	8/9
(110) (1 × 2)	3/3	31/34	3/5	1/3	6/9	2/2	10/10
(17, 17, 1)	0/2	3/29	0/3	0/2	0/8	0/2	2/8
(110) (1 × 3)	0/2	0/29	0/3	1/2	1/8	0/2	0/8
(551) c (1 × 1)	2/2	22/27	1/2	2/2	5/8	2/2	8/8

The crystals were grown under different conditions. 97 crystals were investigated grown from 14 charges of Heraeus Au; 7 crystals from one charge of Johnson-Matthey Au and 15 crystals from 3 charges of IMANCO Au. Table 1 shows how often a structure was found compared to the number of observations. If a superstructure was not found, there was always the diffraction diagram from the bulk crystal. Table 1 summarizes all observations performed under the following conditions:

- (i) The Au charges were etched in aqua regia before the first melting;
- (ii) the crystals were grown in the UHV-RHEED apparatus at 10⁻⁷ torr without baking out or at 10⁻⁹ torr after baking out and further pumping.

All observations were excluded from Table 1 which were done on crystals grown in a modified residual atmosphere or after additional annealing.

As described in Chapt. 2, gold from Heraeus must be preferred for the appearance of supernets. The structure (001)(5 × 20) was observed on all these crystals. (110)(1 × 2) and (551)c(1 × 1) were nearly on all of them. Most of the other structures had a better chance if the crystals were grown at 10⁻⁷ torr without baking out of the apparatus, or if a gold charge was melted and solidified for the first time not before the baking out, but after it.

Acknowledgement

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