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Crystal Growth in the Chemical Displacement
of Metals.

By

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SECTION I.INTRODUCTION.1. General Introduction.

The chemical displacement of metals by base metals has been known for a long time, and the process has important applications in the extraction of metals and in the metal finishing industry. If a metal is immersed in a solution of the appropriate compound of a nobler metal this metal is displaced to form a coating on the baser metal. It is, therefore, quite easy to coat metals like iron and copper with nobler metals like silver and gold which are extensively used as coatings for decoration and prevention of corrosion.

Nowadays electrodeposition is mainly used for coating metal articles. This process provides the best method of obtaining coherent and thick deposits according to requirements. No such thick deposit can be easily obtained by chemical displacement. Besides, in thickness, the deposits obtained by chemical displacement differ considerably in nature from the electrodeposits. All these factors have focussed greater attention to electrodeposition and the process of chemical displacement has been overshadowed.

Since the thinner deposit of metals like silver and

gold can be easily obtained by chemical displacement the substitution of the process of electrodeposition, in some cases, by chemical displacement may prove more efficient and profitable if done under proper conditions. It has been observed in the present research that deposits of silver and gold obtained by chemical displacement on copper from cyanide baths are bright and coherent. As the qualities and properties of the deposits depend on the nature of the crystal growth, a study of various aspects of crystal growth in chemical displacement is desirable.

The most important aspect of the study of crystal growth in chemical displacement is how and whether growth in this process is different from growth in other processes. Crystals can be grown, for example, by (i) condensation from the state of vapour; (ii) from the solution; (iii) from the melt; (iv) by electrodeposition; and also (v) by chemical displacement. Although extensive studies on most of these processes have been made, little work on crystal growth in chemical displacement has been done. A comparative study of crystal growth in this process with growth in other processes is likely to be useful.

A common feature of the crystal growth in different processes is that the nature of growth is very much influenced by the nature of the substrate on which crystals

may be grown. The growing crystals are often influenced in their structure by that of the substrate. This phenomenon was observed long ago by Wakkernagel (1825) and Frankenheim (1836) in crystals obtained from natural sources. Mugge (1903) described many examples of naturally oriented growths of different minerals. After Laue's discovery of the diffraction of X-rays by crystals in 1912, Royer (1928) made an extensive study of the orientations of crystals grown on crystalline substrates, and he used the X-ray results on the crystal structures to interpret his observations in terms of the atomic arrangement. He first used the term "Epitaxy" (Greek: orderly arrangement) for the phenomenon of crystal growth in which the deposited crystals grow in an orientation such that there is a close fit of their atomic arrangement with that of the substrate at the interface. He came to the conclusion that the most important factor promoting epitaxial growth is the similarity of the identity spacings of the parallel rows of atoms of the growing crystals and the substrate surface and that epitaxy cannot take place when the difference in parameters of such parallel rows is more than 15%. Later results (e.g. Wilman, 1951) have shown that such a limit of 15% can no longer be accepted as valid.

Elleman and Wilman (1949) have also shown clearly

that the initial condition of epitaxy is that the local atomic fitting between the deposit and substrate crystals must be good, the lattice fitting being a further secondary consideration.

From the study of adsorption and mixed crystal formation Bunn (1933) concluded that though similarity of the three dimensional lattice is necessary for mixed crystal formation good atomic fit on the interface is necessary for oriented growth.

Epitaxial growth of metals condensed from the state of vapour was studied by Bruck (1936) who postulated that the distance between atoms of the substrate and those of the deposit, averaged over a cell, is minimum. Rudiger (1937) studied the growth of metals evaporated on crystalline substrates and found that the temperature of the substrate must be greater than a certain minimum to allow epitaxial growth of the deposits. From the study of the growth of sodium nitrate on polished faces of calcite Finch and Whitmore (1938) concluded that the forces determining epitaxy are generally short range and the orientation of the deposit is wholly determined by the atomic arrangement on the surface of the substrate.

The influence of the substrate on the growth of crystals during electrodeposition was first observed by

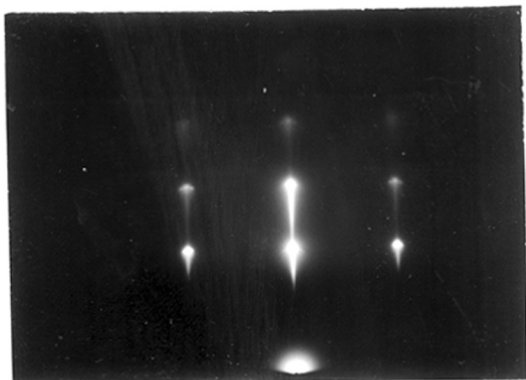


Fig.1(A)
 (111)-orientated silver
 on mica. Azimuth $\langle 211 \rangle$

~~Fig. 2~~

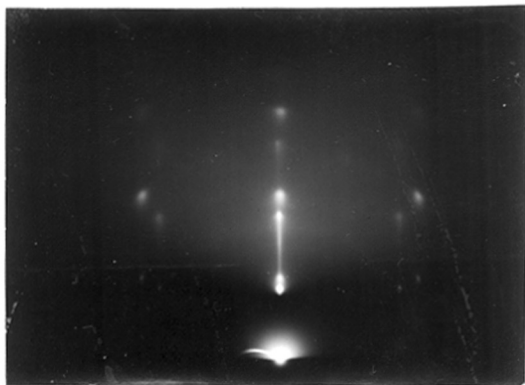
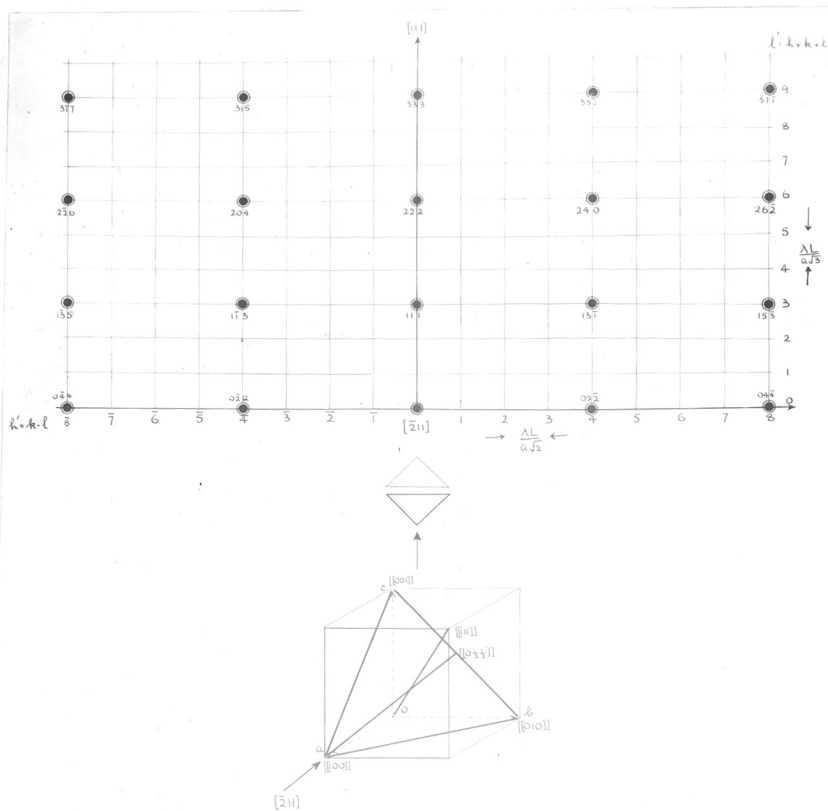


Fig.1(B)
 Nickel on (111)-
 orientated silver
 azimuth $\langle 211 \rangle$

Huntington (1905). Blum and Rawdon (1923) and Hethersall (1935) made some systematic study of crystal growth in electrodeposition, with the help of the optical microscope and observed the influence of the substrate on the orientation of the deposit crystals. Wood (1931) and Hume-Rothery and Wyllie (1943) used X-rays and obtained similar results. The effect of the substrate on the initial thin electrodeposits has been studied by electron diffraction by Thomson (1931), Cochrane (1936) and especially by Finch and collaborators (1936, 1937, 1947) who found many interesting and useful results and definitely established the fact that the substrate influence gradually diminishes with the increase in thickness of the deposit. A similar effect has been observed in the present experiments in the growth of crystals in chemical displacement.

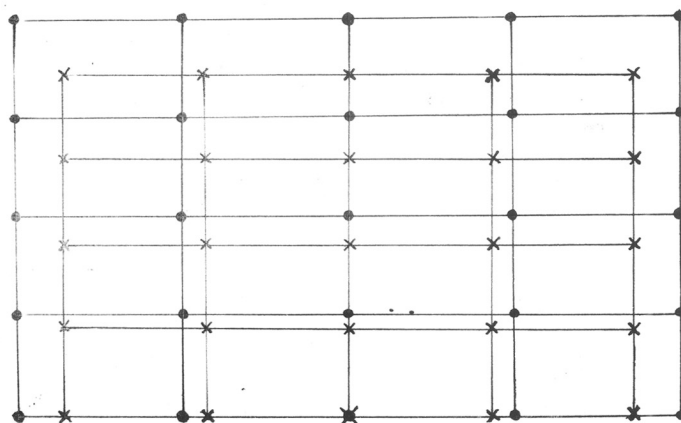
As an illustration of the epitaxial growth of electrodeposits a new example observed by the author may be cited. Fig.1(A) shows the electron diffraction pattern of a thin deposit of silver condensed in vacuo in (111) orientation on a fresh cleavage face of mica at about 200°C. Fig.1(B) shows the diffraction pattern obtained from a thin layer of nickel electrodeposited on the silver for 90 sec. at 55°C. and 3.5 mA. per sq.cm. from a bath containing 240 grams of nickel sulphate and 30 grams of boric acid per litre.



TWO DEGREE ORIENTATION — BEAM ALONG $[211]$.

fig 2 A.

Diffraction pattern from the (111)-orientated parallel layers of Silver and Nickel Crystals with the beam along the $\langle 211 \rangle$ lattice rows.



● ← Diffraction spots due to Nickel
 x ← " " " " Silver

fig 213

The nickel had grown epitaxially on the silver as is evident from the pattern. A theoretical diffraction pattern expected from a (111) face of a face-centred cubic crystal in [211] azimuth is drawn in Fig.2A and the expected pattern from parallel layers of silver and nickel is drawn in Fig.2B. They agree quite well with the diffraction patterns obtained.

The influence of the substrate on the orientation of compounds formed by chemical reactions has also been studied by many workers. A review of the earlier work is given by Thomson and Cochrane (1939). More recent cases of such effects have been studied by Thirsk and Whitmore (1940), Ellisman and Wilman (1949) and Wilman (1940, 1949).

Though the process of chemical displacement has been known for a long time, crystal growth by this method has not been systematically studied. Very little data exists on any aspect of crystal growth in this process. This process differs from other processes by the fact that there is an exchange of ions between the solution and the substrate. Similar exchange does not take place in crystal growth by other methods which are generally one-way processes. The study of the substrate effect on crystal growth in chemical displacement is, therefore, expected to be useful and informative.

Another important aspect of the phenomenon of crystal growth is the effect of the relative lattice parameters

of the deposit and the substrate on the structure of the deposit. It has now been generally agreed that epitaxial growth of crystals takes place by atom-by-atom accretion to the initial crystal nucleus on the substrate. The deposited atoms tend to form an initial monolayer in which they take, as far as possible, the positions that would have been taken up by atoms of the substrate if it were continued in space. If the lattice parameters of the deposit are different from those of the substrate, the deposited atoms remain under a strain which may produce profound effects on the structure of the deposit. The strain may cause even contraction of the lattice parameter for the sake of close fit with the substrate. Such changes have, in fact, been observed by different workers. Finch and Quarrell (1933, 1934) observed, for the first time, contraction of the lattice dimension of zinc oxide formed on zinc: they called this phenomenon "pseudomorphism". Similar pseudomorphic growths have been observed by Cochrane (1936) and recently, by Clark, Pish and Weeg (1944).

Finch and Quarrell concluded that pseudomorphic strain does not persist in the thicker layers and is confined to the first few atom layers adjoining the substrate. As the thickness increases, the strain is generally relieved and the initial orientation may change

a result of twinning and translational or rotational slip (Evans and Wilman 1950). Twinning of deposit crystals has been observed by Bruck (1936), Cochrane (1936), Menzer (1938), Goche and Wilman (1939), Wilman (1940), Finch, Wilman and Yang (1947), during crystal growth in electrodeposition and condensation from vapour. Similar twinning of the deposits of silver, gold and especially platinum has been observed in the present work.

The process of chemical displacement has a greater degree of similarity with electrodeposition than with the other methods of crystal growth. It has now been universally accepted that displacement of one metal by another from solution of salts is an electrochemical phenomenon like electrodeposition. Every metal has a characteristic potential as referred to hydrogen electrode. When a metal having a higher potential is placed in a solution containing ions of a metal having a lower potential the latter is displaced and the displacing metal enters the solution as cations. Hence the mechanism consists of the neutralisation of the cation in solution as in the case of electrodeposition. The essential difference between the two processes is that in chemical displacement the ions which enter the solution are of a different metal from the ions which are neutralised.

Consequently the concentrations of the ions of the two metals involved in the reaction gradually change.

Extensive researches have been carried out on crystal growth by electrodeposition by many workers, notably by Finch and his collaborators who have obtained results which now present a relatively clear picture of the cathodic crystal growth. They have clearly established that two main influences^{govern} the growth of the deposit, namely the influence of the substrate and that of the bath conditions. These two influences are often opposite to each other. The substrate influence when dominating causes the deposit crystals to grow epitaxially. The substrate influence gradually diminishes when the thickness of the deposit increases. When the deposit is sufficiently thick it is the bath conditions which take charge and wholly control the nature of the deposit. As chemical displacement is essentially like electrodeposition, similar effects of the substrate are likely to be produced. These results are, indeed, confirmed by the results obtained in the present work.

It has also been found in electrodeposition that there are many factors which determine the bath conditions. These are temperature, concentration, current density, ion association, over-voltage and presence of foreign materials which may also be deposited on the cathode. The nature of

the ions, especially that of cations, produces profound effects on the nature of the deposits; for example, good electrodeposits of iron can be obtained from ferrous ions but not from ferric ions (D.H.Layton, D.I.C.Thesis, 1950). Amorphous deposits are formed by metals having weak cohesive forces, such as arsenic and antimony (Finch, Wilman and Yang, 1947). In chemical displacement, similar factors which may be present are likely to produce similar results. It has been found in the course of the present work that when silver is displaced from a simple bath of silver nitrate the deposit is dark and non-adhesive, but when displaced from the complex cyanide bath it is bright and adherent. It is, therefore, worthwhile to study the effects of different factors on deposits formed by chemical displacement. In this connection it may be noted that some of the factors such as change of current density and evolution of hydrogen are absent in chemical displacement; so in these ^{respect-} results it provides a simpler system for the study of crystal growth.

The process of chemical displacement differs from electrodeposition in other ways, apart from those mentioned above. In chemical displacement metallic cations from the bath are exchanged with cations formed from the surface of the substrate. This is a two-way process and thus differs from electrodeposition. This factor has an important effect

on the nature of the deposits. In the course of the small amount of research (vide 2 below) done on chemical displacement formation of alloys between the displaced and displacing metals has been reported in most cases. No such formation of alloys has been generally observed in the cases of electrodeposition from a solution containing only one kind of cation, although alloys can be electrodeposited from a mixed cation bath. It is, therefore, highly desirable to compare crystal growth in the two processes from the same bath. Although our knowledge of the mechanism of electrodeposition has considerably increased in recent years a full understanding has^{not} yet been reached. A comparative study of the two processes of deposition may throw new light also on electrodeposition, which is a complex process. In the present researches a comparative study of chemical displacement of silver, gold and platinum with the electrodeposition of the metals has been made using copper single-crystal substrates. The results show some interesting differences in the nature of the deposits obtained by the two processes.

2. Historical Review.

Although the process of chemical displacement has been known for a long time few results on the nature of the crystals formed by this process are known. The earliest

investigation on the structure of chemically displaced metals was made by Tsuboi (1928) by X-ray diffraction. He studied the structure of the spongy deposit of silver obtained by displacement with copper wire from silver nitrate solution. The micro-crystals of the deposit were orientated with (111) plane parallel to the axis of the wire, i.e. parallel to the wire surface. He also obtained by displacement (111) orientation for lead and (0001) orientation for cadmium, on zinc.

Natta and collaborators (1934, 1935, 1937) made an extensive study of silver, gold and platinum deposits obtained by chemical displacement on copper and gold and platinum on silver. They removed the displacing metal from the deposit by the action of nitric acid and then studied the structure of the deposit by the transmission electron diffraction method.

Natta (1934) found the lattice dimension of the deposits to vary between those of the displaced and displacing metals according to composition, and he concluded that alloys of the two metals were formed. He further concluded (1935) that the ordering structure of the alloys so formed depended on atom radii of the alloying metals and he obtained solid solutions of platinum, palladium and silver in the copper lattice by displacing them by copper from

solutions of their salts. The diffraction diagram revealed F.C.C. structure of the precipitates whose lattice constants were found to depend on the thickness of the film obtained and also on the concentration of the nitric acid used.

The result of the study of platinum displaced by silver⁽¹⁷³⁷⁾ was found to be different. The lattice constant of the deposit was found to be equal to that of silver and the value of the lattice constant was found to be diminished when heated. He explained the high value of the lattice constant of platinum obtained, by assuming that an unstable alloy is formed when the lattice dimension of the displacing metal is greater than that of the displaced one. He assumed that the unstable variety of alloy formed changed into a more stable form having lower lattice constant, on heating.

Finch and Sun (1936) investigated, by electron diffraction, the structure of platinum deposits obtained by displacement by polycrystalline silver and copper. They found that the lattice constants of the deposits did not correspond to those of the pure components and that the lattice constant of displaced platinum decreased when silver was kept in contact with solution for a longer time. From these facts they came to the conclusion that alloys of displaced and displacing metals were formed.

Cochrane (1936), while studying the electrodeposition of silver on (001) and (110) faces of single crystals of

copper found that a polycrystalline deposit of silver was formed by simply dipping the copper crystal in a strong solution of complex silver cyanide containing an excess of KCN.

Natta and Guiriani (1937) from a study of the precipitated metals and their alloys came to the conclusion that although displacement of one metal by another is possible, formation of a solid solution is not possible where the atomic diameters of the two metals are widely different and that a compact and coherent deposit is obtained only where solid solution is formed. From their study of the solid solution of copper and platinum (Cu-Pt) obtained by chemical displacement they came to the conclusion that the first step in the formation of alloy is the substitution of the surface atoms of the displacing metal by those of the displaced metal and then the process of diffusion through the surface layer follows.

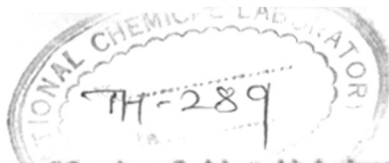
The electrochemical properties of the different faces of copper single crystals were studied by Leidheiser and Gwathmey (1947), who displaced silver and gold on (100) and (111) faces of copper from silver nitrate and gold chloride solutions. They obtained black deposits which, when rubbed with a soft tissue, left a definite pattern on the surface of the copper. Straumanis and Fang (1951) studied by X-ray

diffraction the structure of gold and silver obtained by chemical displacement on zinc. They obtained polycrystalline deposits with lattice constants intermediate between those of the pure components and they concluded that alloys were formed. Goswami (1950) made a brief study of the displacement of silver on (100) and (110) faces of single crystals of copper from a solution of complex cyanide of silver. He was the first author to note a two-degree orientation of a deposit obtained by chemical displacement. He found that silver had the normal lattice dimension. He also studied displacement of copper from copper sulphate solution on polycrystalline mild steel and iron and also on single crystal of ferro-silicon alloy. Polycrystalline deposits were obtained in all cases.

3. The Methods of Study used and the General Nature of the Results Obtained.

It has been mentioned previously that crystal growth has been studied so far mainly by optical microscopy, X-ray diffraction, and recently by electron diffraction which proves to be the most potent technique for the purpose. The growth of crystals takes place atom by atom and layer by layer, though succeeding layers may start to grow before lower layers are complete. It is therefore obvious that X-rays which penetrate deep into the bulk of the specimen

will be unsuitable for study of the nature of the initial layers of thin deposits or of the surface layers of thick deposits. In electron diffraction, even a 60 KV. electron beam used at grazing incidence in the "reflection" method on a highly smooth surface, penetrates only a few tens of angstroms below the surface and thus gives the desired information free from obscurity of details arising from the inner regions. The nature of the orientation has been found to change with increase in thickness of the deposit on the (100) face of copper. In the following researches electron diffraction was, therefore, the principal technique employed to examine the structure of the deposits which, in their initial stages, were so thin as to be scarcely visible to the eye; and even the thicker deposits were featureless when observed in the optical microscope. In all cases the substrate surface was made highly smooth by modern electropolishing technique. The present work studies in detail the epitaxial growth of silver, gold and platinum on (100), (110) and (111) faces of copper single crystals by displacement from both complex cyanide baths as well as simple baths. The results obtained reveal many new interesting features. Perfect epitaxial growth of the deposits of all three metals has been observed, especially from complex bath when the deposit is thick. Silver has the narrowest lattice dimension under all conditions investigated, oriented crystals having two-degree orientation with relative



to the copper substrate. The effect of the thickness of the deposit has been studied by changing the concentration of the baths as well as the time of deposition. The substrate effect on orientation has been found to decrease with increase in thickness, as in certain cases of crystal growth by other processes, especially electrodeposition. The nature of the orientation has been found to change with increase in thickness of the deposit on the (100) face of copper. The cause of this change has been explained and enables a mechanism of deposition to be suggested.

Some interesting points of difference between growths from simple and complex baths have been observed and some points of dissimilarity between growths of the three different metals from baths of similar nature have been noted.

The lattice dimensions of the deposits have been determined by calibration with graphite. The results show ~~some~~ ^{Some} differences in the nature of bonding of the deposits of the three different metals with copper. The lattice constant of platinum is much lower than the normal value; thus suggesting the formation of an alloy with the copper. The lattice dimension of gold also is slightly lower when the deposit is thin but it appears to be normal when the deposit is thick. Silver has the normal value of lattice dimension under all conditions investigated.

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With a view to comparing the nature of the initial stage of the crystal growth by chemical displacement with that by electrodeposition, the electrodeposition of silver, gold and platinum on two surfaces of single crystals of copper from cyanide and complex baths has also been studied under identical conditions. Some remarkable differences between growths in the two processes have been observed.

Displacements of copper, silver, gold, platinum and nickel on single crystal of iron have also been studied, and only random deposits have been obtained. Nickel was found to form only Ni(OH)_2 and copper also formed Cu_2O from dilute solutions. No deposits of the above metals could be obtained by displacement by iron from cyanide baths.

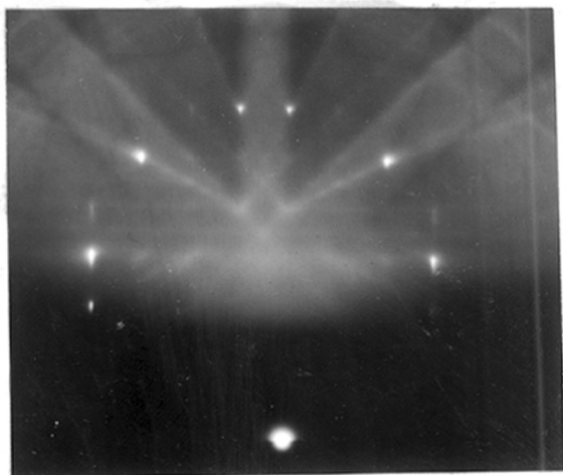
SECTION II.

EXPERIMENTAL OPERATIONS.

1. Preparation of Single Crystal Faces of Copper.

The copper single crystals used for the present work were cut from a copper single crystal rod which was kindly lent by Professor Finch. The rod was carefully cut with a jeweller's saw lubricated with oil so that the crystal might not be distorted during cutting. The cut pieces of the crystal were ground with emery on a revolving wheel moistened with benzene, until suitable faces were obtained. The faces were then polished with emery of grades 1, 0, 00, 000 and 0000, moistened with benzene. The faces thus polished were etched with nitric acid (1:1) to remove the distorted layer. After etching, the crystal faces were electropolished in a phosphoric acid bath containing 63% H_3PO_4 and 37% water (Jacquet 1936). The cathode was a sheet of copper, cut into strips to allow free evolution of hydrogen. The voltage of the circuit was carefully regulated between 2 and 2.5 volts to prevent anodic oxidation of the face of the crystal. After electropolishing, the crystal was taken out, washed with water and then etched by a 10% KCN solution for about 30 seconds to remove any oxide which might have been left on the copper surface after electropolishing.

Cu

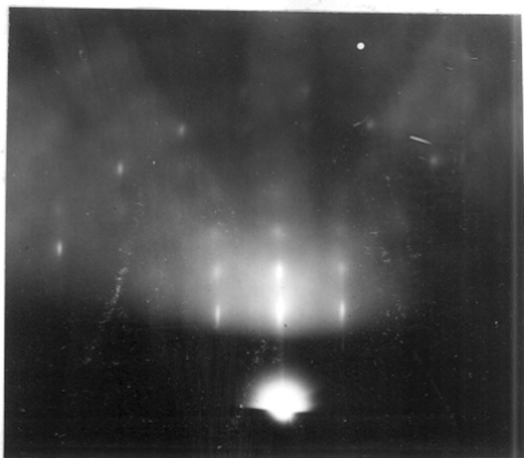


Electropolished (001)
face of copper.
azimuth $\langle 001 \rangle$



Electropolished (001)
face of copper.
azimuth $\langle 110 \rangle$

Cu



#18.7
Electropolished (111)
face of copper.
azimuth $\langle 211 \rangle$

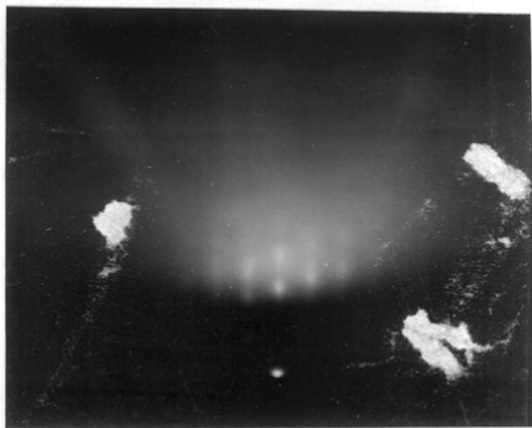


Fig.6
Electropolished (111)
face of copper.
azimuth $\langle 110 \rangle_{cu}$

Cu

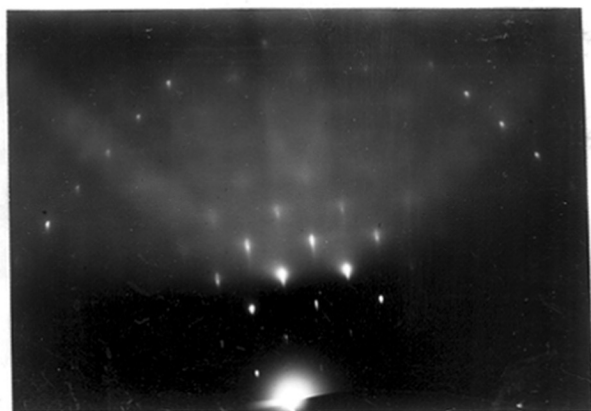


Fig.7
Electropolished (110)
face of copper.
azimuth $\langle 001 \rangle$

Finally it was thoroughly washed with distilled water and acetone and then transferred to the camera under propyl alcohol, which was used to prevent oxidation by air. From the diffraction pattern the type of face obtained was identified. The crystals were further ground and polished as above until the appropriate faces were obtained. From the diffraction pattern the direction of a suitable main azimuth on the crystal face was identified and marked on the crystal. The (100), (110) and (111) faces of the copper single crystals that were prepared yielded the diffraction patterns shown in Figs. 3-7. The elongated diffraction spots and Kikuchi bands indicate the atomically smooth surface of the crystals and their high lattice perfection.

2. Preparation of Single Crystal Surfaces of Iron.

The single crystals of iron used in these experiments were lent by Professor Finch. These were each about 2 mm. thick and about 4 sq.cm. in area, and were cut from a sheet of decarbonised mild steel in which large crystals had been grown by the strain-anneal method. Every possible care was taken so that the crystal might not be distorted during cutting. The surfaces were polished with graded emery in sequence of grades as was used for polishing copper and then electropolished in a bath containing 185 cc. perchloric acid, 80 cc. acetic anhydride and 50 cc. water per litre of solution (Jacquet and Rocquet, 1939).

Fe

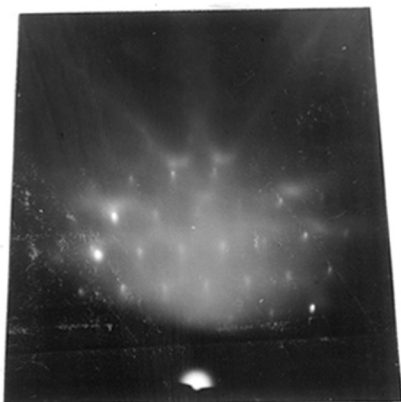


Fig. 8
Electropolished (211)
face of iron.
azimuth $\langle 111 \rangle$

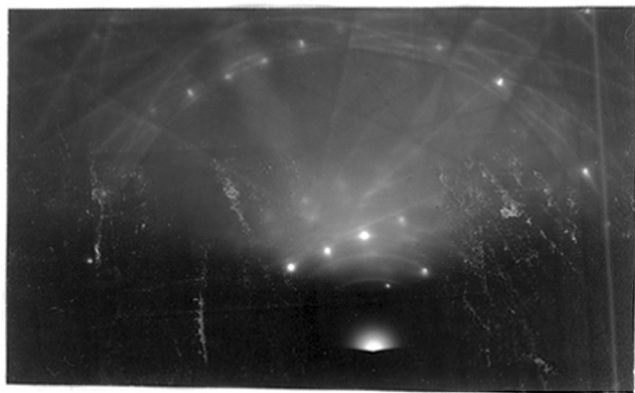


Fig. 9
Electropolished approx
(001) face of iron.
azimuth $\langle 110 \rangle$

TABLE I.

Composition of the Baths Used.Simple Baths *

Silver bath		AgNO_3	dissolved in distilled water				
Gold bath		$\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$	"	"	"	"	"
Platinum bath		$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	"	"	"	"	"
Copper bath		$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	"	"	"	"	"
Nickel bath		$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	"	"	"	"	"

The concentrations used are expressed in terms of molarity (M).

Complex Cyanide Baths.

Silver bath		"A"	AgCN	3.5	grams/litre
			KCN	3.6	grams/litre
			K_2CO_3	3.7	grams/litre
Gold bath		"B"	AuCN	11.5	grams/litre
			KCN	15	grams/litre

The concentrations used are expressed in terms of "A" and "B".

* The term "simple bath" is rather loosely used in the case of gold and platinum. In solution the gold chloride and chloroplatinic acid form more or less complex anions containing the metal anions; but these anions are much less stable than the complex anions in the cyanide baths.

After electropolishing, the crystals were washed with water and then etched for a few seconds by a 1% solution of picric acid in absolute alcohol to remove the film of oxide that otherwise tends to be present on the surface. The de-oxidised crystals were washed thoroughly with water and acetone and then transferred to the camera under propyl alcohol to avoid oxidation by contact with air. The approximate (100) and (112) faces when examined in the diffraction camera produced diffraction patterns like Fig.8 and 9.

3. Displacement of Metals.

For displacement of any of the metals, the appropriate solution (Table I) of desired concentration was placed in a clean porcelain basin. After electropolishing and de-oxidation of the substrate it was thoroughly washed with distilled water and most of the water still adhering to the polished face was drawn off with the edge of a clean piece of filter paper. The rest of the body of the crystal was dried with the help of filter paper. The crystal was then put into the reaction bath with a pair of tweezers coated with insoluble varnish, so that no reaction with the metal of the tweezers could take place. After the desired period of reaction the crystal was taken out, transferred

quickly to another pair of clean metal tweezers and then washed thoroughly with distilled water followed by acetone. The washing was done as quickly as possible to avoid oxidation and the specimen was immediately transferred under propyl alcohol to the diffraction camera.

4. Electrodeposition.

For electrodeposition on faces of single crystals of copper the desired crystal face was electropolished and de-oxidised as before and then thoroughly washed with distilled water. The face and body of the crystal were dried as described before and electrodeposition was carried out. A sheet of the pure metal to be electrodeposited on the copper face was used as anode and the crystal forming the cathode was held in position with its polished face just in contact with the bath. The current was drawn from a 12 volt battery and it was regulated by a variable series resistance. The current was measured with a milliammeter. When the time of deposition was short the adjustment of the resistances in the circuit was made before electropolishing was done for the purpose of electrodeposition so as to keep the current density at the desired limit. After the electrodeposition, the crystal was washed with water, followed by acetone, and then transferred under propyl alcohol to the diffraction camera.

5. Electron Diffraction Study.

The specimens were examined by electron diffraction with the help of the usual type of Finch camera (Finch and Quarrell 1933, Finch and Wilman 1937). The accelerating voltage producing the electron beam was between 45 and 60 KV. The diffraction patterns were examined and interpreted in the way described by Finch and Wilman in the publication mentioned above.

SECTION III.DISPLACEMENT ON THE (001) FACE OF COPPER SINGLE CRYSTAL.A. Displacement from Simple Baths.

The results on displacement of silver from silver nitrate solution and of gold and platinum from gold chloride and chloroplatinic acid are set forth in Figs. 10-29 and Tables 2-4. The deposits of all these metals, when thin (after a few seconds deposition) were not visible and the colour gradually increased from faint greyish-pink to deep grey as the thickness increased. In the case of silver, ^{it was} ~~deep~~ when the deposit was very thick.

The deposits of all the three metals consisted of both random and oriented crystals in varying proportions as is evident from the diffraction patterns. The proportion of orientated growth was highest for the thinnest deposit. As the thickness of the deposit increased the proportion of the orientated crystals diminished and ultimately the surface region consisted of only random crystals. It is therefore clear that the influence of the substrate on the orientation of the deposit gradually falls off as the thickness increases. The nature of the substrate influence in chemical displacement of these metals is thus similar to that in the electrodeposition of metals.

TABLE 2.

DISPLACEMENT OF SILVER FROM SILVER NITRATE
SOLUTION ON THE (001) FACE OF COPPER.

Concentration	Time	Colour of deposit	Structure and Orientation of the deposit*	Figs.
M/2000	1 sec	No colour	C(001)+C(111) +H(101) + R.	10-12
M/2000	30 sec	No colour	C(001)+C(111) +H(101) + R.	13
M/2000	5 min	Light grey	R+C(001)+C(111) +H(101)	14
M/2000	10 min	Dark grey	R+very little C(111) +little H(101)	15
M/100	1 sec	Greyish	C(001)+C(111) +H(101) + R	16
M/10	1 sec	Light grey	R+C(001)+C(111) + H(101)	17

* C(001) = cubic, (001)// Cu(001), $\langle 110 \rangle_{\text{cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

C(111) = cubic, (001)// Cu(111), $\langle 110 \rangle_{\text{cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

R = random (cubic)

H(101) = hexagonal, (101)// Cu(001), $\langle 010 \rangle_{\text{hex}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

TABLE 3.

DISPLACEMENT OF GOLD FROM GOLD CHLORIDE SOLUTION
ON (001) FACE OF COPPER.

Concentration	Time	Colour	Structure and Orientation of the Deposit.*	Figure
M/2000	10 sec	No colour	C(111) + R	
M/2000	30 sec	No colour	C(111) + R	18
M/2000	3 min	Grey	R + C(111)	19
M/2000	7 min	Grey	R + Cu ₂ O(111)	20
M/1000	30 sec	No colour	C(111) + R	21
M/500	30 sec	Greyish	R + C(111)	22
M/250	30 sec	Grey	R + Cu ₂ O(random)	23

* C(111) = cubic_c (111) // Cu(001), $\langle 110 \rangle_{\text{cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$
 R = random (cubic)

TABLE 4.

DISPLACEMENT OF PLATINUM FROM CHLOROPLATINIC
ACID ON (001) FACE OF COPPER.

Concentration	Time	Colour	Structure and Orientation of the Deposit*	Figure
M/4000	30 sec	No colour	C(111) + R(little)	24
M/2000	10 sec	No colour	C(111) + R	25
M/2000	20 sec	No colour	C(111) + R	
M/2000	30 sec	No colour	C(001)+C(111)+R	26, 27
M/2000	5 min	Light grey	C(001) + R	28
M/2000	10 min	Grey	R	29
M/1000	30 sec	Very light grey	C(111) + R	

* C(001) = cubic (001) // Cu(001) $\langle 110 \rangle_{\text{Cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$
 C(111) = cubic (111) // Cu(001) $\langle 110 \rangle_{\text{Cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

Silver Displaced on (001) Face of Copper from Silver Nitrate

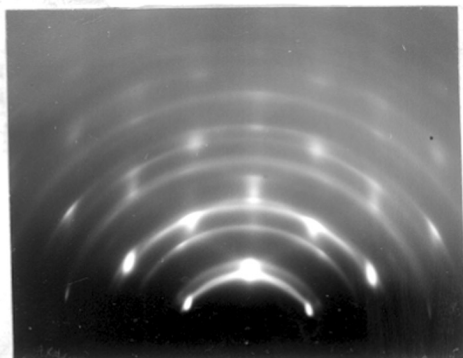


Fig. 10
M/2000 1 sec
azimuth $\langle 110 \rangle_c$

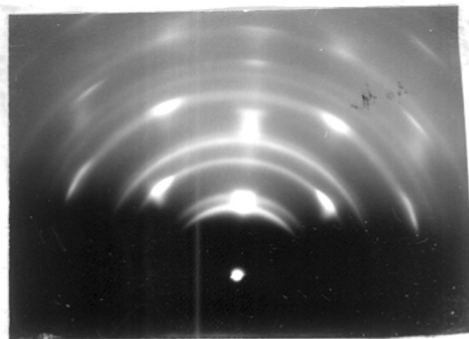


Fig. 11
M/2000 1 sec.
azimuth $\langle 001 \rangle_c$

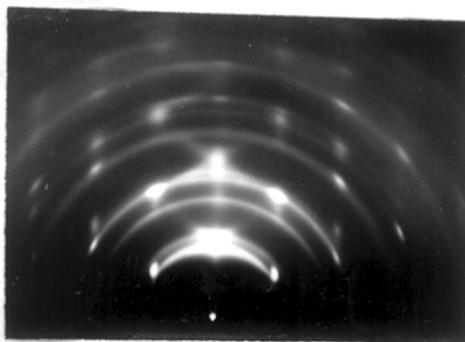


fig 12 -
12
M/2000, 1 sec., $\langle 110 \rangle$

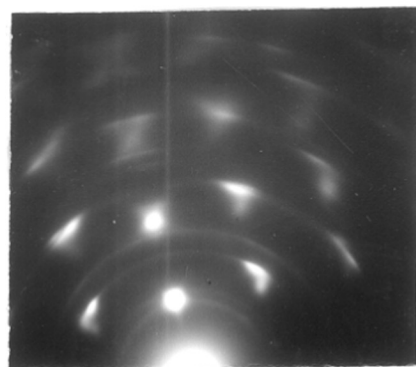


fig 13
M/2000, 30 sec $\langle 001 \rangle$

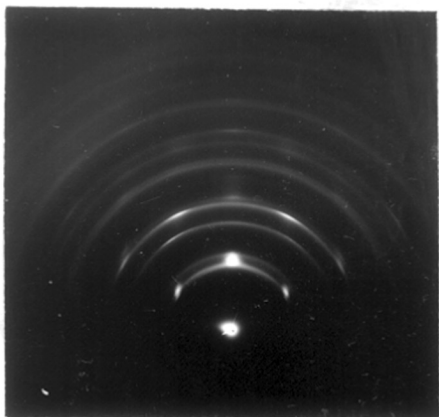


Fig.14
M/2000 5 mins.
azimuth $\langle 110 \rangle$ Cu

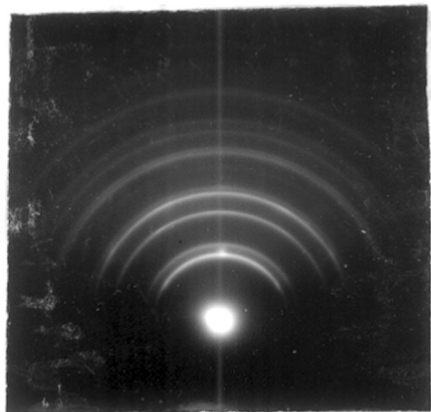


Fig.15
M/2000 10 mins.
azimuth $\langle 110 \rangle$ Cu

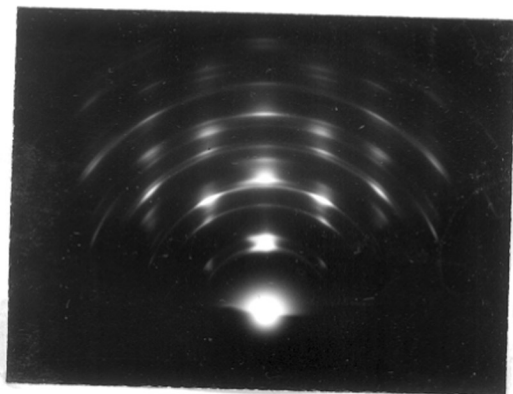


Fig.16
M/100 1 sec
azimuth $\langle 110 \rangle$ Cu

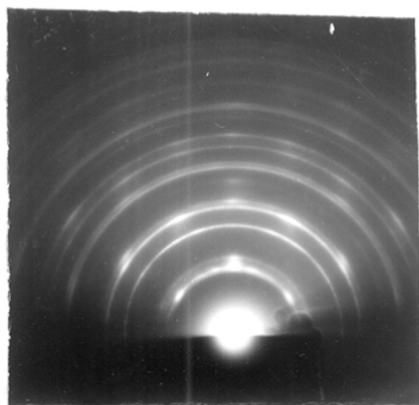


Fig.17
M/10 1 sec
azimuth $\langle 110 \rangle$ Cu

Gold Displaced from Gold Chloride Solution on
(001) Face of Copper.

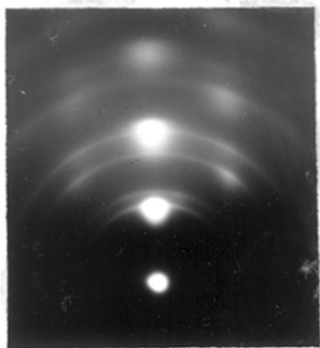


Fig. 18
M/2000 30 sec
azimuth 110 Cu

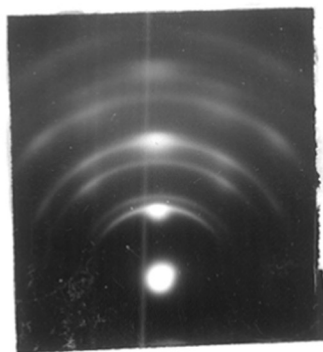


Fig. 19
M/2000 3 mins.
azimuth 110 Cu

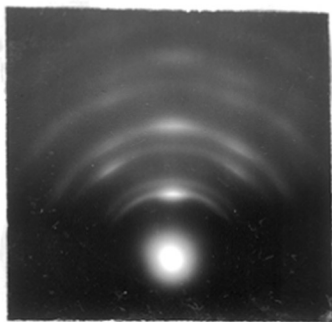


Fig. 20
M/2000 7 mins.
azimuth 110 Cu



Fig. 21
M/1000 30 sec
azimuth 110 Cu

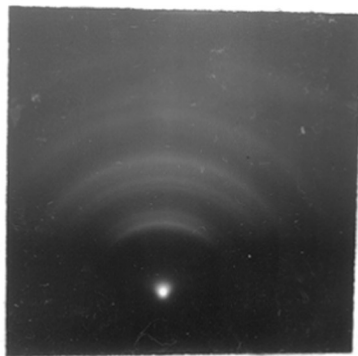


Fig. 23
M/250 30 sec

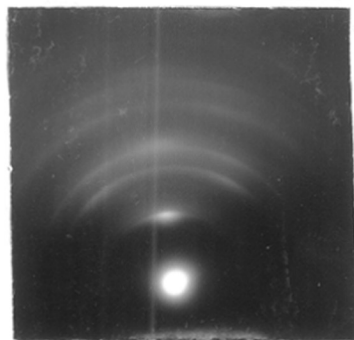


Fig. 22
M/500 30 sec
azimuth 110 Cu

Platinum Displaced from Chloro-platinic Acid on
(001) Face of Copper.

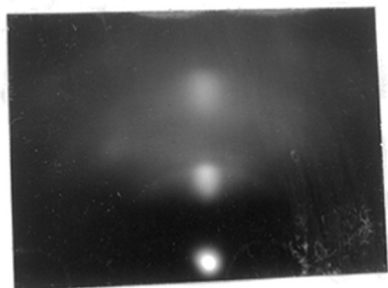


Fig. 24
M/4000 30 sec
azimuth 110 Cu

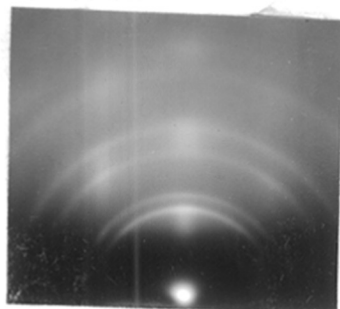


Fig. 25
M/2000 10 sec
azimuth 110 Cu

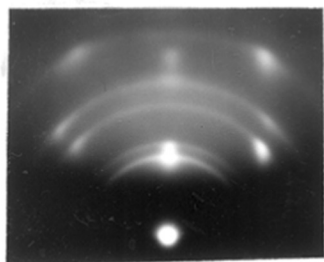


Fig. 26
M/2000 30 sec
azimuth 001 Cu

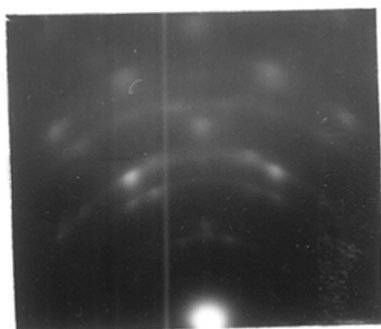


Fig. 27
M/2000 30 sec
azimuth 110 Cu

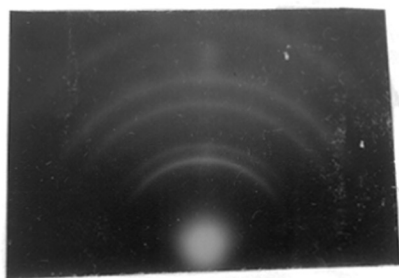


Fig. 28
M/2000 5 mins.
azimuth (110)Cu

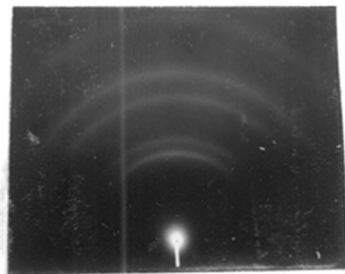


Fig. 29
M/2000 10 mins.
azimuth

The orientated deposits had two-degree orientation with relation to the substrate but the nature of the orientation differed in some respects for the three metals.

Silver deposits : The diffraction patterns of silver deposits (Figs. 10-17) show, in the plane of incidence, orders of 001 and 111 diffractions from normal face-centred-cubic silver crystals and orders of 101 diffractions from close-packed hexagonal Ag crystals. The diffraction pattern obtained from these silver deposits is thus a composite pattern consisting of a number of independent patterns corresponding to the (001) and (111) orientated cubic crystals and (101) orientated hexagonal crystals in various azimuthal orientations. For clarification the theoretical patterns expected from the suggested azimuths are drawn in Figs. 31-36 explained below.

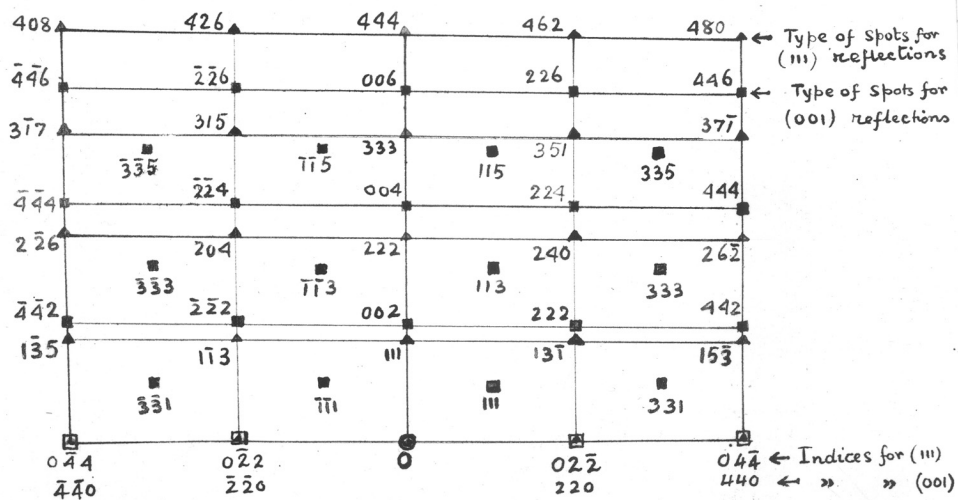
The diffraction pattern Fig.10 of the deposit, taken in the $\langle 110 \rangle$ azimuth of the substrate, shows a centred $\sqrt{2}$ rectangular pattern, showing that the (111) orientated cubic deposit crystals have their $\langle 110 \rangle$ lattice row parallel to $\langle 110 \rangle$ of the substrate surface. The expected theoretical pattern, Fig.31, from a face-centred cubic crystal when the beam grazes a (111) face in the $\langle 110 \rangle$ azimuth is a network of spots in a centred $\sqrt{2}$ rectangular pattern with one of the diagonals along the plane of incidence. As the (111)-orientated cubic crystals in $\langle 110 \rangle$ azimuth can occupy two

equivalent asymmetric positions the diffraction pattern contains a second rectangular pattern of spots which can be obtained by reflection of the first pattern across the plane of incidence.

The diffraction pattern Fig.10 from the deposit, taken in the $\langle 110 \rangle$ azimuth of the substrate, also shows a $\sqrt{2}$ rectangular pattern with the longer side along the shadow edge. It is therefore clear that some cubic crystals of the deposit had (001) orientation with a $\langle 110 \rangle$ lattice row parallel to $\langle 110 \rangle$ of the substrate surface. It is clear from the body-centred reciprocal lattice of face-centred-cubic crystals that the pattern from the (001) oriented crystals in $\langle 110 \rangle$ azimuth is a set of $\sqrt{2}$ centred rectangles with longer side along the shadow edge as drawn in Fig.32.

The second rectangular spot pattern drawn in this diagram is associated with the (111) orientated cubic crystals with the beam in $\langle 211 \rangle$ azimuth. The (111) orientated cubic crystals can occupy four equivalent positions relative to the substrate, such that a $\langle 110 \rangle$ lattice row is along $\langle 110 \rangle$ of the substrate surface. In two of these positions the crystals will give the pattern shown in Fig.31 as already described. The remaining two components will be symmetrically placed with relation to the beam with their $[211]$ row along 110 of the substrate. These two components

Reflections from the
(111) and (001) planes
of F.C.C. Crystals.



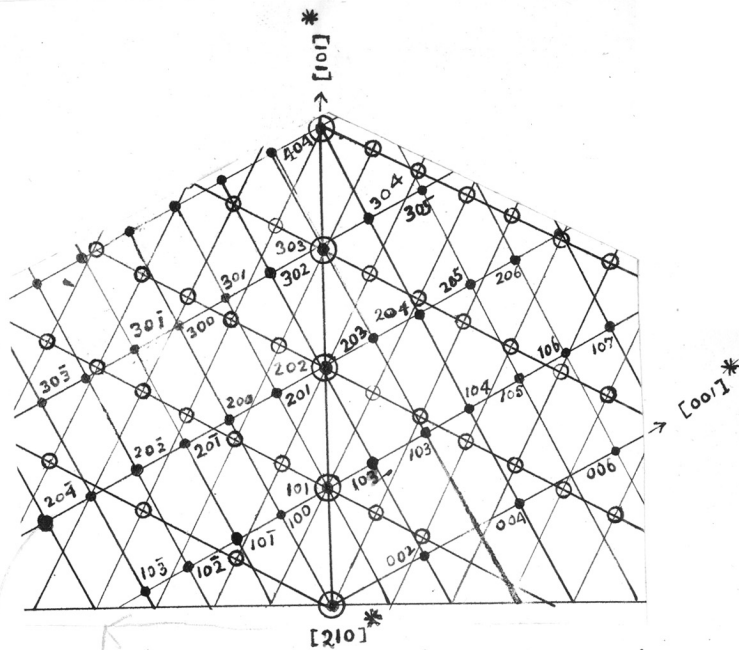
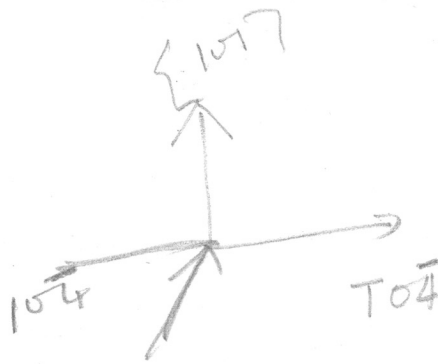
Beam along $[211]$ of (111) plane
" " $[101]$ of (001) "

fig 32

will give the rectangular pattern with sides in the ratio $= \sqrt{3} : \sqrt{8}$. The construction of the pattern has already been explained in Section I (Fig.2A).

The diffraction patterns, such as Fig.10, from the deposits of silver on the (001) face of copper show strong (101) type of hexagonal diffractions in the plane of incidence, and the hexagonal diffractions elsewhere in the pattern appear in the same vertical rows (Laue zones for 110 rows of the cubic crystals) as the cubic diffractions (Figs.10-12). This suggests that a $\langle 010 \rangle$ row of the hexagonal silver is parallel to a $\langle \bar{1}10 \rangle$ row of the (001) face of the copper substrate. These hexagonal crystals so orientated may occupy four equivalent positions with relation to the substrate. In two of these positions the electron beam passes along a $\langle 010 \rangle$ type of lattice row and the [001] row is orthogonal to the beam and is at an angle of 28° with the (101) face, i.e. with the substrate surface. The expected diffraction pattern, Fig.33, from the (101) face of the hexagonal crystals with the beam grazing along the [010] row, will be two sets of rectangular networks of spots with one diagonal of each set parallel to the plane of incidence. One set of rectangles is the reflection of the other set across the plane of incidence.

But these expected diffractions do not appear in the

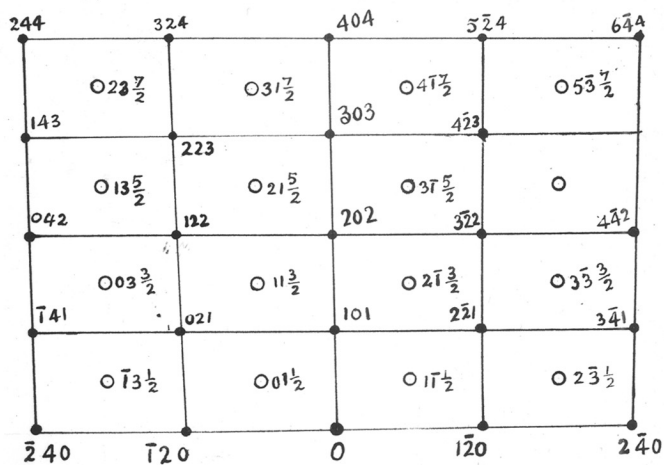


Reflection from (101) plane of hexagonal Crystal.
with the beam along [010] now.

fig 33

$$\begin{array}{r} 203 \\ 101 \\ \hline 104 \end{array} \quad \begin{array}{r} 101 \\ T04 \\ \hline 005 \end{array}$$

Diffraction pattern from (101)-orientated hexagonal crystal with beam at the grazing incidence at right angle to [010] row



• = The main diffractions from the (101) plane

○ = Diffractions corresponding to the reciprocal lattice points at lateral distances equal to $\frac{1}{2} \pm 1, 2, 3, \dots \times T_{[210]}$ from the plane of incidence.

along the shadow edge. These spots are indeed strong in Fig.10 and their form shows that they are due to transmission of the beam through the thin (0001) lamellae.

It is further noticed that there ^{are}/weaker and more diffuse spots which appear at the points of intersections of the diagonals of the rectangular pattern of strong spots. In view of the above evidence of the formation of the (0001) lamellae, these spots can be accounted for in terms of the very extensive elongation and almost coalescence of the reciprocal-lattice intensity regions along $[C]^*$.

Fig.35 shows the elongated intensity regions as mentioned above. These elongated intensity regions will touch the approximately plane central region (near the origin) of the Ewald sphere at points indicated by circular spots in Fig.34, which is the expected diffraction pattern from those two components of the (101) orientated hexagonal crystals situated with their $[010]$ row normal to the beam.

The complete pattern has been drawn in Fig.36 to the same scale for the cubic and hexagonal crystals. It agrees with the diffraction pattern obtained (Fig.10).

The hexagonal deposit of silver as mentioned above is not due to twinning of the cubic deposits on (111) planes. Such twinning has been observed in many cases in the following researches; but in this particular case of

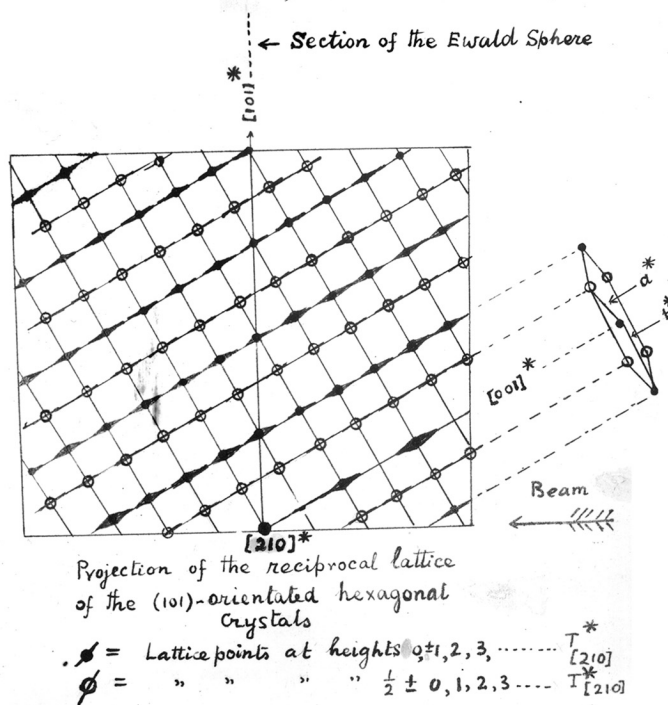


fig 35

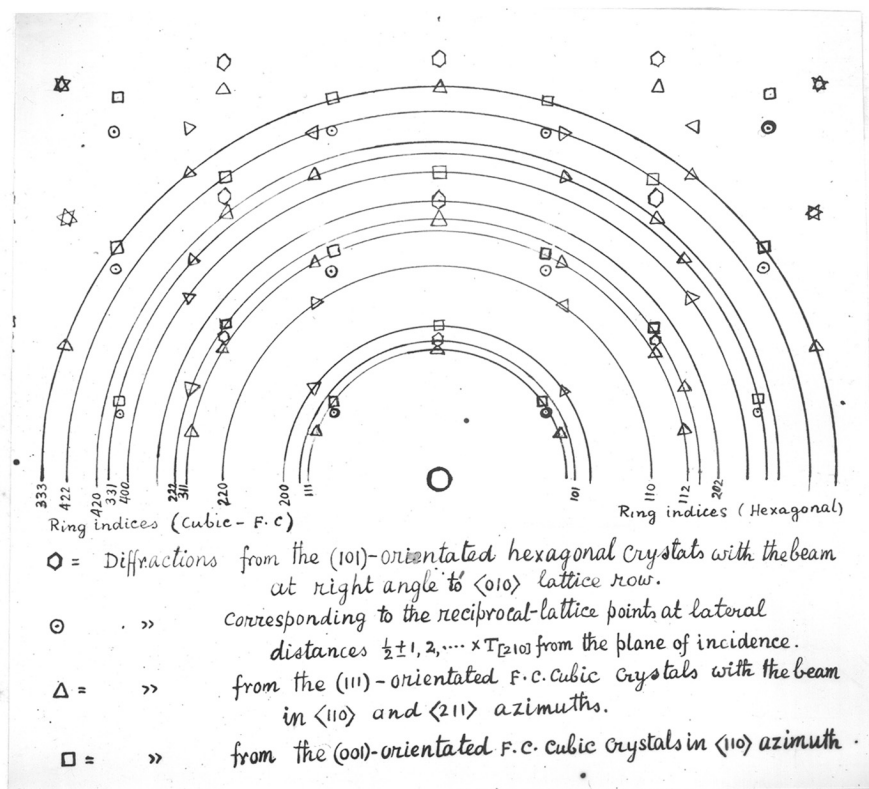


fig 36

deposition of silver on the (001) face, no formation of twinned cubic crystals was observed. If the hexagonal crystals had arisen from twinning of the cubic crystals the [001] lattice row of the hexagonal deposit would have been at an angle of $35^{\circ}16'$ with the (001) plane of the (001) orientated cubic deposit, since the angle between (001) and (111) planes of cubic crystals is $54^{\circ}44'$.

On the other hand if the (111) orientated cubic deposit crystals had twinned on another (111) face to form the hexagonal crystals then the [001] hexagonal row would have been inclined at 19° to the substrate surface. From the (101) orientation of the hexagonal crystals it is clear that the [001] hexagonal row is at an angle of 28° with the substrate surface. Hence the hexagonal deposits must be formed from the beginning as hexagonal crystals which are stabilised as such by their epitaxial relationship with the copper substrate.

Gold and Platinum deposits : In the case of gold only random and (111) orientated cubic crystals were formed and this orientation persisted even in the thicker deposits. The deposits of platinum contained random and (111)-orientated cubic crystals at the beginning (10 seconds deposit) but when the thickness was increased (001)-orientated deposits appeared. Gold and platinum did not form any hexagonal

crystals like silver. In some cases platinum in (001) orientation was twinned on the octahedral planes (Fig.27).

Origin of the (111) orientation of the Ag, Au and Pt deposits on Cu (001).

The (111) orientation of the deposits of all the three metals on the (001) face of copper is rather unusual at first sight. This apparent disagreement between the substrate effects in the present case and in electrodeposition (see Section I) can be explained by the fact that some cuprous oxide is always present on the (001) face of copper, which is a metal susceptible to easy oxidation. In some cases definite evidence of the presence of Cu_2O on the (001) face after electropolishing and etching was obtained (Fig.30). The spot pattern in this figure was identified as being due to Cu_2O . The value of the lattice dimension was calculated from the pattern by calibration with graphite. It was found to be $4.29 \pm 0.03 \text{ \AA}$ which fairly agrees, within the experimental error, with the normal value ($4.26^{kx}_{\text{\AA}}$) of the lattice dimension of Cu_2O (Wyckoff, 1948). In some cases Cu_2O was present along with the metal deposits formed from dilute solutions by reactions for longer times (Fig.20) and also from stronger solutions, especially when the deposit was random (Fig.23).

It is evident from Fig.30 that the Cu_2O crystals have (111) parallel to the substrate Cu (001) surface, with a 110 lattice row parallel to a 110 row of the Cu (001) face. The (111) orientation of the displaced-metal deposits on the (001) face is, therefore, due to the substrate influence produced by Cu_2O . The nature of the substrate influence on deposits formed by chemical displacement is thus similar to that of the substrate effect on electrodeposits. The substrate effects observed in the present researches are further discussed in Section IV.

The lattice dimensions of the deposits of the three metals (Table 14) were determined by calibration with graphite (Finch and Wilman, 1937). Silver was found to have effectively the normal lattice constant. The lattice dimension of gold was found to be appreciably low, especially for thin deposits. The lattice dimension of platinum deposits was always found to be much lower than the normal value, thus indicating the formation of an alloy of platinum with the substrate copper. The lattice dimensions of these metals are more fully discussed in Section IV.

B. Displacement from Complex Baths on the (001) Face of Copper.

The results of displacement of silver and gold from cyanide baths are shown in Table 5 and Figs.37-48. Platinum

Table 5.

Displacement from Cyanide Baths on (001) Face
of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*.	Figure
<u>A. Silver.</u>				
A/25	1 sec	No colour	C(111)	37
A/10	1 sec	No colour	C(111)	38-39
A/10	30 sec	No colour	C(001)	40
A/10	5 min	Silvery	C(001)	41
A	1 sec	Very faintly silvery.	C(001)	42
<u>B. Gold</u>				
B/100	5 sec	No colour	Cu ₂ O(111)	similar to 30.
B/25	10 sec	No colour	C(111)	43
B/25	30 sec	No colour	C(111)	-
B/25	1 min	Very light golden	C(001)	44
B/25	10 min	Golden	C(001)	45
B/10	5 sec	No colour	C(111)	46
B/10	5 min	Light golden	C(001)	47

* C(111) = Cubic (111)//Cu(001), $\langle 110 \rangle_{\text{cubic}}$ // $[110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

C(001) = Cubic (001)//Cu(001), $\langle 100 \rangle_{\text{cubic}}$ // $\langle 100 \rangle_{\text{Cu}}$

Silver Displaced from Cyanide Bath on (001) Face of Copper.

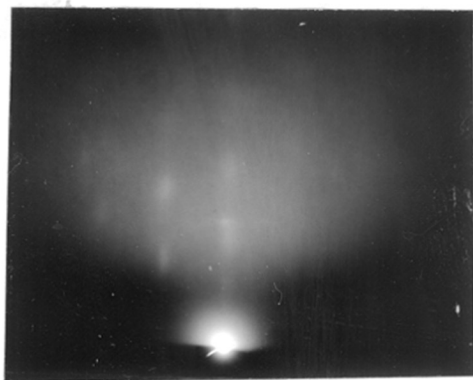


Fig. 37
A/25 1 sec
azimuth [001]_c

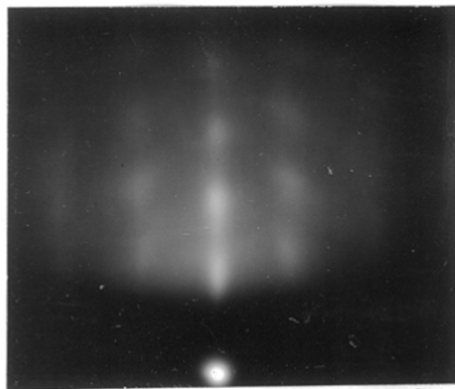


Fig. 38
A/10 1 sec
azimuth [001]_c

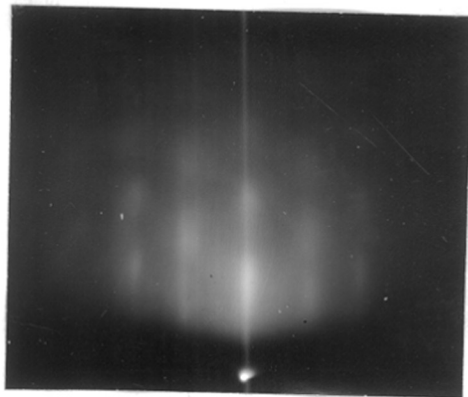


Fig. 39
A/10 1 sec
azimuth [110]_c

Silver Displaced from Cyanide Bath on (001) Face of Copper.



Fig. 40
A/10 30 sec
azimuth $[001]_a$

Fig. 42

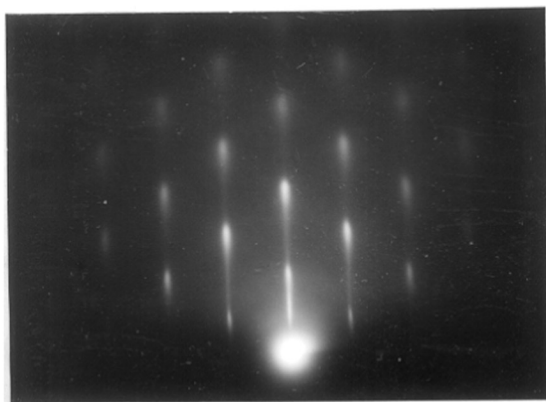


Fig. 42
A 1 sec
azimuth $[110]_a$

Fig. 45

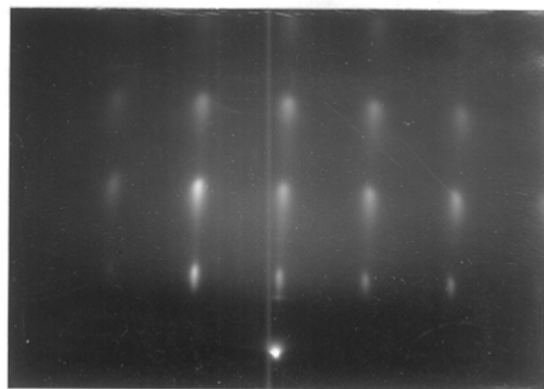


Fig. 41
A/10 5 mins.
azimuth $[001]_a$

Fig. 44

Gold Displaced from Cyanide Bath on (001) Face of Copper

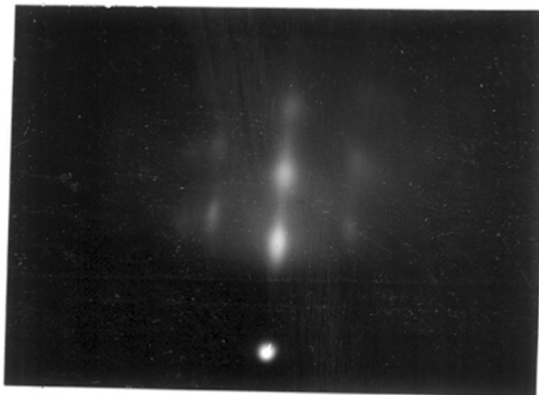


Fig 43

B/25 $\lambda = 0.071$ nm
10 sec
azimuth $[001]_c$



Fig 44

B/25 $\lambda = 0.071$ nm
1 min
azimuth $[001]_c$

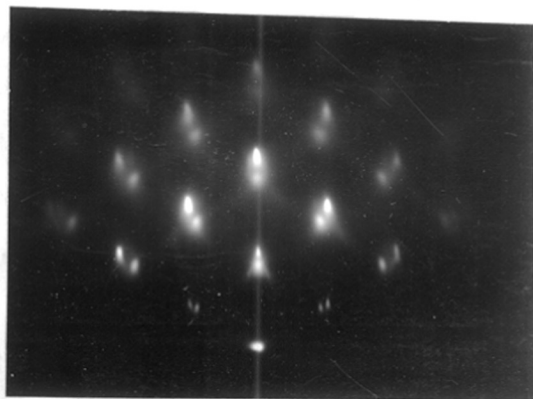


Fig 45

B/25 $\lambda = 0.071$ nm
10 mins.
azimuth $[110]_c$

Gold Displaced from Cyanide Bath on (001) Face of Copper.



Fig. 46
B/10 5 sec
azimuth $[001]_{\text{Cu}}$

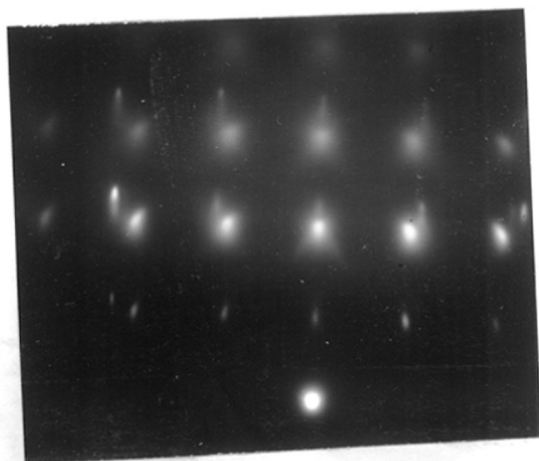


Fig. 47
B/10 5 mins.
azimuth $[001]_{\text{Cu}}$

was found to be not displaced on copper from the cyanide bath. From the diffraction patterns it is evident that only two-degree orientated crystals are formed and no random deposit was obtained, such as was found in the case of deposition from simple baths. The deposits of both silver and gold, when thin, appeared in (111) orientation on the (001) copper face, but the orientation of the surface regions of the thick deposits of both the metals was parallel to that of the substrate. There is therefore an apparent change in orientation of the deposits from (111) to (001) with relation to the substrate. The (111) orientation of the deposit is evidently due to the influence of the Cu_2O , such as was found in the case of the deposition from the simple baths. Definite evidence of the formation of cuprous oxide was also obtained from dilute cyanide baths (Table 5).

There is a general similarity in orientation of the deposits of gold and silver on this face of copper and also a similar increase in crystal size with increasing time of deposition. On the other hand there are some differences in the nature of the silver and gold deposits. The diffraction patterns from both short time and long time deposits of gold show spots due to the copper substrate and correspond to atomically rough surfaces. Similar spots due to the substrate are, however, not found in the

diffraction patterns obtained from the silver deposits, and there the elongated diffractions show the surface to be highly smooth and parallel to the substrate surface. Silver deposits form a uniform layer on the substrate surfaces whereas gold deposits are not uniformly distributed.

The diffraction spots due to the copper substrate in the patterns obtained from specimens of gold deposits for longer times are bifurcated at the lower end (Fig.45). Similar bifurcation of the diffraction spots was observed when the face was etched for 10 minutes in a solution of KCN alone, of strength equal to the calculated strength of the free KCN in the solution of gold used for displacement. It is therefore concluded that the effect is due to the formation of facets on the copper due to etching by the excess KCN. The observed angle between the facets and the $\{001\}$ planes of copper is found to be $25^{\circ}30'$, whence it follows that the facets are of $\{311\}$ type.

In the case of the gold deposits some additional diffraction spots were observed (Fig.47). These additional diffractions were due to secondary diffraction of the main primary diffractions as they pass through neighbouring parts of the deposit. The lattice dimension of silver (Table 14) was found to be normal, as in the case of deposition from the simple bath. The lattice dimension

of the gold was found to be appreciably lower when the deposit was thin and showed a tendency to increase with the thickness of the deposit. This is further discussed in Section IV.

2. Displacement on the (111) Face of Copper.

A. From Simple Baths.

The results of displacement of silver, gold and platinum from simple baths (Table 1) are shown in Tables 6-8 and Figs. 49-67. The results are much more straightforward than those obtained on the (001) face.

In this case also the deposits contained both random crystals and orientated face-centred cubic crystals having relatively perfect two-degree orientation with relation to the substrate. No change in orientation of the deposit crystals with increase in thickness was found, such as occurred in the case of deposition on the (001) face. There was evidence of the formation of Cu_2O on this face also (Fig.60) but the Cu_2O produced no change in orientation of the deposits like that in the case of the (001) face. The reason is obvious from the diffraction pattern (Fig.60) given by the Cu_2O on this face. The cuprous oxide had grown with its axes parallel to those of the copper substrate;

Table 6.

Displacement of Silver from Silver Nitrate Solution
on (111) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals *	Figure
M/2000	1 sec	No colour	C(111) + R + H	49
M/2000	30 sec	No colour	C(111) + R + H	50
M/2000	5 min	Grey	R + C(111) + H	51
M/2000	10 min	Deep grey	R + C(111) + H	52
M/100	1 sec	Greyish	R + C(111)	53
M/10	1 sec	Deep grey	R + trace of C(111) + H	54

* C(111) = cubic(111)// Cu(111), $\langle 110 \rangle_{\text{cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

R = Random (cubic)

H = hexagonal (0001) // 111 Cu (See discussion on page 37)

Table 7.

Displacement of Gold from Gold Chloride Solution
on (111) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
M/2000	5 sec	No colour	C(111) + R	55
M/2000	10 sec	No colour	C(111) + R	-
M/2000	30 sec	No colour	C(111) + R	56
M/2000	2 min	Greyish	C(111) + R	-
M/2000	7 min	Grey	R + Cu ₂ O(111)	57
M/1000	30 sec	No colour	C(111) + R	58
M/500	30 sec	Greyish	R + C(111)	59
M/100	30 sec	Grey	R + Cu ₂ O(random)	similar to 23

* C(111) = cubic(111)// Cu(111), $\langle 110 \rangle_{\text{cubic}} // [110]_{\text{Cu}}$ or $[\bar{1}\bar{1}0]_{\text{Cu}}$

R = random(cubic)

Table 8.

Displacement of Platinum from Chloroplatinic Acid
Solution on the (111) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
M/10,000	30 sec	No colour	$\text{Cu}_2\text{O}(111) +$ trace of C(111)	60
M/4000	2 sec	No colour	C(111)	61
M/4000	10 sec	No colour	C(111) + R(little)	62
M/4000	30 sec	No colour	C(111) + R	63
M/4000	10 min	Grey	C(111) + R	64
M/1000	2 sec	No colour	C(111) + R	65
M/1000	10 sec	No colour	C(111) + R	-
M/1000	30 sec	very light greyish	C(111) + R	66
M/1000	3 min	grey	R + trace of C(111)	67
M/1000	10 min	grey	R	
M/200	30 sec	grey	R + trace of C(111)	

* C(111) = Cubic(111) // Cu(111), $\langle 110 \rangle_{\text{cubic}}$ // $[110]_{\text{Cu}}$ or $[\bar{1}10]_{\text{Cu}}$

Displacement of Silver from Silver Nitrate Solution
on (111) Face of Copper.

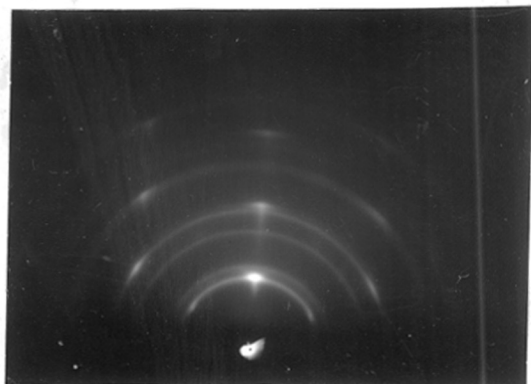


Fig. 49
M/2000 1 sec
azimuth $[211]_{\text{Cu}}$

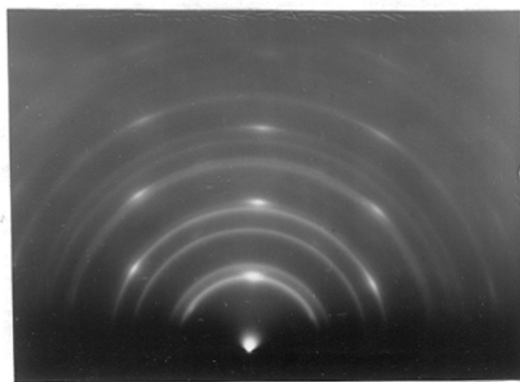


Fig. 50
M/2000 30 sec
azimuth $[211]_{\text{Cu}}$

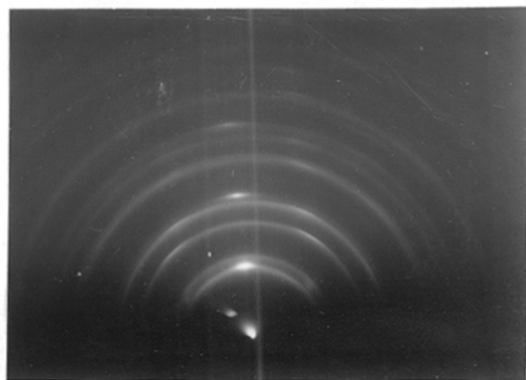


Fig. 51
M/2000 5 mins
azimuth $[110]_{\text{Cu}}$

Displacement of Silver from Silver Nitrate Solution
on (111) Face of Copper.

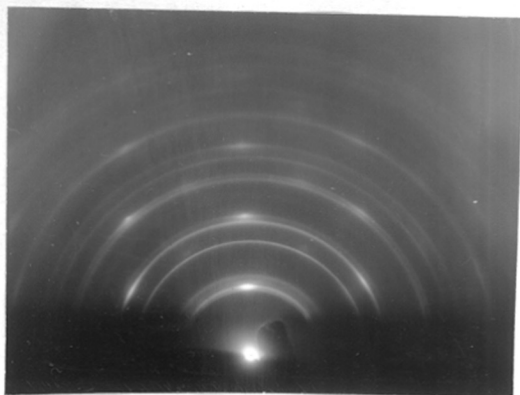


Fig. 52
M/2000 10 mins
azimuth $[211]_{Cu}$

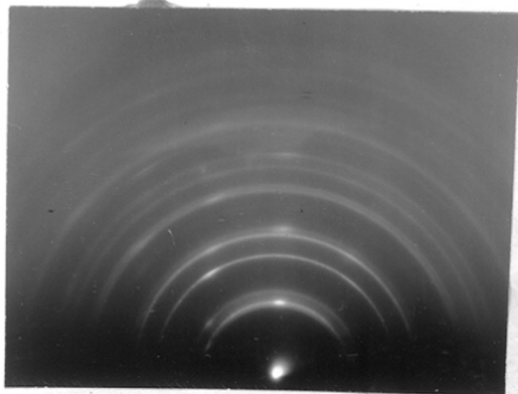


Fig. 53
M/100 1 sec
azimuth $[110]_{Cu}$

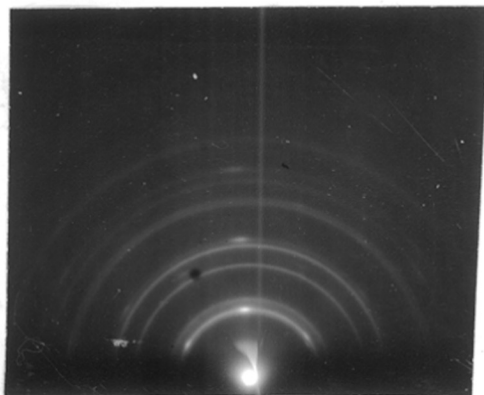


Fig. 54
M/10 1 sec

Displacement of Gold from Gold Chloride Solution
on (111) Face of Copper.

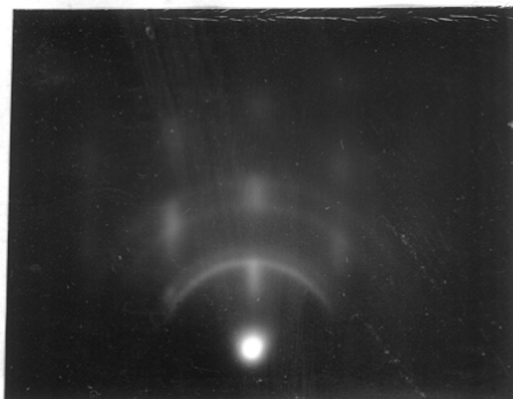


Fig. 55
M/2000 5 sec
azimuth [110]_{Cu}

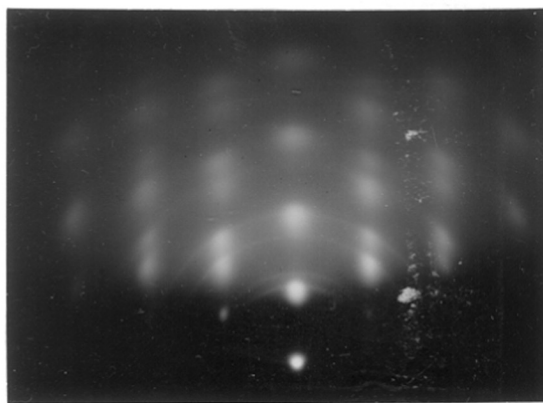


Fig. 56
M/2000 30 sec
azimuth [110]_{Cu}

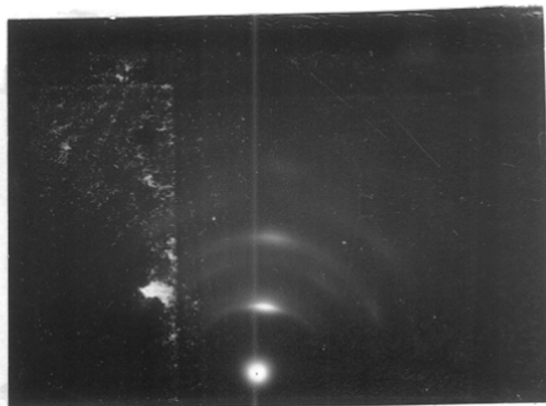


Fig. 57
M/2000 7 mins.
azimuth [211]_{Cu}

gold from gold chloride on (111) face

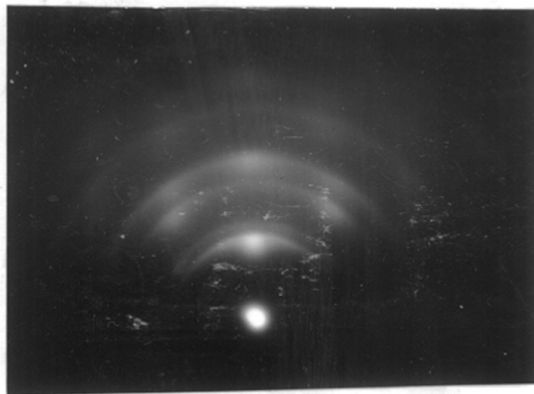


Fig. 58
M/1000 30 sec
azimuth [110]_{cr}

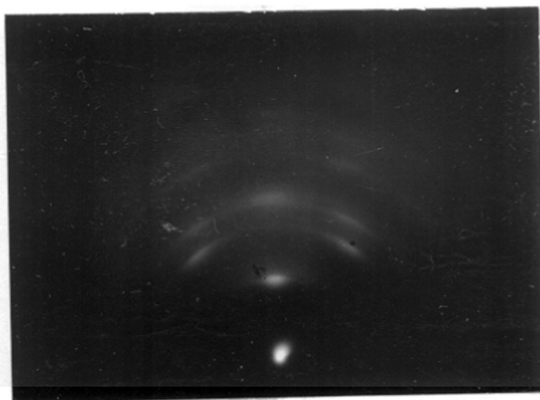


Fig. 59
M/500 30 sec
azimuth [110]_{cr}

Displacement of Platinum from Chloro-platinic Acid
on (111) Face of Copper.



Fig. 60
M/10000 30 sec
azimuth [211] *cu*

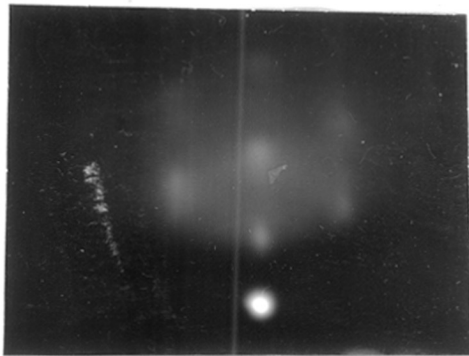


Fig. 61
M/4000 2 sec
azimuth [110] *cu*



Fig. 62
M/4000 10 sec
azimuth [110] *cu*

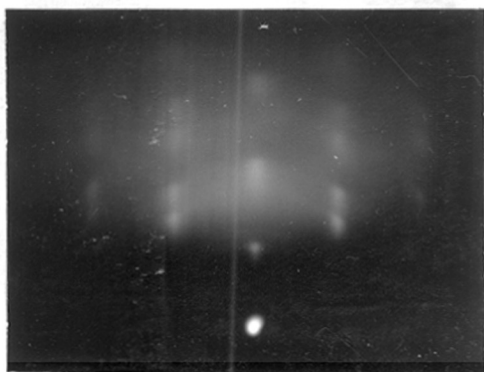


Fig. 63
M/4000 30 sec
azimuth [110] *cu*

Pt from chloroplatinic acid on (111) face

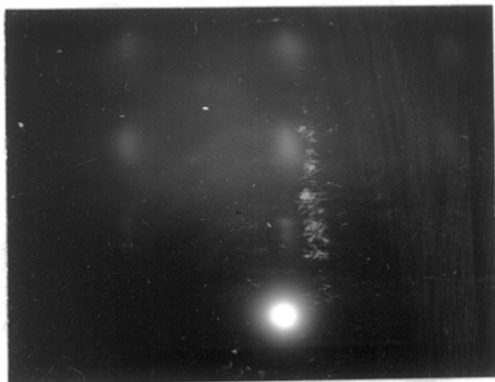


Fig. 64
M/4000 10 min
azimuth $[211]_{cu}$

Fig. 67

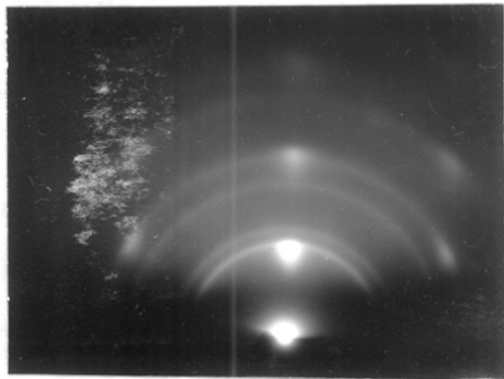


Fig. 65
M/1000 2 sec
azimuth $[211]_{cu}$



Fig. 66
M/1000 30 sec
azimuth $[211]_{cu}$

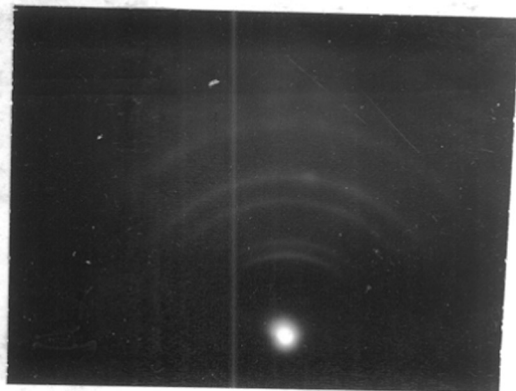


Fig. 67
M/1000 3 min
azimuth $[211]_{cu}$

consequently these deposit crystals which followed the orientation of the Cu_2O were also orientated with their axes parallel to those of the substrate.

There was, however, a point of particular interest observed in the orientation of some of the deposits. Two equivalent azimuthal orientations of the (111)-orientated deposit crystals often occurred on the (111) copper face in mirror symmetrical relation to the vertical plane through the [110] azimuth, but one of the orientations (the "antiparallel" one) appeared in greater proportion in some cases, especially thin deposits and those from dilute solutions (Fig. 55). This must be due to the substrate influence of the Cu_2O because the cuprous oxide formed on the copper (111) face had also in some cases only this "antiparallel" orientation with relation to the substrate (Fig. 6). The crystals of the metal deposit thus tended to follow the orientation of the cuprous oxide. This fact lends further support to the view that it is largely the Cu_2O which exerts the main influence on the orientation of the deposit crystals, in the initial stages.

In the case of silver displaced from silver nitrate solution a small proportion of hexagonal crystals was found to be formed, as in the case of deposition on the (001) face. From the patterns, Figs. 49-54, it is concluded that the orientation of this hexagonal part of the deposits is such

that the (0001) plane is parallel to an octahedral plane of the cubic silver crystals whose normal is inclined at $19^{\circ}30'$ to the copper substrate (111) surface. In this position those hexagonal crystals which have their c axis in the plane of incidence when the beam is along a symmetrical azimuth of the substrate, as in Figs. 49, 50 and 52, give rise, near the undeflected beam, to a pattern of diffractions some of which coincide with the strong cubic diffractions in the $\sqrt{3}/3$ -rectangular array, while the remaining diffractions lie at the centre of these rectangles. The latter set of diffractions lie on ring positions corresponding to the hexagonal structure. These conclusions follow by imagining first the hexagonal silver crystal with a (100) plane parallel to the substrate and its c axis along the beam; then rotating this crystal through $\cos^{-1}(2\sqrt{2}) = 19^{\circ}30'$ about the [010] axis, which lies in the substrate plane and normal to the beam. If the reciprocal lattice intensity regions are elongated along c^* , corresponding to a (0001)-lamellar shape of the hexagonal crystals, then these elongated regions intersect the Ewald sphere at the points described above.

Further evidence for such an elongation of the reciprocal lattice intensity regions is provided by Fig. 54, which was obtained at an azimuth a few degrees away from the symmetrical $\langle 211 \rangle$ type of azimuth. Here the short arcs lying between the cubic 220 and 311 rings occur practically

midway between these rings instead of close to the 220 ring as in Figs. 49, 50 and 52.

The hexagonal diffractions of 101 type observed in Fig. 51, in the symmetrical azimuth, also support the above conclusions on the orientation of the hexagonal crystals. Thus it seems clear that these hexagonal crystals are of lammellar type and are probably associated with abnormal stacking sequence of the initially-formed cubic crystals whose lattice is parallel to that of the copper substrate.

The effect of the thickness of the deposits of gold, silver and platinum on the orientation is found to be normal as in the case of the deposition from similar baths on the (001) face of copper; the proportion of random deposits increased with increase in the thickness. The deposits of silver generally formed bigger crystals in a given time, than those of gold and platinum, as is evident from the patterns. The values of the lattice dimensions were found to be the same as in the case of deposits from similar baths on the (001) face of copper.

B. Displacement from the Complex Baths on the (111) Face of Copper.

As in the case of the displacement on the (001) face, platinum was not displaced from the complex cyanide bath.

The deposits of silver and gold showed perfect epitaxial growth with relation to the substrate. The results are shown in Table 9 and Figs. 68-81. Like the deposits from the simple baths also these deposits did not show any change in orientation with increasing time of deposition, as was observed in the case of the deposits on (001) face of copper. The reasons have already been explained in connection with deposition on this face from simple baths.

As in the case of the deposition from simple baths some of the deposits from cyanide baths also showed a greater proportion of antiparallel orientation, as is evident from their diffraction patterns (Fig.74). When the deposit was thick both the 111 orientations generally appeared in equal proportions. The reasons have already been explained.

Like the gold deposits from the cyanide bath on the (001) face of copper, the deposits of gold on this face also gave diffraction patterns showing diffractions from both the deposit and the substrate, and like the silver deposits on the (001) face the silver deposits on this face did not show diffractions from the substrate. The reasons were the same as described previously, i.e. deposits of gold were not uniform like those of silver. In this case there was no clear formation of facets on the substrate such as were formed on the (001) face.

Table 9.

Displacement of Ag and Au from the Cyanide Baths
on the (111) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
<u>A. Silver.</u>				
A/25	1 sec	No colour	C(111)	68
A/25	30 sec	No colour	C(111)	69
A/25	5 min	Light silvery	C(111)	70-71
A/25	10 min	Silvery	C(111)	72
A/10	1 sec	No colour	C(111)	73
A	1 sec	Very light silvery	C(111)	74
<u>B. Gold.</u>				
B/25	5 sec	No colour	C(111)	75
B/25	30 sec	No colour	C(111)	-
B/25	1 min	No colour	C(111)	76
B/25	5 min	light golden	C(111)	77
B/25	10 min	Golden	C(111)	78
B/5	5 sec	No colour	C(111)	79
B	5 sec	No colour	C(111)	80-81

* C(111) = Cubic(111) // Cu(111), $\langle 110 \rangle_{\text{cubic}}$ // [110] Cu^{or} [110]

Displacement of Silver from the Cyanide Bath on
the (111) Face of Copper.

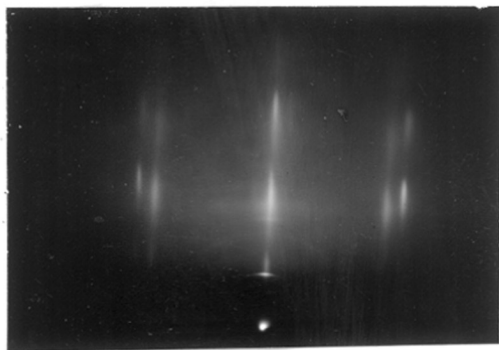


Fig.72
A/25 10 mins
azimuth [211]_m

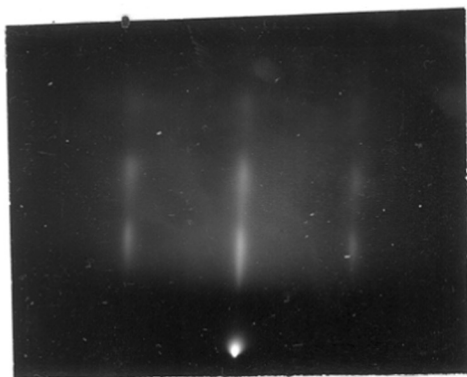


Fig.73
A/10 1 sec
azimuth [211]_m

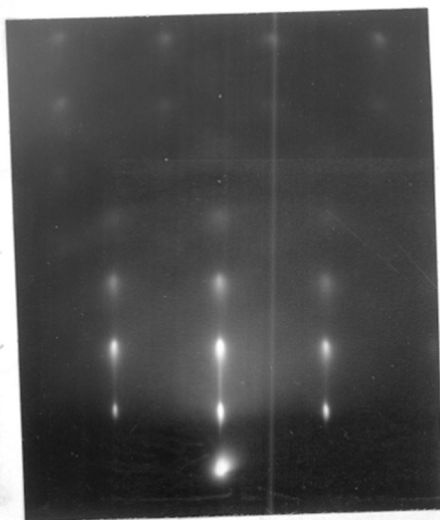


Fig.74
A 1 sec
azimuth [211]_m

Displacement of Gold from the Cyanide Bath on
the (111) Face of Copper.

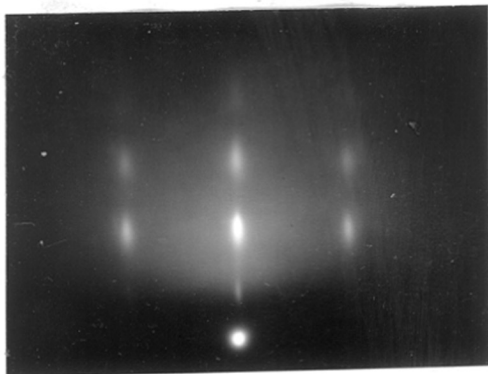


Fig. 75
B/25 5 sec
azimuth [211]_{an}



Fig. 76
B/25 1 min
azimuth [211]_{an}

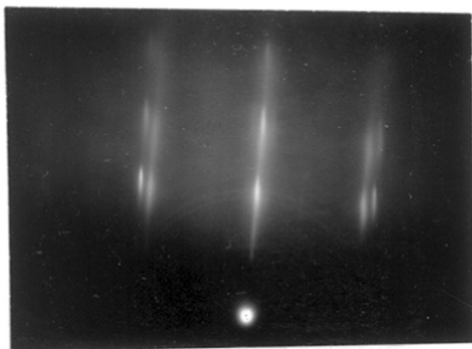


Fig. 77
B/25 5 mins.
azimuth [211]_{an}



Fig. 78
B/25 10 mins.
azimuth [211]_{an}

Displacement of Gold from the Cyanide Bath on
the (111) Face of Copper.

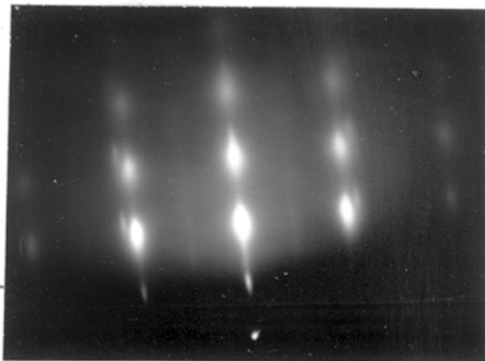


Fig.79
B/25 5 mins.
azimuth [211]_a

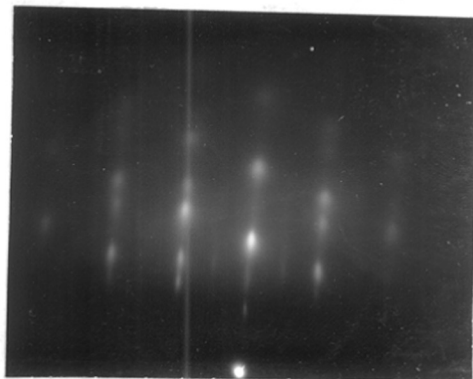


Fig.81
B 5 sec
azimuth [110]_a



Fig.80
B 5 sec
azimuth [211]_a

There was, however, indication of the formation of projections or steps on this face of the substrate due to etching by KCN. The more intense points at the upper end of the elongated diffraction spots due to the substrate (Fig.78) are due to transmission of the electron beam through such projections.

As in the case of the deposits on the (001) face there are additional diffractions due to secondary diffraction from some gold deposits on this face also (Fig.77) the cause being that mentioned previously. The values of the lattice dimensions of silver and gold deposits have been found to be similar to those of the deposits on the (001) face. This is further discussed in Section IV.

It is clear from the diffraction patterns that most of the surface of the substrate was atomically smooth although it was more or less wavy. The highly elongated diffraction spots indicating a greater degree of refraction are due to extreme general smoothness of the surface. The degree of refraction was greater in the case of deposition of gold from the cyanide bath, especially for longer duration. It is likely to be due to etching by the free KCN present in the bath.

One particular feature of some of the diffraction patterns obtained from gold deposits from the cyanide bath

could not be explained. In some patterns (Figs. 79, 80) some unexpected diffractions appeared midway between the normal diffraction spots. These could not as yet be clearly accounted for and further study is necessary to clarify them.

3. Displacement of Silver, Gold and Platinum on the (110) Face of Copper.

A. From the Simple Baths.

The results are set forth in Tables 10-12 and Figs. 82-99. The results of displacement on this face were simple and straightforward. As on the other faces, both random and orientated deposits crystals were obtained and the orientated fraction of the deposit had perfect epitaxial growth.

There was evidence of the formation of Cu_2O on this face as well, especially from the simple bath of gold (Fig. 87) but it produced no change in orientation of the deposits such as was observed in the case of deposition on the copper (001) face because the orientation of the Cu_2O was parallel to the substrate copper as was observed in the case of the (111) face. Cuprous oxide orientated with its axes parallel to those of the copper substrate was formed on the copper (110) face in the case of the deposition of gold for longer time (Fig. 90). The electron diffraction arc pattern was due to Cu_2O , which can be readily identified from the relative spacings of the

Table 10.

Displacement of Silver from Silver Nitrate
Solution on (110) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the deposit Crystals.	Figure
M/2000	1 sec	No colour	C(110) + R	82-3
M/2000	30 sec	No colour	C(110) + R	84
M/2000	10 min	Grey	R + trace of C(110)	85
M/500	1 sec	very faint greyish	C(110) + R	86
M/100	1 sec	Grey	R	

Lattice dimension of silver displaced from M/2000 solution for one second is normal (4.077 Å.)

C(110) = cubic (110) // Cu(110), $\langle 110 \rangle_{\text{cubic}} // \langle 100 \rangle_{\text{Cu}} // [100]_{\text{Cu}}$

R = Random (cubic).

Table 11.

Displacement of Gold from Chloro-auric acid on
the (110) face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
M/4000	30 sec	No colour	Cu ₂ O (110)	87
M/2000	10 sec	No colour	C(110)	88
M/2000	30 sec	No colour	C(110) + R	
M/2000	3 min	Greyish	C(110) + R	89
M/2000	7 min	Grey	R + Cu ₂ O (110)	90
M/1000	30 sec	very faint grey	C(110) + R	91
M/500	30 sec	Light-grey	R + Cu ₂ O(R)	92

* C(110) = cubic(110) // Cu(110), $\langle 110 \rangle_{\text{cubic}}$ // $\langle 110 \rangle_{\text{Cu}}$

R = random (cubic)

Table 12.

Displacement of Platinum from Chloroplatinic Acid
on the (110) Face of Copper.

Concentration	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
M/4000	30 sec	No colour	C(110)	93
M/2000	5 sec	No colour	C(110)	94
M/2000	10 sec	No colour	C(110)	95
M/2000	30 sec	No colour	C(110)	96-97
M/2000	2 min	Light grey	R + C(110)	98
M/2000	5 min	Grey	R + C(110)	
M/1000	30 sec	very faint grey	C(110) + R	99

* C(110) = cubic(110) // Cu(110), $\langle 100 \rangle_{\text{cubic}}$ // [100] Cu

R = random (cubic) deposit.

Displacement of Silver from AgNO_3 Solution on
the (110) Face of Copper.

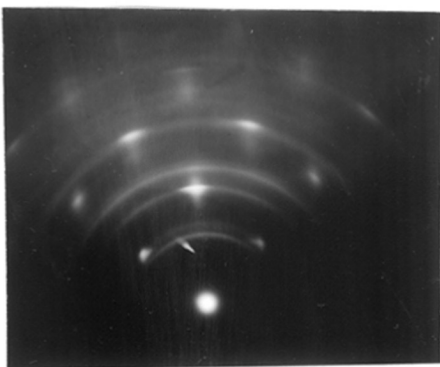


Fig. 82
M/2000 1 sec
azimuth [001] μ

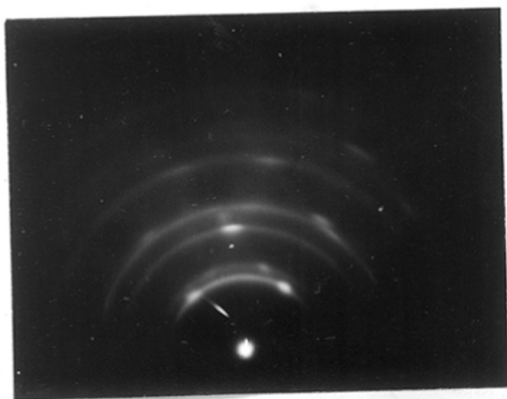


Fig. 83
M/2000 1 sec
azimuth [110] μ

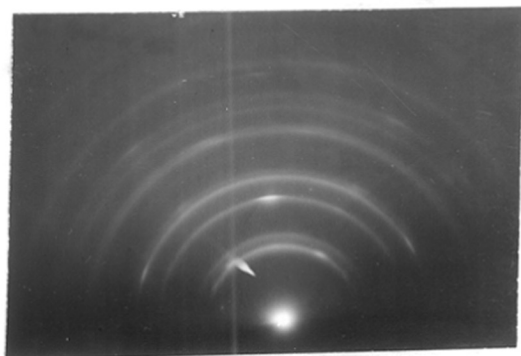


Fig. 84
M/2000 30 sec
azimuth [110] μ

Displacement of Gold from Gold Chloride on
the (110) Face of Copper.

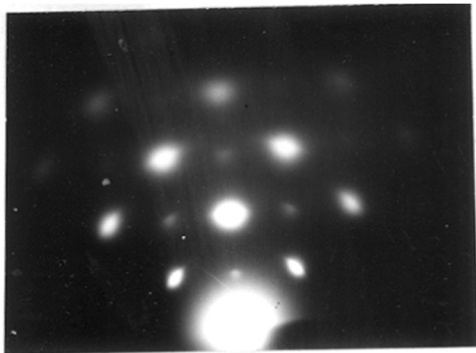


Fig. 87
M/4000 30 sec
azimuth [001]

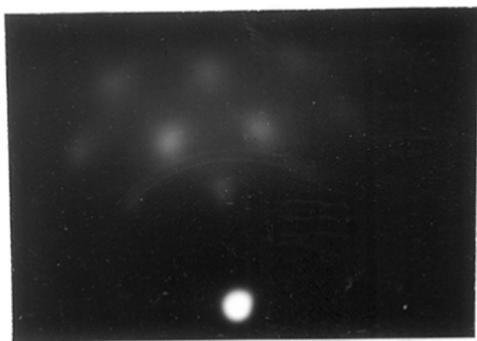


Fig. 88
M/2000 10 sec
azimuth [110]

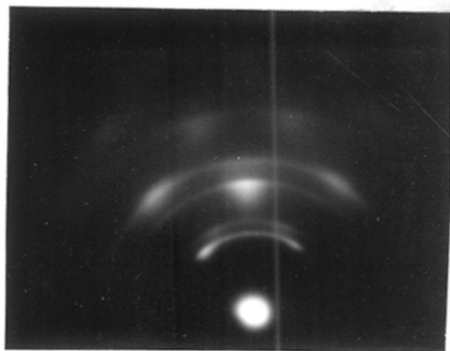


Fig. 89
M/2000 3 mins.
azimuth [110]

Displacement of Gold from Gold Chloride on
the (110) Face of Copper.

An

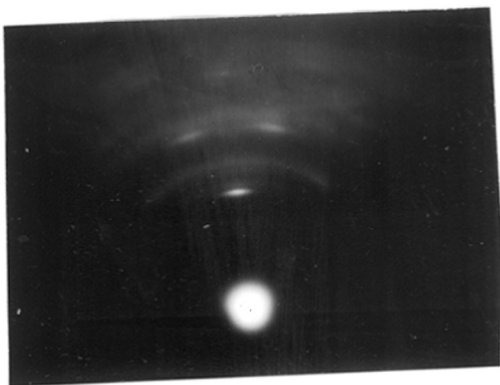


Fig. 90
M/2000 7 mins.
azimuth [001]

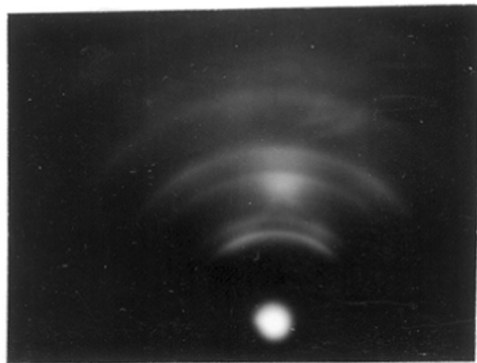


FIG. 91
M/1000 30 sec
azimuth [110]

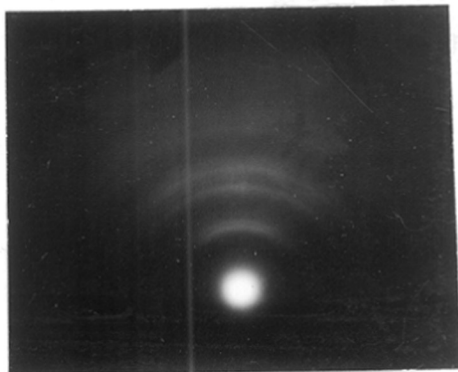


Fig. 92
M/500 30 *su*

Displacement of Silver from the Cyanide Bath on
the (111) Face of Copper.

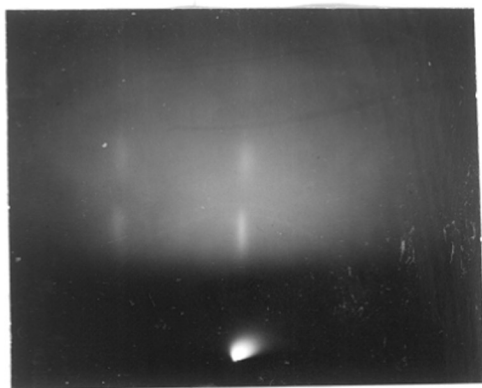


Fig.68
A/25 1 sec
azimuth [211] *an*

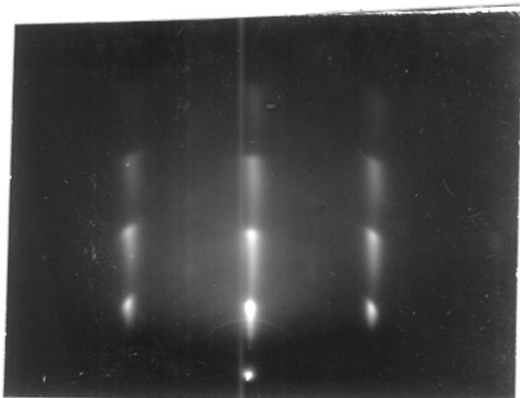


Fig.69
A/25 5 mins.
azimuth [211] *an*



Fig.70
A/25 5 mins.
azimuth [110] *an*



Fig.71
A/25 5 mins
azimuth [110] *an*

Displacement of Platinum from Chloroplatinic Acid on
the (110) Face of Copper.



Fig. 93
M/4000 30 sec
azimuth [001]



Fig. 94
M/2000 5 sec
azimuth [110]

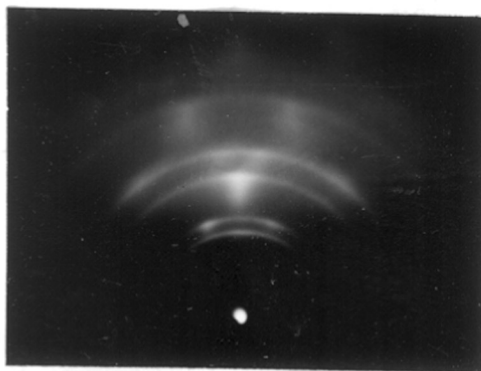


Fig. 95
M/2000 10 sec
azimuth [110]

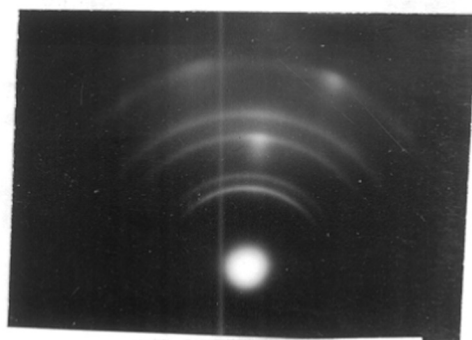
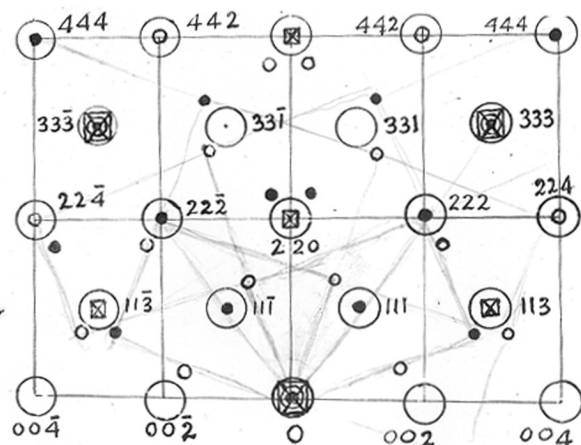


Fig. 96
M/2000 30 sec
azimuth [001]



○ = The main diffractions from the (110)
 face of platinum in $\langle 110 \rangle$ azimuth
 □
 ○
 ●
 × } = The diffraction spots from the
 twins formed on the
 octahedral planes.

fig 94 A

Displacement of Platinum from Chloroplatinic Acid on
the (110) Face of Copper.



Fig. 97
M/2000 30 sec
azimuth [110]

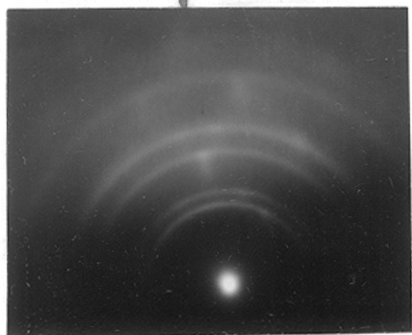


Fig. 98
M/2000 2 mins.
azimuth [110]

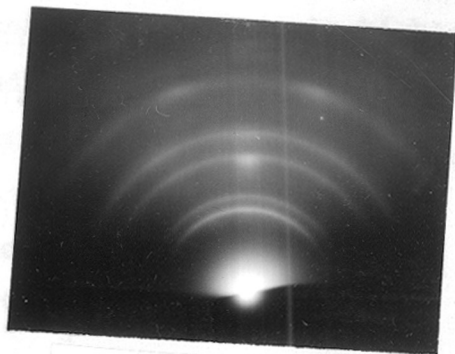


Fig. 99
M/1000 30 sec
azimuth [001]

rings due to Cu_2O and due to the gold, which appeared as random crystals.

The deposits of all the three metals on this face of copper contained (111) -twinned crystals, as is evident from some of the patterns. The twin spots appeared prominently in the diffraction patterns obtained in the [110] azimuth of the substrate (Fig.97). Similar (111) twinning has been observed by Cochran (1936) in electrodeposited nickel on copper, and by Goche and Wilman (1939) and other workers on silver crystals formed by condensation from vapour on a hot cleavage face of NaCl. A theoretical pattern showing (111) twinning of face-centred cubic crystals is shown in Fig.97A, and it agrees fully with the diffraction pattern obtained with the beam in the [110] azimuth of the substrate.

The proportion of twinning was found to be highest in the deposits of platinum, and among the three faces of the copper substrate, the (110) face produced the largest proportion of the twinned crystals. The value of the lattice dimensions were found to be of the same order as in the case of the deposits on the other faces of copper (Table 14).

In the deposits from simple baths the effect of the deposit thickness on the orientation was the same as in the

other cases of deposition i.e. the proportion of the random
Displacement of Silver from Cyanide Bath on the
crystals in the deposit increased with increase in the
(110) face of copper.
 thickness until the crystals in the uppermost regions of the
 deposits were completely randomly disposed.

B. Displacement from the Complex Baths.

Even gold formed very little deposit from the
 cyanide bath on the (110) face of copper. The deposits of
 silver had perfect two-degree orientation with relation to
 the substrate. The results are shown in Table 13 and Figs.
 100-104.

There was evidence of (111) twinning (Fig. 103) as in
 the case of deposition from the silver nitrate bath. The
 size of the silver crystals increased with increase in the
 thickness of the deposits. Among the three faces of copper
 on which deposition by displacement has been studied the
 (110) face appeared to be the least active. This face
 appeared most polished of the three faces, and this may be
 the main cause of its relative inactivity.

Displacement of Silver from Cyanide Bath on
the (110) face of Copper

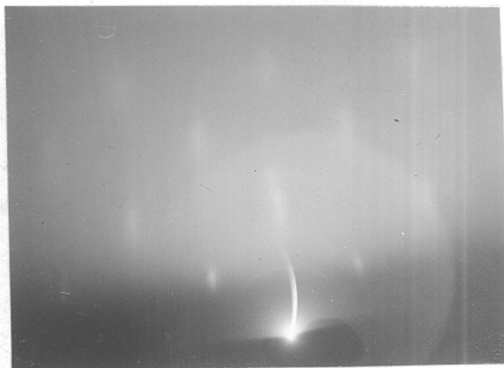


Fig.100
A/25 1 sec
azimuth [001]_{cu}



Fig.101
A/25 10 mins
azimuth [001]_{cu}

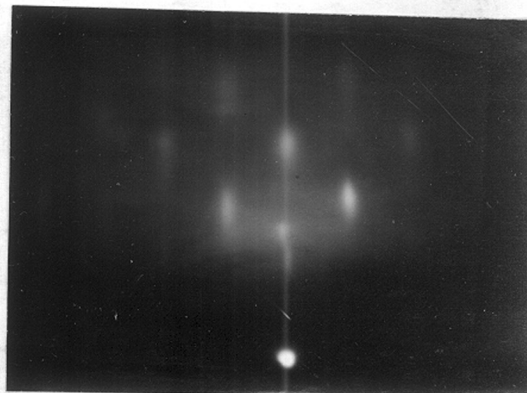


Fig.102
A/10 1 sec
azimuth [001]_{cu}

Displacement of Silver from Cyanide Bath on
the (110) Face of Copper.

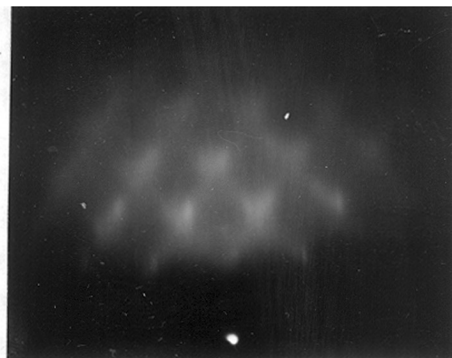


Fig.103
A/10 1 sec
azimuth $[110]_{\text{Cu}}$



A Fig.104
1 sec
azimuth $[001]_{\text{Cu}}$

Table 14.

Comparative view of the results of Chemical Displacement of Silver, Gold and Platinum from Simple and Complex Baths on Copper.

Page	Displacement from simple baths.				Displacement from cyanide baths.			
	Bath	Time secs	Nature of the deposit	Lattice Dimension A.	Bath	Time secs	Nature of the deposit	Lattice Dimension kx
001	H/2000 AgNO ₃	1	C(001)+C(111) +H(101)+R	Normal	A/10 AgCN KCN	1	C(111)	4.07±.02
		300	C(001)+C(111) +H(101)+R	"		30	C(001)	
		600	^{v-tlle} R+C(001) ^{+little} H(101)	"		300	C(001)	4.08±.02
	H/2000 gold chloride	10	C(111)+R	4.01±.02	B/25 AuCN KCN	10	C(111)	4.01±.01
		180	R+O(111)			60	C(001)	4.03±.01
		420	R+Cu ₂ O(111)	4.06±.02		600	C(001)	4.04±.01
111	H/2000 chloro- platinic	10	C(111)+R	3.79±.02	No displacement of platinum from cyanide baths.			
		30	C(001)+ C(111)+R					
		300	C(001)+R					
		600	R					
	H/2000 AgNO ₃	1	C(111)+R	Normal	A/25 AgCN KCN	1	C(111)	
		600	R+C(111) +H(100)	"		600	C(111)	
	H/2000 gold chloride	10	C(111)+R	4.02±.02	B/25 AuCN KCN	5	C(111)	4.012±.008
		120	C(111)+R			60	C(111)	4.033±.005
		420	R+Cu ₂ O(111)	4.06±.02		600	C(111)	3.94 ±.005

4A. Electro-deposition from Simple Baths on the
(001) Face of Copper.

The results of electrodeposition of silver, gold and platinum from simple baths (Table 1) are shown in Table 15 and Figs. 105-113. These results are considerably different from the results of chemical displacement on this face from identically similar baths.

Silver deposits.

The electrodeposits of silver contained both orientated and random face-centred cubic crystals but did not contain any hexagonal crystals such as occurred in the chemical deposits. The two-degree orientated crystals had (001) and (111) orientations with relation to the substrate, as in the case of chemical displacement, *but* the (111) orientation was more prominent than the (001) orientation.

The electrodeposits of silver had some (111)-orientated crystals twinned on the (111) planes (Fig.107). Silver deposited in some cases of chemical displacement studied in the present work had shown some twinning (Fig.83),

Table 15.

Electrodeposition from the Simpler Baths on the
(001) Face of Copper.

Bath	Conc ⁿ .	Time	Colour	Structure and Orientation of the Deposit Crystals*	Fig.
1. AgNO ₃	N/2000	3 sec	No colour	C(111)+C(001) + R	105
	N/2000	10 sec	No colour	C(111)+C(001) + R	106-7
	N/2000	5 min	very light grey	R + little C(111)	108
2. AuCl ₃ ·2H ₂ O	N/2000	5 sec	No colour	C(001)	109
	N/2000	10 sec	No colour	C(001)	
	N/2000	10 min	Slightly greyish	C(001) + R(trace)	110
11. H ₂ PtCl ₆ 6H ₂ O	N/2000	10 sec	No colour	C(001)	111
	N/2000	45 sec	No colour	C(001)	112
	N/2000	2 min	No colour	C(001)	
	N/2000	10 min	very light grey	C(001) + little R	113

C(111) = cubic(111) // Cu(001), <110>_{cubic} // <110>_{Cu} or ~~110~~_{Cu}

C(001) = cubic(001) // Cu(001) <100>_{cubic} // <100>_{Cu}

R = random (cubic).

Electrodeposition from Gold Chloride on the (001) Face
of Copper.

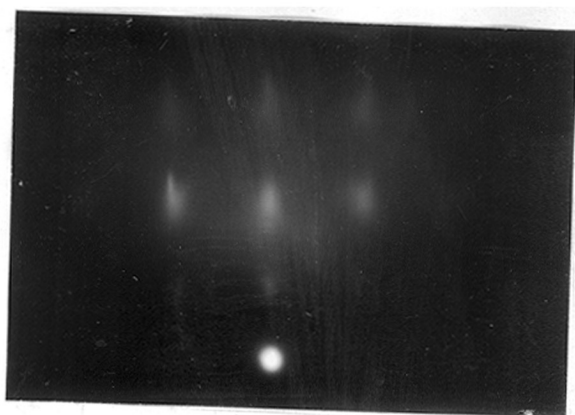


FIG. 109
M/2000 5 secs
azimuth [001]_{Cu}

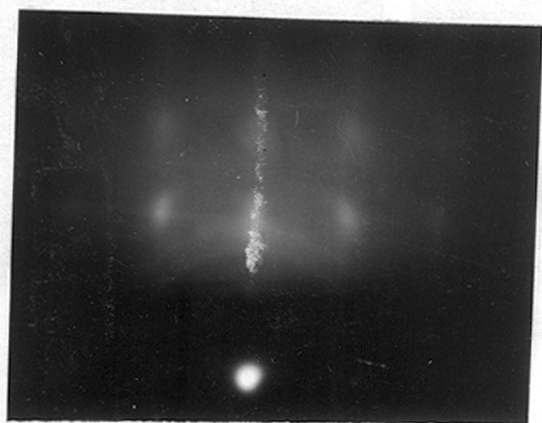


FIG. 110
M/2000 10 sec
azimuth [110]_{Cu}

Electrodeposition from Chloroplatinic Acid on the (001)
Face of Copper.

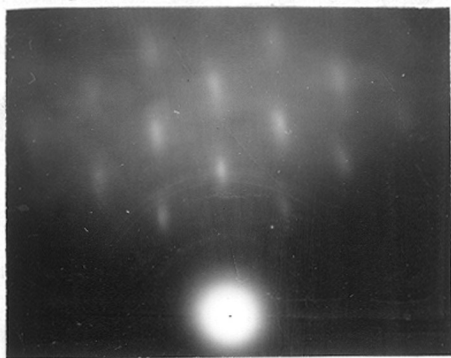


Fig. 111
M/2000 45 sec.
azimuth [001]_C

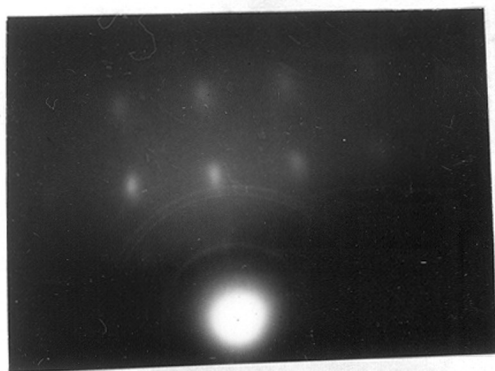


Fig. 112
M/2000 10 mins.
azimuth [001]_{Cu}

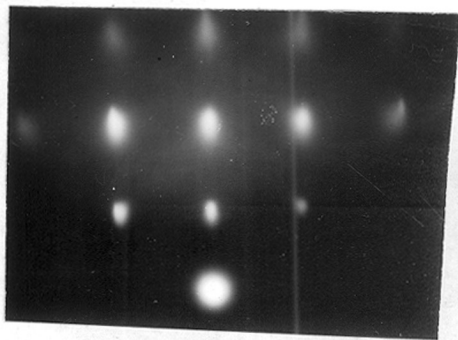


Fig. 113
M/2000 10 mins.
azimuth [001]_{Cu}

but no (111)-orientated silver was found to be twinned on the (111) planes. In all the cases of chemical displacement there was no case of twinning of the (111) orientated crystals except in chemical deposits of platinum from chloro-platonic acid on the (111) face of copper (Fig.62). The absence of the hexagonal deposits and the presence of the (111)-orientated twinned crystals may be due to the influence of the stronger electric field force present in the electrodeposition bath.

The general nature of the substrate effect was similar to that observed in chemical displacement; the proportion of orientated crystals diminished as the thickness of the deposit increased. The electrodeposits, especially the (111) orientated crystals had a perfectly smooth surface as is evident from the highly elongated spots and streaks along $\langle 111 \rangle$ * directions (Fig.107).

Gold and Platinum deposits: The electrodeposits of gold and platinum from gold chloride and chloroplatinic acid were strikingly different from the deposits obtained from the same baths by chemical displacement. The electrodeposits of gold and platinum contained when thin no random crystals such as were found in chemical deposits. Only traces of random crystals were found in 10 minute deposits of both gold and platinum. This difference in the nature of the deposits obtained by the two processes appears to be due to the slow rate of deposition of the electro-

deposits. The solutions of gold chloride and chloroplatinic acid were found to evolve hydrogen on the cathode during electrodeposition. The rate of evolution was quite high and it appeared to be higher in the case of gold bath. It is therefore probable that the rate of deposition of these metals was very low. This is also supported by the fact that the grey colour of the deposits from simple baths developed much more slowly in the case of electrodeposits.

The orientated crystals of the electrodeposits had perfect two degree orientation with relation to the substrate. The (111)-orientated crystals found in the deposits formed by chemical displacement from these baths were not found to be present in the electrodeposits. There was no indication of the formation of Cu_2O on the copper substrate during electrodeposition. These results are accounted for by the fact that hydrogen is evolved on the cathode during electrodeposition. It appears that Cu_2O , which was the cause of the (111)-orientated crystals formed on the copper (001) face during chemical displacement, is reduced by hydrogen and thus its effect on the orientation of the electrodeposited crystals is removed.

The lattice dimension of the electrodeposits of silver, gold and platinum are similar to those of the deposits formed by chemical displacement. The results are shown in Table 25 and are discussed in Section IV.

4B. Electrodeposition from Cyanide Baths on the Copper
(001) Face.

The results on electrodeposition of silver and gold from cyanide baths are set forth in Table 16 and Figs. 115-122. The results differ considerably from the results of chemical displacement of these metals from identically similar baths.

The electrodeposits show, like the chemical deposits perfect two-degree orientation with relation to the substrate, but both the nature and degree of orientations are different in the two cases. In electrodeposition both (111)- and (001)-oriented crystals appear from the beginning and both the orientations persisted as the thickness of the deposits increased. In chemical displacement only a small proportion of (111) orientations in the deposits of both silver and gold was noticed at the beginning when the deposit was very thin (a few seconds deposition). As the thickness increased the (111) orientations disappeared and (001) orientation appeared and gradually became stronger with increase in thickness. The causes of these differences in the results are discussed in Section IV. The absence of the (111) oriented deposits crystals in the electrodeposits from simple baths on the (001) face and their presence in the electrodeposits from cyanide baths is associated with the fact that cyanide baths

Table 16.

Electrodeposition from Cyanide Baths on the
(001) Face of Copper.

Current density in all cases was 2 ma/sq.cm.

Bath	Conc ⁿ .	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
i. AgCN KCN	A/10	3 sec	No colour	C(111) + C(001)	115
	A/10	1 min	Very light silvery	C(111) + C(001)	116-7
	A/10	5 min	Silvery	C(111) + C(001)	118-9
ii. AuCN KCN	B/25	5 sec	No colour	C(111) + C(001)	120
	B/25	10 sec	No colour	C(111) + C(001)	121
	B/25	7 min	Golden	C(111) + C(001)	122

* C(111) = cubic(111) // Cu(001), $\langle 110 \rangle_{\text{cubic}}$ // $[110]_{\text{Cu}}$ or $[\bar{1}\bar{1}0]_{\text{Cu}}$
 C(001) = cubic(001) // Cu(001), $\langle 100 \rangle_{\text{cubic}}$ // $\langle 100 \rangle_{\text{Cu}}$

Electrodeposition of Silver from Cyanide Bath on
the (001) Face of Copper.

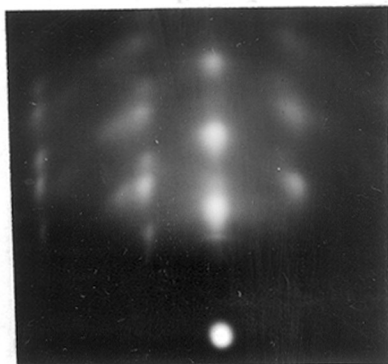


Fig. 115
A/10 3 sec
azimuth [001]-Cu

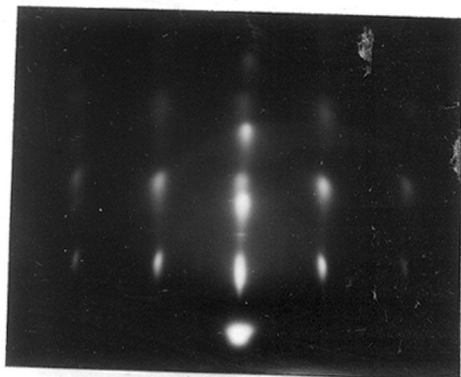


Fig. 116
A/10 1 min
azimuth [001]-Cu

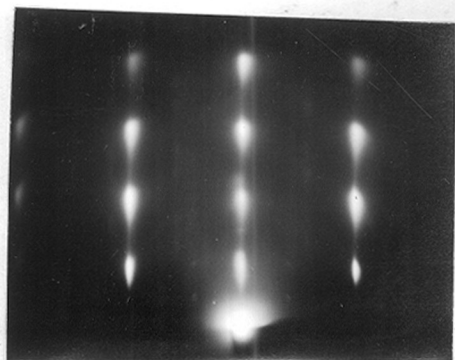


Fig. 117
A/10 1 min
Beam along 15°
with [001]-Cu

Electrodeposition of Silver from Cyanide Bath on
the (001) Face of Copper.

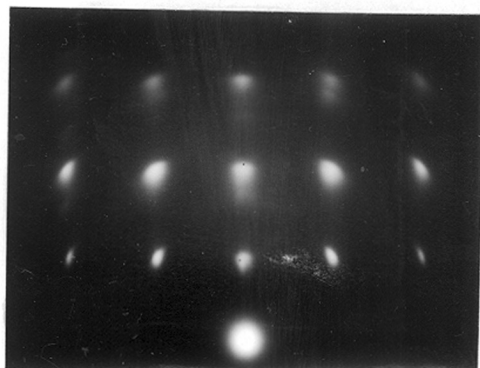


Fig. 118
A/10 5 mins
azimuth $[001]_{\text{Cu}}$

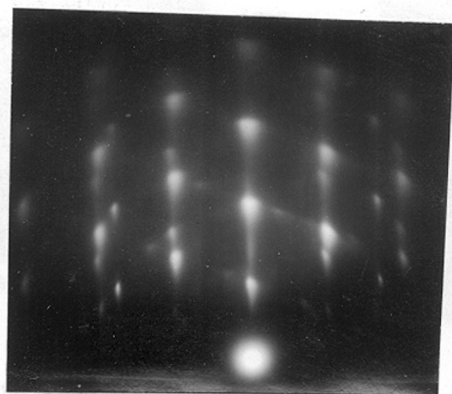


Fig. 119
A/10 5 mins.
azimuth $[110]_{\text{Cu}}$

Electrodeposition of Gold from Cyanide Bath on
the (001) Face of Copper.

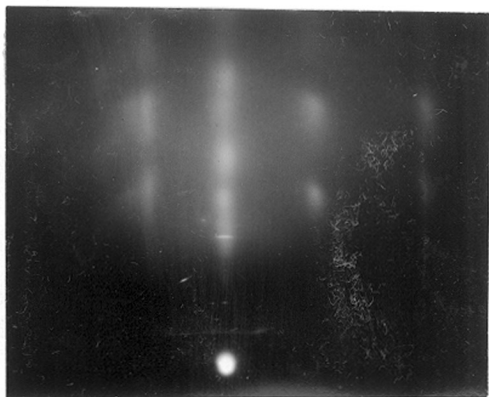


Fig. 120
B/25 5 sec
azimuth [001] Cu

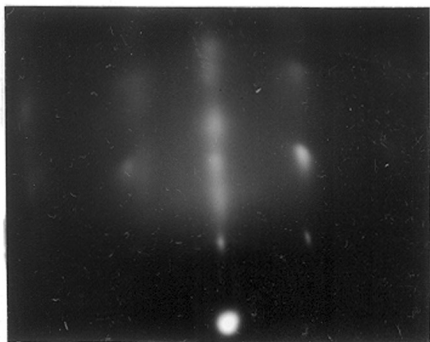


Fig. 121
B/25 10 sec
azimuth [110] Cu

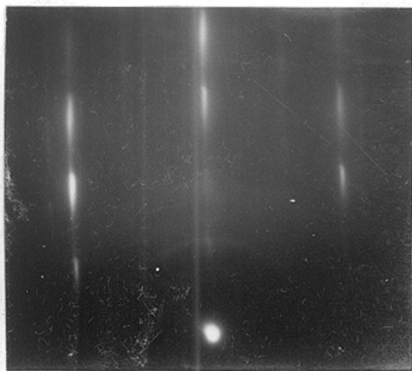


Fig. 122
B/25 7 mins

were not found to evolve hydrogen on the cathode like the simple baths; so the substrate effect of the Cu_2O is observed.

A further important observation in connection with the electrodeposition of gold and silver from cyanide baths is that the same specimen of the deposits sometimes showed one or other of these two types of orientations when the beam fell on different parts, especially in certain azimuths. This is evident from the different diffraction patterns obtained from the same specimen (Figs. 116-7) and (118-9). It is thought to be connected with the presence of Cu_2O on some parts of the surface of the substrate more than on others.

5A. Electrodeposition from Simple Baths on the (110) Face of Copper.

The results are set forth in Table 17 and Figs. 123-130. The results of electrodeposition of silver, gold and platinum on this face are straightforward and simpler than those on the (001) face of copper. As expected from the results on the (001) face, the deposits of silver contained both random and orientated crystals whereas most of the deposits of gold and platinum contained only orientated crystals in perfect two-degree orientation with relation to the copper substrate. The cause of this difference is the same as explained in Section IV, ^{1,6}. The rate of deposition

Table 17.

Electrodeposition from Simple Baths on the
(110) Face of Copper.

The current density was 2 ma./sq.cm. in all cases.

Bath	Conc ⁿ .	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
i. AgNO ₃	N/2000	3 sec	No colour	C(110)	123
	N/2000	6 min	Greyish	C(110)	124
ii. AuCl ₃ 2H ₂ O	N/2000	10 sec	No colour	Very little deposit	
	N/2000	30 sec	No colour	C(110)	125
	N/2000	7 min	No colour	C(110)	126
iii. H ₂ PtCl ₆ 6H ₂ O	N/2000	5 sec	No colour	C(110)	127-8
	N/2000	10 sec	No colour	C(110)	
	N/2000	10 min	Very faintly grey	C(110) + R	129-30

* C(110) = cubic(110) // Cu(110), $\langle 100 \rangle_{\text{cubic}}$ // $\langle 100 \rangle_{\text{Cu}}$

C(111) = cubic(110) // Cu(110) $\langle 110 \rangle_{\text{cubic}}$ // $\langle 110 \rangle_{\text{Cu}}$

R = random (cubic).

Electrodeposition of Silver from AgNO_3 solution on
the (110) Face of Copper.

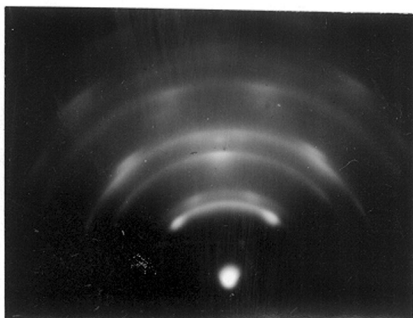


Fig. 123
M/2000 3 sec
azimuth $[110]_{\text{Cu}}$



Fig. 124
M/2000 6 mins
azimuth $[110]_{\text{Cu}}$

Electrodeposition of Gold from Gold Chloride Solution on
the (110) Face of Copper.

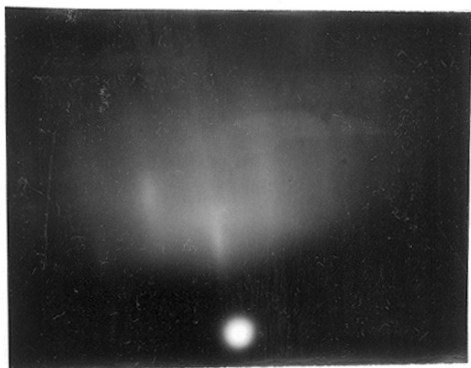
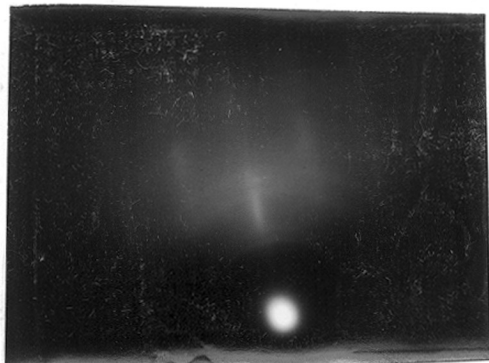


Fig. 125
M/2000 30 sec
azimuth [001] Cu



tp 26

M/2000 7 mins
azimuth [001] Cu

Electrodeposition of Platinum from Chloroplatinic Acid
on the (110) Face of Copper.

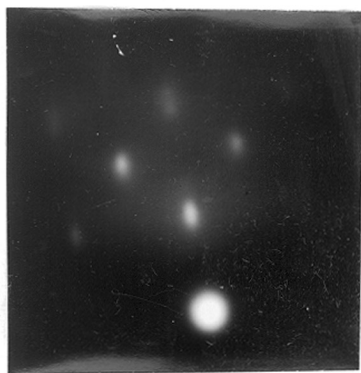


Fig. 127
M/2000 5 sec
azimuth $[001]_{\text{Cu}}$

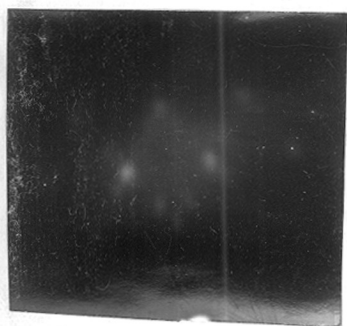


Fig. 128
M/2000 5 sec
azimuth $[110]_{\text{C}}$

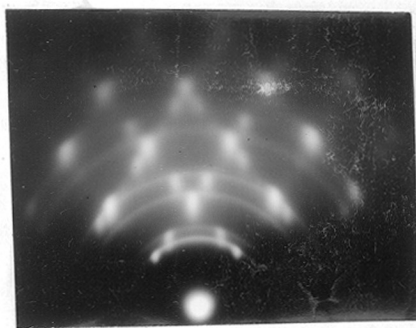


Fig. 129
M/2000 10 mins.
azimuth $[110]_{\text{Cu}}$

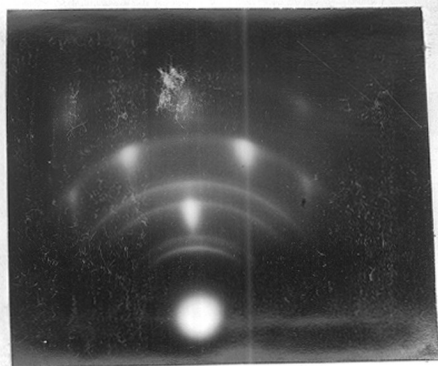


Fig. 130
M/2000 10 mins
azimuth $[001]_{\text{Cu}}$

of gold and platinum was low, as is evident from the colour of the deposits. The platinum deposits were found to be highly twinned (Fig.129) in the octahedral plane. The degree of twinning in this case is much higher than that of the chemical deposits. Even thin silver deposits showed appreciable twinning in the octahedral plane (Fig.123).

5B. Electrodeposition from Cyanide Baths on the Copper (110) Face.

The electrodeposition of silver and gold from cyanide baths has been studied and the results are shown in Table 18 and Figs. 131-133. As expected from the previous results the deposits contained only orientated crystals deposited epitaxially on the substrate.

The deposits had a highly smooth surface parallel to the substrate as is evident from the highly elongated diffraction spots which almost coalesce in some cases (Fig. 132).

The diffraction patterns from the silver deposits contained some faint vertically elongated streaks midway laterally between the main diffraction spots (Figs. 131 and 132). Similar spots were observed in the case of the chemical deposits of gold from the cyanide bath on the (111) face of copper. The cause of these diffractions cannot as yet be explained. Further work is necessary on this point.

Table 18.

Electrodeposition from Cyanide Baths on
the (110) Face of Copper.

Bath	Conc ⁿ	Time	Colour	Structure and Orientation of the Deposit Crystals*	Figure
AgCN KCN	A/10	5 sec	No colour	C(110)	131
	A/10	10 min	Silvery	C(110)	132
AuCN KCN	B/25	10 sec	No colour	C(110)	133
	B/25	5 min	Golden	C(110)	Similar to 133

* C(110) = cubic(110) // Cu(110), $\langle 100 \rangle$ cubic // $\langle 100 \rangle$ Cu

The current density was 2 ma./sq.cm. in all cases.

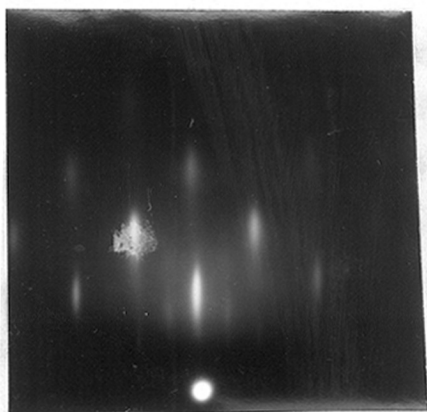


Fig.131
Silver electro-
deposited from
cyanide solution
on copper (110)
A/10, 5 sec.
azimuth $[001]_{Cu}$



Fig.132
Silver electrodeposited
on copper (110) from
cyanide solution.
A/10, 10 mins.
azimuth $[001]_{Cu}$



Fig.133
Gold electrodeposited
from cyanide soln. on
Cu(110) B/25 10 sec
azimuth $[001]_{Cu}$

6. Chemical Displacement on the Electropolished Surface
of a Single Crystal of Iron.

The chemical displacement of copper, silver, gold, platinum and nickel from simple baths (Table 1) was studied and the results are set forth in Table 19 and Figs. 134-141. The displacement of these metals from the solutions of their cyanide complexes was tried but none of the metals could be displaced by iron.

Deposits of Silver, Gold and Platinum: The deposits of these three metals were found to consist of randomly disposed crystals with lattice dimensions approximately the normal values (Table 19). The deposits of silver contained crystals of larger size than those of the gold and platinum as is evident from the patterns. From very dilute solutions of gold and platinum traces of iron oxide were formed due to oxidation of the substrate.

Deposits of Copper and Nickel: The deposit formed from M/500 solution of copper sulphate contained mostly Cu_2O mixed with a small amount of copper (Fig. 134). A stronger solution produced a greater proportion of copper as is evident from the pattern obtained from M/50 solution (Fig. 135). The lattice dimension of the Cu_2O and copper (Table 20) were found to be normal within the limits of experimental error.

In the case of nickel no metallic deposit could be obtained by displacement with iron from nickel sulphate solution but instead deposit of random crystals of some other substance was obtained. From the diffraction pattern the substance was identified to be nickel hydroxide, which was the only product formed also from stronger solution of nickel sulphate. The value of the basal axial dimension of the hexagonal lattice was calculated (Table 24) to be $3.05 \pm .02$ kx. The value is rather too low compared with the value of the lattice dimension (3.11 Å.) found by Germer (1938). The total absence of metallic nickel is in agreement with the results obtained by Germer, who observed electron diffraction rings due to contamination by Ni(OH)_2 formed from German silver alloy which he used as a support for specimens in some electron diffraction experiments. In the present case displacement of nickel by iron must be very slow due to their close positions in the electromotive series. It is therefore clear that a small amount of nickel is displaced by iron and it is completely oxidised to nickel hydroxide.

Table 19.

Results of Displacement on Single Crystal Surfaces of Iron

Bath	Conc ⁿ	Deposit	Nature of the Deposit	Lattice Dimensions (Calculated in kx)	Fig.
CuSO ₄	N/500	Cu ₂ O + small amount of Cu.	Polycryst. random	$a_{Cu} = 3.61 \pm .02$ $a_{CuO_2} = 4.27 \pm .02$	134
	N/50	Cu + traces of Cu ₂ O	Polycryst. random.		135
AgNO ₃	N/10	Ag	" "	$4.06 \pm .02$	136
	N/2000	Ag	" "		137
<i>Gold Chloride</i> chloroauric acid	N/1000	Au	" "	$4.08 \pm .03$	138
Chloro-platinic acid.	N/2000	Pt	" "	$3.90 \pm .03$	139
	N/200	Pt	" "		140
Nickel sulphate	N/125	Ni(OH) ₂	Hexagonal Polycryst. random	$3.05 \pm .02$	141
	N/10	Ni(OH) ₂	as above		similar to 141

Table 20.

Lattice Dimensions of Copper and Cuprous Oxide
formed on Iron from M/500 CuSO₄ Solution (Fig.134).

$\lambda \lambda L = 2.598$ kx from $R_{Fe110} = 1.284$ cm. and $a_{Fe} = 2.86$ kx.

	Intensity*	Radius cms.	hkl Cu	a_{Cu} (kx)	hkl Cu ₂ O	a_{Cu_2O} (kx)
1	V.F.	0.962	-	-	110	(4.35)
2	M.	1.058	-	-	111	4.23
3	M	1.246	111	3.61 $\pm 0.01 \lambda$	200	(4.17)
4	V.V.F.	-	200	-	-	-
5	V.V.F.	-	-	-	211	-
6	S.	1.721	-	-	220	4.27
7	S.	2.021	220	3.63 λ	311	4.26
8	M.	2.375	311	3.62 λ	400	(4.38)
9	F.	2.628	-	-	331	4.31
10	V.F.	2.964	-	-	422	4.29
11	F.	3.168	331	3.58 λ	-	-
				3.61 ± 0.02		4.27 ± 0.02

* S = strong, M = medium, F = faint, V = very.

Table 21.

Silver displaced on Iron from N/10 Silver

Nitrate Solution (Fig.136).

$\lambda_L = 2.448$ kx from $R_{Fe\ 110} = 1.21$ cm. and $a_{Fe} = 2.86$ kx.

	Intensity	Radius cms	hkl	a Ag(kx)
1	S	1.055	111	(4.022)
2	S	1.212	200	4.05
3	S	1.704	220	4.06
4	S	2.003	311	4.04
5	V.P.	2.085	222	4.07
6	M	2.628	331	4.06
7	M	2.705	420	4.05
8	F	2.933	422	4.09
9	F	3.131	333	4.06

Mean $4.06 \pm .02$

Table 22.

Gold displaced from N/1000 Gold Chloride on Iron (Fig.138)

$L = 2.41$ kx calculated from $R_{Fe\ 110} = 1.192$ cm. $a_{Fe} = 2.86$ kx

	Intensity	Radius	hkl	a Au(kx)
1	V.S.	1.028	111	4.06
2	M	1.179	200	4.09
3	S	1.676	220	4.07
4	S	1.986	311	4.06
5	M	2.615	420	(4.12)

$4.08 \pm .03$

Table 23.

Platinum displaced on Iron from M/2000 Chloroplatinic
Acid Solution (Fig.139).

$\lambda L = 2.961 \text{ kx}$ calculated from $R_{Fe \ 110} = 1.466 \text{ cm.}$ $a_{Fe} = 2.86 \text{ kx}$

Intensity	Radius cms.	hkl	$a \text{ Pt(kx)}$
S	1.298	111	3.96
F	1.530	200	3.88
F	2.149	220	3.90
H	2.501	311	3.92
F	3.400	420	3.89
Mean			$3.90 \pm .03$

Table 24.

Nickel Hydroxide formed on Iron from M/125 Nickel Sulphate
Solution (Fig.141)

$\lambda L = 2.53 \text{ kx}$ from $Fe_{110} = 1.252 \text{ cm.}$ and $a_{Fe} = 2.86 \text{ kx.}$

Intensity	Radius cms	hkl	$a_0 \text{ (kx)}$
S	0.968	110	3.02
V.S	1.663	110	3.04
F	1.915	200	3.05
F	2.515	210	3.07
F	2.873	300	3.05
Mean			$3.05 \pm .02$

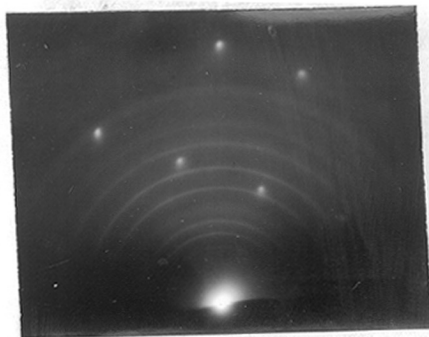


Fig.134
Cu displaced on
iron from M/500
 CuSO_4 solution

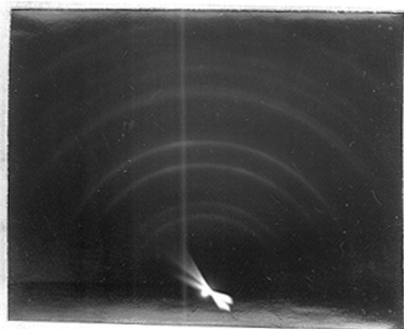


Fig.135
Copper displaced on
iron from M/50 CuSO_4
solution.

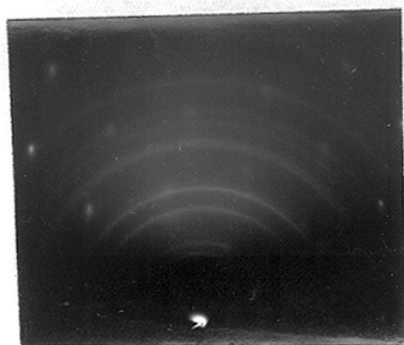


Fig.136
Silver displaced on
iron from M/10
 AgNO_3 solution.

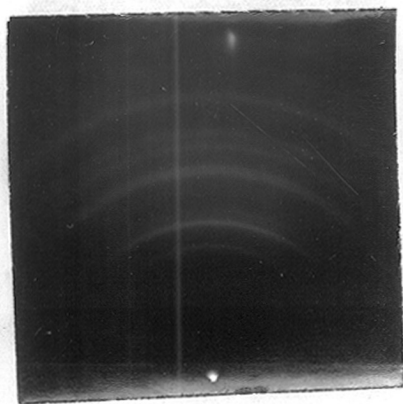


Fig.137
Silver displaced
on iron from M/2000
 AgNO_3 solution.

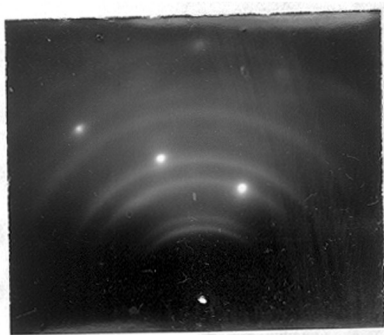


Fig.138
Gold displaced on iron
from M/1000 gold
chloride solution.



Fig.139
Platinum displaced
on iron from M/2000
chloroplatinic acid

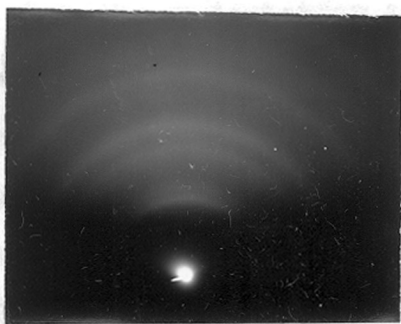


Fig.140
Platinum displaced
on iron from M/200
chloroplatinic acid.

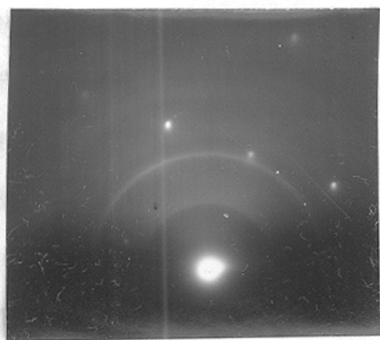


Fig.141
Nickel hydroxide on
iron formed from M/125
 NiSO_4 solution.

SECTION IV.

GENERAL DISCUSSION.

It has been pointed out in Section I that chemical displacement as a process of crystal growth has not been systematically studied. The present work was undertaken with a view to studying it in detail as far as practicable. The results described in Section III are discussed below in the light of present knowledge of the other main processes of crystal growth, especially the process of electrodeposition.

1. Orientation of the Deposit Crystals.

The orientation of the deposit crystals obtained in different processes is found to be dependent on various factors such as the nature and surface form of the substrate, the rate of growth, and the nature of the substance forming the crystals. In electrodeposition the bath characteristics play a very prominent part in determining the deposit orientation. The effects of these factors on orientation of the deposit crystals obtained by chemical displacement of silver, gold and platinum on copper are discussed below.

- a. Effect of the concentration of the cations and of the rate of deposition.

The degree of orientation of the deposits

obtained by chemical displacement was found to be very much dependent on the nature of the bath. The deposits of silver, gold and platinum obtained from the simple baths on the single crystal face of copper contained both orientated and random crystals, whereas the crystals obtained from the cyanide baths all had two-degree orientation with relation to the substrate. In the case of electrodeposition a proportion of randomly disposed crystals of silver from a silver nitrate solution was formed but no randomly disposed crystals were found in the deposits from simple baths of gold and platinum. In the case of chemical deposition on iron single crystals only random crystals are obtained from simple baths.

The formation of random crystals on copper substrate is associated with the higher rate of displacement caused by higher concentration of the cations in the simple baths. Similar results were obtained by Cochrane (1936) and Finch, Wilman and Yang (1947) in electrodeposition, where high rate of deposition tends to lead to the formation of randomly disposed crystals. In deposition of metals by condensation from vapour and in formation of deposits by rapid reaction of gases on single crystal substrates deposits of randomly disposed crystals are produced (Wilman 1940). In chemical displacement the rate of displacement will

increase with increase in concentration of the cations in the baths. In the present work the formation of random crystals on copper from the simple baths, which have a relatively high ionic concentration is, therefore, in agreement with the results obtained in other processes of deposition. The formation of random crystals on iron appears to be associated not with high rate of deposition but disorientated or amorphous oxide films.

The absence of the random crystals in the deposits obtained on copper single crystals from the cyanide baths is evidently due to low concentration of the ions of the metals to be displaced. The coinage metals are well-known for their ability to form complex cyanides in solution. The metal atoms are firmly bound with the cyanide groups in the form of complex anions such as $\text{Ag}(\text{CN})_2^-$. These anions undergo secondary dissociation only to a limited extent to set free some metal as cations. The dissociation constant of these complex cyanide anions of silver, gold and platinum are also low.

The dissociation constant of $\text{Ag}(\text{CN})_2^-$ is 3.8×10^{-19} that of $\text{Au}(\text{CN})_2^-$ is 5×10^{-39} (Latimer 1938). The dissociation constant for the platinum anion must be still lower as the platinum complex is the most stable amongst them. It is thus clear that the concentration of the metal ions in the cyanide baths is low, and consequently no random deposit

is formed from the cyanide baths of silver and gold. The same reason accounts for the absence of any appreciable displacement of platinum from the cyanide baths on copper. From the above results it is clear that the effect of the rate of reaction on the orientation of the chemical deposits is similar to that in other crystal growth processes, including electrodeposition.

b. Effect of the Substrate.

The effect of the substrate on the orientation of the deposit crystals on (111) and (110) faces of copper is found to be normal, that is the deposits assume an epitaxial orientation continuing as far as possible the atomic arrangement and co-ordination of the substrate. In the case of chemical displacement on the (001) face of copper the orientation of the deposit is found to be different from that of the substrate, having (111) orientation instead of the (001) of the substrate copper. It has already been pointed out (see article 1A., Section III) that the (111) orientation of the deposit is due to the presence of (111)-orientated Cu_2O which acts as the effective substrate producing this orientation of the deposits. It is clear from the results that the (111) orientation of Cu_2O is consistently obtained on the smooth electropolished copper cube face when this is oxidised in moist conditions. It is, therefore, worth while to examine first of all the causes

of the (111) orientation of Cu_2O on the (001) face of copper.

Cause of (111) orientation of Cu_2O on the Copper (001) Face.

The (111) orientation of Cu_2O on this face appears rather unusual at first sight, but closer examination reveals that this gives a less strained fitting together of the Cu_2O with the underlying copper at the interface than would the growth in parallel (001) orientation on the copper. Fig.142 shows the atomic fit of the copper atoms between (111)-orientated Cu_2O on the (001) face of copper, and Fig.143 shows the atomic fit between Cu-atoms on the (001) faces of both Cu_2O and copper. It is seen from the two diagrams that the (111) orientation of Cu_2O gives better atomic fit with the (001) face of copper.

It has already been mentioned (see Section I) that of all the factors promoting orientated growth of crystals consideration of the atomic fit at the interface is the most important (Elleman and Wilman 1949) although lattice fitting is an important secondary consideration. A typical example in the case of electrodeposits is provided by the growth of gold crystals on iron with their (001) face parallel to (001) face of the iron and [001] row parallel to [110] of iron instead of [001] row of iron for the sake of better atomic fit (Finch and Layton 1951).

In the present case the (111)-orientated Cu_2O has its

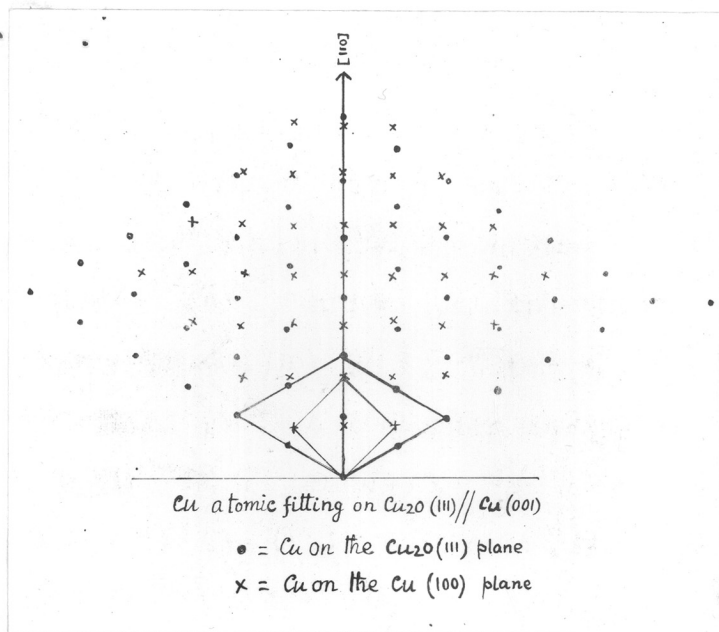


fig 142

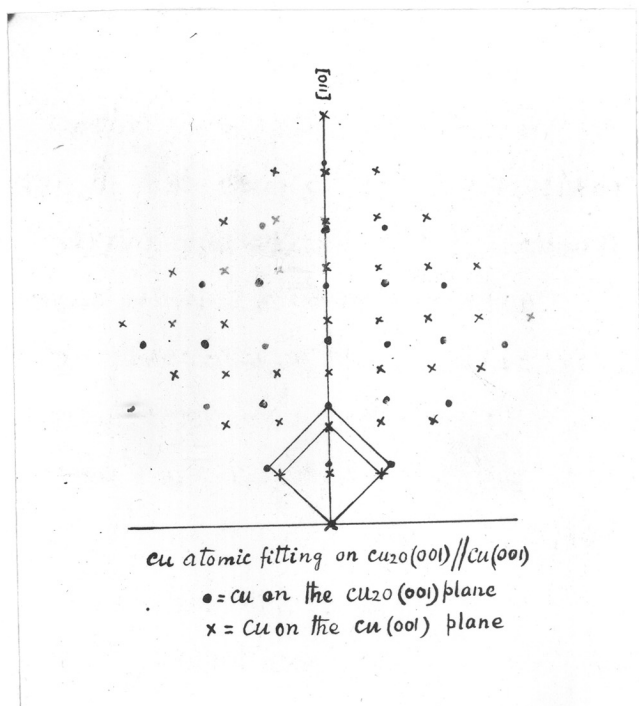


fig 143

[110] lattice row parallel to [110] of copper. The lattice misfit along this row is 18% which is also the misfit along this row for the parallel orientation of Cu_2O on copper.

Along the perpendicular 110 row of the (001) face of copper there is a 211 row of the (111) orientated Cu_2O with a period of 10.4 Å. ($=T[211]$ of Cu_2O) which is very nearly *double* that of (T_{110}) of the (001) face of copper, thus giving a much smaller lattice misfit of about 2% only. This case of Cu_2O provides a new example where consideration of atomic fit at the interface caused orientation other than parallel orientation although parallel growth is normally expected.

It may further be noted that this orientated growth of Cu_2O on (001) face of copper is a case where the lattice misfit along the common lattice rows of the deposit and the substrate is more than 15%, which was formerly considered to be the maximum limit below which orientated growth may take place (Royer 1928). It, therefore, lends further support to the later view (Wilman 1951) that the limit of 15% can no longer be accepted as valid. In the present case of metal crystals grown by chemical displacement the lattice misfit between the deposit and the substrate is much lower than 15% in every case (Table 27). So far as the effect of lattice dimension on orientation of the deposits is concerned no strong adverse effect on the orientated growth can be

caused by this factor.

Some Special Features of the Orientation of the Deposits on the Copper (001) Face. (See Table 14) & (Table 25)

In addition to the presence of (111) orientation the following peculiarities of the nature and change of orientations of the deposits on this face were observed.

i. In the case of the silver nitrate solution the cubic silver deposit had (111) and (001) orientations from the start and both these orientations persisted effectively until ultimately the top layer of the deposit became completely random.

ii. In the case of the gold deposit from the gold chloride solution there was no (001) orientation, only (111) orientation which gave way to randomly disposed crystals as the deposits became thicker.

iii. The platinum deposits from the simple bath and the silver and gold deposits from the cyanide baths started with (111) orientation which soon disappeared to make room for (001) orientation.

The above results appear very diverse at first sight but these results can be seen to be due to the effect of certain factors (see further discussion below) that are operative in these processes. The most important factor is the presence of Cu_2O which plays an important role to determine the mechanism in the present cases of displacement on copper substrate.

2. Suggested Mechanism of Displacement on Copper
and its Agreement with Results Obtained.

While considering the orientation of the deposits obtained in the present work the following factors must be taken into account: (i) The displacement was studied on a highly smooth electropolished surface of the substrate and (ii) this surface contained some crystals of cuprous oxide which are likely to provide the main points of discontinuity on the polished surface. In the normal case of displacement the precipitation of the nobler metal by displacement probably begins at such projecting parts of the surface of the displacing metal whose ions enter into solution from the remaining parts of the surface. When the initial nuclei have been formed further precipitation on these requires less energy than the formation of new nuclei for precipitation on the surface (Straumanis and Fang 1951) On the electropolished smooth surface of copper such points of discontinuity must be very rare; on the other hand there will always be some Cu_2O crystals present on the surface. The deposition evidently starts on the projecting semi-conducting cuprous oxide crystals and this is the cause of the initial predominance of the (111) orientation of the deposit.

As the deposition continues the deposits will grow outwardly and laterally, and this lateral growth will extend

the deposits on to the surface of the copper. It is, therefore, reasonable to think that growth of the crystals will first begin on the surface of Cu_2O and the growth on copper will begin later. The deposits that will grow on copper will assume the (001) orientation of the copper face because this deposition will continue the same atomic arrangement and will not involve large misfit relative to the substrate.

On the basis of the above suggested mechanism of the process of displacement let us examine the peculiarities that are observed in the nature and change of orientation of the deposits formed on (001) face of copper.

The presence of only (111) orientation at the beginning directly follows from the above suggested mechanisms which appears to be quite probable under the conditions of the experiments. If the rate of growth of crystals be slow the time taken by the deposits to extend to the surface of copper will be longer and consequently the diffraction pattern will show at the beginning only (111) orientation due to the deposit crystals formed on the Cu_2O . Even if there may be some initial deposit at a few points on the copper substrate, the diffractions from such deposits are not likely to appear strongly on the electron diffraction pattern from the short-time deposits, as the deposits on top of the Cu_2O will occupy a relatively higher position than the deposits on the copper

surface. This type of effect is quite expected in view of the fact that an electron beam at grazing incidence and under an accelerating voltage of even 50 to 60 KV. can penetrate only a few tens of angstroms below the surface.

The deposits obtained from dilute solution of chloroplatinic acid and of complex cyanides of silver and gold show at the beginning only (111) orientation which subsequently changes to (001) orientation. This result is in full agreement with the reasons stated above because the rate of deposition must be low due to low ionic concentration in the baths, particularly the cyanide baths. If the rate of deposition is high such as is observed in the case of deposition from silver nitrate solution, the time lag between the start of (111) and (001) orientations will be negligible and both the orientations will appear simultaneously; this is indeed found in the case of deposition from silver nitrate solution.

The disappearance of the initial (111) orientation of the deposits obtained from the baths having low ionic concentration appears to be due to relatively higher rate of growth of the deposits on copper than the rate of growth of those on Cu_2O . Although the deposition will start earlier on the Cu_2O according to the suggested mechanism the higher rate of growth on copper which will follow will make the latter deposits thicker than the former in course of time,

which will depend on the rate of deposition.

Due to the relatively non-conductivity of Cu_2O such a higher rate of growth on the surface of copper is not unlikely. Consequently only (001) orientation of the deposit is likely to appear in the diffraction patterns obtained from deposits for comparatively longer time.

In the case of displacement from the cyanide baths the (111) orientation of the deposits disappears much more quickly than in the other cases. This can be ascribed to the effect of the free cyanide which dissolves Cu_2O and removes its effect quickly.

In the case of the displacement from gold chloride solution, the (111) orientation is the only type of orientation exhibited by the deposit crystals. This orientation does not disappear and it persists up to the end. It is due to the formation of a thick layer of cuprous oxide which covers the face of copper almost completely. As a result the deposits are formed only on Cu_2O . The copper ions formed from the surface of the substrate seem to enter the solution by diffusion through the intercrystalline boundaries of this layer of cuprous oxide crystals. Such a process is not impossible. The above view about the presence of a thick layer of Cu_2O formed on copper in the gold chloride bath is supported by the facts that even thick random deposits of gold obtained from gold chloride baths on all the three faces

contained crystalline cuprous oxide (Figs. 20, 57⁹⁰), and even a very dilute solution of gold chloride formed a large quantity of Cu_2O on (110) face of copper (Fig. 87) in a short period. Such formation of cuprous oxide from any other bath was not observed particularly on the (110) face, which rarely formed any cuprous oxide when put in any other bath.

The rapid oxidation of copper substrate in the gold chloride bath was due to the presence of free chlorine which could be easily identified by the starch-iodide test. This fact further supports the view that the (111) orientation of the deposits on the (001) face of copper is due to the substrate effect produced by Cu_2O .

3. Comparison of the Present Results on Electrodeposition with those on Chemically Formed Deposits from the Same Baths.

In the case of electrodeposition from the same baths used for chemical displacement the results on the (110) and (001) faces of copper were studied and those on (110) were found similar to the results of chemical displacement on the same face. The following points of difference in the results obtained in the two processes on only the (001) face of copper were observed.

- i. The electrodeposits from the gold chloride bath had only (001) orientation unlike the chemical deposits which

Table 25.

Comparative view of the results of Chemical Displacement and Electrodeposition of Silver, Gold and Platinum from identical Baths on Copper.

Face	Bath and Concentration	Chemical displacement			Electrodeposition (c.d. = 2 amp)		
		Time secs.	Nature of deposit	Lattice Dimension kx	Time secs.	Nature of deposit	Lattice Dimension kx
001	M/2000 AgNO ₃	1	C(001)+C(111)+H(101) <i>300 C(001)+C(111)+H(101)+R</i>	Normal	3	C(111)+C(001)+R	
		600	R+C(001)+ <i>little</i> H(101)		300	R+ <i>little</i> C(111)	
	A/10 AgCN KCN	1	C(111)	Normal	3	C(111)+C(001)	
		30	C(001)				
		300	C(001)	Normal	300	C(111)+C(001)	
	M/2000 gold chloride	10	C(111)+R	4.01±.02	5	C(001)	3.98±.02
		180	R+C(111)		10	C(001)	4.02±.02
		420	R+Cu ₂ O ₁₁₁	4.06±.02	600	C(001)+R traces	
	B/25 gold cyanide	10	C(111)	4.01±.01	5	C(111)+C(001)	4.03±.02
		60	C(001)	4.03±.01			
		600	C(001)	4.04±.01	420	C(111)+C(001)	4.08±.02
	M/2000 chloro platinic acid	10	C(111)+R	3.79±.02	5	C(001)	3.80±.02
		30	C(001)+C(111)+R	3.79±.02	10	C(001)	3.79±.02
		300	C(001)+R		600	C(001)+R	3.81±.02
		600	R				

Table 25 (continued)

Face	Bath and concent- ration.	Chemical displacement			Electrodeposition		
		Time secs	Nature of deposit	Lattice Dimension kx	Time secs	Nature of deposit	Lattice Dimension kx
110	M/2000 AgNO ₃	1	C(110)+R	Normal	3	C(110)+R	
		10	R + trace of C(110)		300	R+C(110)	
	N/25 AgON soln.	1	C(110)		5	C(110)	
		600	C(110)		600	C(110)	
	M/2000 gold chloride	10	C(110)		10	C(110)	
		180	C(110)+R				
		420	R+Cu ₂ O(110)		600	C(110)	
	R/25 gold cyanide	Very little displacement			10	C(110)	
					300	C(110)	
	M/2000 chloro platinic acid	5	C(110)	3.78 $\pm$.02	5	C(110)	3.78 $\pm$.02
		300	R+C(110)	3.80 $\pm$.02	600	C(110) + R (small amount)	3.83 $\pm$.02

had only (111) orientation.

ii. The electrodeposits of gold and platinum from the simple baths contained very little randomly disposed crystals such as were observed in the chemical deposits from the same baths.

iii. The electrodeposits of platinum from chloroplatinic acid had only (001) orientation unlike the chemical deposit which had (111) orientation followed and displaced by (001) orientation.

iv. The electrodeposits of silver and gold from the cyanide baths showed both (001) and (111) orientation which persisted throughout whereas the (111) orientation of the chemical deposits from the cyanide baths disappeared quickly to make room for (001) orientation which then persisted all throughout.

v. The electrodeposits of silver obtained from the silver nitrate solution started with both (111) and (001) orientations as in the case of chemical displacement but there was no hexagonal crystals as were found in the chemically formed deposits. Moreover the (111) orientations of the electrodeposits persisted longer.

These points of difference are discussed below.

The absence of the (111) orientation of the electrodeposits of gold and platinum from the simple baths can be ascribed to the fact that in electrodeposition from these

baths hydrogen was evolved on the cathode. The nascent hydrogen on the cathode is likely to reduce the Cu_2O and thus cause the absence of the orientation corresponding to that of Cu_2O .

The absence of the random crystals in the electrodeposits from these baths is partly due to hydrogen evolution and partly to the low rate of deposition. The evolution of hydrogen indicates that the rate of deposition of the metal atoms on the surface of the substrate must be low in relation to the bath current, and hydrogen must have produced a stirring action and so helped quick supply of ions from the bath to the substrate surface. Both these factors, i.e. good supply of ions to the substrate and low rate of deposition, favour orientated growth. It is therefore clear that the observed absence of random and (111)-orientated crystals is in agreement with expectation.

The persistence of the (111) orientation of the electrodeposited crystals from the cyanide baths and its quick disappearance in the chemical deposits from the same baths is accounted for by the fact that in electrodeposition there exists a tendency for outward growth from the projections on the surface of the cathode (Finch, Wilman and Yand 1947). Although the rate of deposition on the top of the Cu_2O appears to be slower than the rate of deposition on the surface of copper this factor is counterbalanced by the tendency of

outward growth on the top of Cu_2O . Hence in electrodeposition the growth on both substrates appears to proceed at equal rate and thus both types of orientations are observed even in the long time deposits. This also appears to be the cause of the persistence of the (111) orientation longer than the (001) orientation in the electrodeposits from the silver nitrate solution.

The effect of the free cyanide to cause quick disappearance of the (111) orientation by dissolving the Cu_2O such as was observed in chemical displacement from cyanide baths, cannot be expected in the case of electrodeposition. The cyanogen ions which act on the Cu_2O are drawn towards the anode and thus kept away from the substrate which forms the cathode.

From the above discussions it is clear that the differences in the nature of orientation of the electrodeposits and the chemical deposits are due to well founded reasons. The absence of the hexagonal crystals in the electrodeposits of silver is discussed below in connection with the abnormal structure of the deposit crystals.

Before discussions on orientation of the deposit crystals obtained are concluded it should be pointed out that in the present work on chemical displacement the one-degree orientation of the thick deposits, often obtained by electrodeposition, is due to the specific effect of the bath

conditions (Vinch, Wilman and Yang 1947). In chemical displacement such thick deposits cannot be easily prepared due to the fall in concentration of the metal ions in the bath as well as due to increase in the thickness of the deposit. Both these factors cause lowering of the rate of deposition which gradually becomes slower and slower, and may ultimately stop completely.

4. Abnormal Structure of the Deposit Crystals.

The structure of the chemical deposits of gold and platinum was always found to be face-centred cubic, except in the case of silver deposited from silver nitrate solution on copper. In the case of AgNO_3 hexagonal crystals of silver were obtained in addition to the cubic crystals. The tendency to form hexagonal crystals was observed even in silver compounds by other workers (Bloch and Moller 1931). It has been suggested that many metals including silver generally form hexagonal crystals in the first deposited layers and that there is a gradual transition from hexagonal to face centred cubic arrangement with increasing thickness (Quarrell 1937).

In the present case of chemical displacement the silver deposits contained some hexagonal crystals which persisted in even long time deposits. It appears that a high rate of displacement is responsible for the formation

of hexagonal crystals. When the rate of growth is rapid, the deposited crystals do not get opportunity to undergo its change to cubic structure before the succeeding layers begin to form. In the hexagonal and face centred cubic crystals the array of atoms in the first two layers of (0001) and (111) type respectively are similar. The difference begins with the third layer (see e.g. Hume-Rothery 1936). In the close packed hexagonal arrangement an atom in the third layer is directly above an atom in the first layer whereas in the face centred cubic arrangement it is situated directly above an empty space in the first layer. The latter arrangement is more stable than the former. When the rate of deposition is rapid all the atoms may not find the most stable position of minimum potential before the next layers begin to form. Consequently crystals of hexagonal structures may be formed with the cubic crystals.

That the formation of hexagonal crystals is due to the high rate of deposition is borne out by other facts: Of the faces of copper the (001) face formed a greater proportion of hexagonal Ag deposits than the (111) face and the (110) face formed no hexagonal deposit at all. This is in order of the observed reactivity of the three faces of which the (001) face was the most active. No hexagonal crystal was formed from the silver cyanide baths, which have low ionic concentration. Hence it is concluded that a high

rate of deposition was responsible for formation of hexagonal crystals. The absence of hexagonal crystals in the electrodeposits from the silver nitrate solution appears to be due to the effect of the greater field force in electrodeposition baths which helped the deposited atoms to find the places of minimum potential corresponding to the face centred structure of the crystals.

5. Lattice Dimension of the Deposits.

The lattice dimension of all the chemically displaced silver deposits had under all conditions the normal value within the limits of experimental error. This result is in general agreement with the results obtained by other workers. Sacklowski (1925) stated that the solubility of silver in copper is very limited. The alloy with less than 9.2% Cu has lattice dimension between 4.03 and 4.07 Å., while alloys richer in copper are not homogeneous and give a composite diffraction pattern from the two solid solution limits. Erdal (1927) concluded that the solubility of Cu in silver is still lower, only up to 6.3%. Natta (1937) calculated the lattice dimension of silver precipitated on polycrystalline copper to be 4.023 Å. but at the same time he admitted that he found it very difficult to get a precipitate of silver suitable for electron diffraction study. His results thus appear to be rather doubtful.

Goswami (1950) observed the lattice dimension of chemically displaced silver to be normal.

From the other results in conjunction with the results obtained in the present work it can be concluded that silver obtained by displacement on copper is either pure silver or a solid solution containing only a few per cent of copper which will change the lattice constant of silver by a very narrow margin. It will thus be of the same order as the possible experimental error. It is therefore not possible to state definitely that pure silver is deposited on copper in the present case, although the observed lattice dimension suggests it.

The lattice dimension of gold has been found to vary between 3.99 and 4.04 kx (Table 26). These results are in general agreement with the values found by Natta (1937) for gold chemically displaced on polycrystalline copper. He found the value to vary between 4.02 and 4.04 Å. corresponding to 89.5% and 93.3% of gold in the solid solution respectively. He further stated that at least in one case the deposit was pure gold. In the present work the lattice dimension of gold has been found to vary with the time of deposition (Table 26) except in the case of deposition on the (111) face from the cyanide bath. It is clear from the general trend of the results that an alloy of gold and copper in variable composition is formed. The lowest value of the

Table 26.

Lattice Dimensions of Gold chemically displaced from Cyanide Baths.

Displaced on (001) face of copper			Displaced on (111) face of copper.		
Conc.	Time	Lattice dimension (kx)	Conc.	Time	Lattice dimension (kx)
B/25	5 sec	3.99 ± .01	B/25	5 sec	4.012 ± .008
	10 sec	4.01 ± .01		1 min.	4.033 ± .005
	30 sec	4.01 ± .01		5 min	3.96 ± .005
	1 min	4.03 ± .01		10 min	3.94 ± .005
	10 min	4.04 ± .01	B/5	5 sec	4.04 ± .01
			B/1	5 sec	4.04 ± .01

Table 27.

Lattice Misfit along corresponding Lattice Rows on similar planes.

Deposit	a _{dep.} in kx	Lattice misfit	= $\frac{(a_{sub} - a_{dep})}{a_{sub}} \times 100$
		For substrate Cu ₂ O a Cu ₂ O = 4.26 kx.	For substrate Cu a _{Cu} = 3.61 kx.
Ag	4.078	4.27%	12.9%
Au	4.07	4.46%	12.74%
Pt	3.91	8.2 %	8.3 %
Cu ₂ O	4.26	-	18%

lattice dimension of gold observed in the present work is approximately equal to the lattice dimension of the hexagonal alloy AuCu which has the basal parameter of 3.98 Å. In the present cases of chemical displacement the deposition of the metals must have taken place atom by atom as is evident from the highly orientated parallel growths of the crystals on the surface of the substrate. It is therefore not unlikely that at the initial stage the alloy Au Cu may be formed. The abnormally low value of the lattice dimension of a 10 minute deposit of gold on the Cu (111) face from a cyanide bath is not clearly understood. It may be connected with some physical change produced as result of etching by free cyanide from the bath.

The lattice dimension of platinum (Table 25) was low, indicating the formation of alloy with copper. The values of the lattice dimensions did not show much change with the time of deposition, although a slight trend to increase is observed. Ordered alloys of platinum and copper with values of lattice dimension comparable to the lowest value of the lattice dimension obtained in the present case are known. Similar alloys may be formed in these cases.

The lattice dimensions of the electrodeposits of gold and platinum on copper are of the same order as those of the chemical deposits. These also indicate formation of alloys. Although alloy formation from baths containing one

type of metal ions is not common, such cases have been reported (Clark, Pish and Weeg, 1944). The formation of alloy of gold and platinum with copper is so common that alloy formation by electrodeposition is not unlikely.

6. Brightness and Adhesion of the Deposit.

The adhesion and brightness of the deposits obtained by chemical displacement are found to be dependent mainly on the orientation of the deposit crystals. All the deposits obtained from the cyanide baths were bright and adherent, and these were in strong two-degree orientation relative to the copper. The thick deposits of random crystals obtained from the simple baths were grey and comparatively softer, being partly removable by rubbing with a finger. The strong adhesion obtained with epitaxially orientated deposits is a consequence of the close fitting together of the atoms of the deposit crystals with the substrate on which they grew.

These results are in general agreement with the results obtained in electrodeposition. The brightness and adhesion of the electrodeposits are proportional to the degree of orientation of the deposit crystals (Wood, 1935; Polatnik, 1936). Small size of the crystals is also considered to be a factor contributing to brightness although crystals of large size are sometimes found to be bright (Jacquet 1936). Hence it is concluded that the factors contributing to brightness

and adhesion of the deposits are similar in the cases of deposition formed by both chemical displacement and electro-deposition.

7. Twinning of the Deposit Crystals.

The deposit crystals of silver, gold and platinum obtained by chemical displacement were found to be (111)-twinned in some cases. The degree of twinning was more prominent in the case of silver and platinum deposits (especially in the platinum deposits). In every case twinning appeared to be more prominent on the copper (110) face and is more easily seen when viewed on the Cu 110 azimuth. In all the cases twinning occurred on the (111) plane. These results are in general agreement with the results obtained by other workers in the cases of electro-deposition (Cochrane, 1936; Finch, Wilman and Yang, 1947). In the present cases of electrodeposition of silver and platinum, similar prominent twinning has been observed.

Twinning is generally considered to occur due to the strain at the interface. This strain is proportional to the lattice misfit between the deposit and the substrate. In the present case strong twinning of platinum can occur in this way, due to local strains associated with the formation of an alloy in which the metal atoms are of different sizes. The reason why twinning was much less prominently observed

in the gold deposits is not at present clear.

8. General Conclusion.

From the above results and discussions it can now be seen that the growth of crystals in chemical displacement occurs atom by atom to form the deposits and under favourable conditions the crystals, which are however in some cases solid solutions containing substrate metal atoms, are built up on single crystal substrates in definite orientation with relation to the substrate. The orientation produced is such that there is a close fitting together of the atoms of the deposit and the substrate at the interface, tending in effect to continue the substrate structure. Similar results are obtained in the processes of crystal growth such as by condensation from the vapour, crystallisation from solution or a melt or by electrodeposition. The general nature of the growth is the same in all the processes but the results vary widely according to the conditions like the nature of the substrate surface, nature of bath and presence of foreign crystalline materials, such as oxide films, on the surface of the substrate.

From these facts a general conclusion can be drawn that crystal growth in chemical displacement is essentially similar to that in other processes, especially the process of electrodeposition which bears a great degree of similarity with the process of chemical displacement.

SUMMARY.

The investigation of the process of crystal growth which by chemical displacement/has not been systematically studied so far, was undertaken with a view to getting clear ideas about the mechanism of the growth of the deposits in this process and to get a comparative view of this process with relation to the other processes of crystal growth, especially the process of electrodeposition.

With this end in view crystal growth by displacement of silver, gold and platinum from both simple baths and complex cyanide baths have been studied on the (001), (111) and (110) faces of copper single crystals, and the results have been compared with those obtained by the study of electrodeposition of these metals from identically similar baths on two of the same copper faces. The displacement of these three metals as well as those of copper and nickel from simple baths on a single crystal iron substrate has also been studied. The main results are enumerated below.

1. The Results on the Deposits formed by Chemical Displacement.

1. The deposits of silver, gold and platinum displaced from solutions of silver nitrate, gold chloride and chloroplatinic acid contained both orientated and random crystals of the three metals having normal face centred cubic structure

and the deposits of silver on (001) and (111) faces contained hexagonal crystals in addition to the cubic crystals. The deposits on iron contained only random crystals.

ii. The deposits of the three metals obtained from the cyanide baths contained only orientated crystals in two degree orientation with relation to the substrate.

iii. The orientated crystalline deposits on the (111) and (110) faces of copper had always parallel orientation with relation to the substrate, but the deposits on the (001) face were found to have (111) orientation in addition to (001) orientation and sometimes only one of the two orientations.

iv. The deposits of platinum from chloroplatinic acid and those of silver and gold from cyanide baths on the copper (001) face had at the beginning only (111) orientation which soon gave way to (001) orientation.

v. The deposit of gold from gold chloride on copper (001) face had only (111) orientation which persisted throughout.

vi. The hexagonal deposits of silver from silver nitrate solution on the (001) face of copper had (101) orientation and the crystals had (0001) lamellar shape; the hexagonal deposits on the (111) face of copper had orientation intermediate between (101) and (100) orientations with

relation to the substrate but it corresponded to (0001) layers built up on the inclined (111) faces of the (111) orientated face centred cubic crystals.

vii. The lattice dimensions of silver on copper and those of ^{all}the metals deposited on iron were practically normal. The lattice dimensions of gold and platinum on copper were lower than the normal values indicating formation of alloys of variable composition with copper.

viii. The deposit crystals of silver and platinum, especially platinum, were found to be twinned on the octahedral plane. Twinning of gold deposits was rather rare.

2. Results on the Electrodeposits.

i. Of the electrodeposits only the silver from the AgNO_3 baths contained random crystals but it contained no hexagonal crystals like the chemical deposits. The electrodeposits of gold and platinum from the simple baths contained no random crystals.

ii. The electrodeposits of gold and platinum from the simple baths on the (001) face of copper did not show (111) orientation, as were shown by the chemical deposits.

iii. The electrodeposits from the cyanide baths on the (001) face of copper had persistent (111) orientation unlike the chemical deposits from the same baths.

iv. The lattice dimensions and the twinning of the

electrodeposits were more or less similar to those of the chemical deposits.

3. Interpretation and Correlation of the Results.

The above results obtained on copper substrates have been compared and explained on the basis of a mechanism in which Cu_2O was formed on the surface of the copper took a prominent part.

i. The cuprous oxide had parallel orientation on the (111) and (110) faces of copper but it had (111) orientation on the (001) face, giving better atomic fit at the interface.

ii. The rate of deposition had been found to influence the structure and degree of orientation. High rate of deposition was found to be responsible for formation of hexagonal silver and random deposits.

iii. The absence of random crystals in the deposits from the cyanide baths was due to the low rate of deposition caused by low concentration of the metal ions in the bath.

iv. The quick disappearance of the (111) orientated of the deposits from the cyanide baths on copper (001) face was found to be due to the effect of free cyanide which dissolves Cu_2O .

v. The (111) orientation occurring alone in the gold deposits on the (001) face of copper from the gold chloride

bath was found to be due to the formation of excessive quantity of Cu_2O on copper due to oxidation by free chlorine present in the solution.

vi. The lowering of the lattice dimensions of the deposits of gold and platinum was due to the formation of alloys of these metals with copper.

vii. The absence of the random crystals in the electrodeposits of platinum and gold from the simple baths was due to comparatively lower rate of deposition.

viii. The absence of the (111) orientation of the platinum and gold electrodeposits from simple baths on the (001) face of copper was due to evolution of hydrogen on the cathode. It reduced the Cu_2O and its effect on the orientation of the deposits.

ix. The persistence of the (111) orientation in the electrodeposits on the (001) face of copper was found to be due to the tendency of deposition to occur on the projections

x. In electrodeposition the absence of the effects of free cyanide in stepping the (111) orientation of the deposit crystals on the (001) face of copper, was due to the fact that the cyanide ions are drawn away from the cathode.

xi. The lattice dimensions of also the thin electrodeposits of gold and platinum were found to be similar to those of the chemical deposits due to formation of alloys.

4. Conclusion.

The results obtained in the present work are found to show a clear analogy between the nature of the crystal growth in chemical displacement and that in the other processes of crystal growth, especially the process of electrodeposition. It is, therefore, concluded that the nature of the crystal growth in chemical displacement is essentially similar to the nature of growth in the other processes.

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