

Thesis Presented by P. R. Rowland  
for the  
Degree of Doctor of Philosophy  
in the  
University of London

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COMPUTERISED

The Chemical Properties of  
Isolated Metallic  
Crystals



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The author wishes to express his gratitude to Professor G. I. Finch, F.R.S., of Imperial College for constant encouragement and to the late Professor C. S. Gibson of Guy's Hospital Medical School, for much help and advice.

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Introduction

Reactions which occur at the boundaries between solids and the gaseous phase have been much investigated, but, in general, the experimental conditions have been such as to introduce so many uncontrolled variables as to obscure the issues. In the case of the study of the oxidation of metal surfaces, for example, the metals have almost invariably been polycrystalline, which in itself tacitly assumes that the atomic packing density within the surface is of no importance or at least exerts no more than a second order effect on the results of surface reaction. It also assumes that the reaction mechanism at a crystal grain surface is comparable to, or even identical with that which occurs at the boundaries between grains. Such a priori assumptions could only be justified by experimental. In the few cases, however, where the matter has been subjected to experimental test, it has been found that such assumptions are untenable. Therefore, in planning this study of surface oxidation, it was decided to confine the experiments to the oxidation of single crystal surfaces of known atom population density and configuration. Copper was used for this purpose because it is easily obtained in a high degree of purity and can be grown into large single crystals without great difficulty.

The three halogens chlorine, bromine and iodine were chosen as reactants with the copper single crystal surfaces because, by suitable temperature choice it would be possible to study oxidations in which all reactants and products other than the copper

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could be obtained in the vapour state and also because, by choice of a lower temperature, the reaction products could further be obtained as solids in situ on the copper.

Little previous work directly on the type of reaction studied has been done. Hausser & Tamman<sup>2</sup> introduced the idea of using spherical crystals for the study of etching, and Hausser & Scolz<sup>1</sup> showed that they appreciated the value of studying action with the gas phase. Nevertheless, it was left to Benton & Gwathmey<sup>3</sup> to study the interaction between metal crystals and gases in any detail. Finally the author<sup>4</sup> pointed out that for the systems to be as simple and clearly understandable as possible both reactants and products must be gaseous. After the work was completed it was found that Stranski<sup>5</sup> had worked with similar systems during the war of 1939-45 but using polycrystalline aluminium, <sup>and</sup> etching with HCl gas. However, the implications of the method as a general type of reaction, and the necessity of studying all possible surface planes (i.e. using spherical crystals) do not appear to have been fully appreciated.

This literature appeared to form too narrow a foundation on which to build and therefore a much wider review was made.

This may appear disproportionately long, but since it is intended to form the basis for work in what is virtually a virgin field, it was considered imperative, not only that all relevant material should be gathered under one head, but that at the same time it should be critically examined in order to prevent the incorporation of erroneous concepts (e.g. p. 92) or

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faulty interpretations of experimental work (e.g. p. 76) into the literature of the subject.

The following results and discoveries are claimed:

1. A fundamental investigation of the reactions between copper and the halogens  $I_2$ ,  $Br_2$  and  $Cl_2$  has been carried out on the surfaces of copper single crystalspheres and it has been clearly demonstrated that the
  - (a) appearance or non-appearance of a face as an etch microfacet depends on the particular halogen used.
  - (b) There are two distinct types of reaction, etching and "polish-etching", the former taking place at elevated temperatures and the latter at about room temperature.
2. These results, together with many related phenomena, have been successfully and simply explained on the theory that adsorption at the metal surface is the most important factor in determining the course of such reactions.
3. A method of growing metal single crystals of high purity and high quality has been developed. The purity of those used was the highest yet recorded in the literature and electron diffraction photographs obtained from them by Professor G.I. Finch and his collaborators are the most perfect yet published for copper.

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## 2. Experimental

### (A) The Growth of Metal Single Crystals

#### I. METHODS

The methods of producing large single crystals of metals (and other solids) have been reviewed many times<sup>6.7</sup>. For this reason only a brief outline will be given here. The techniques available are:-

- (a) Growth from the vapour phase either by depositing the metal itself or by decomposing a vaporised compound of the metal.
- (b) Growth from solution, e.g. by electrodeposition.
- (c) Growth from the molten metal by slow cooling.
- (d) Recrystallisation of polycrystalline metal in the solid state.

Methods (a) and (b) are of no great practical value in work of the sort carried out in this research, (a) may be useful as a last resort and method (b) appears to be of a purely academic interest, for, although orientated deposits have been obtained<sup>8.9</sup> the rates of deposition required to give homogenous material are inconveniently low.

Of the latter two methods, (d) would be the most convenient to apply in any case where it is desired to obtain crystals with a fairly accurately known external shape.

The method may be subdivided into two.

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(i) The strain-anneal method. The metal is given a slight strain (C 1%) and annealed at a high temperature for several hours. Frequently, one of the micro crystals originally present will grow at the expense of all the other strained lattices and the metal will therefore become a single crystal. The method is sensitive to the amount of strain and probably to the temperature. Sufficient strain must be applied just to distort most of the lattices without destroying them, while the application of too high a temperature may allow the lattices to come to equilibrium by internal re-arrangement rather than by movement of an unstable intercrystalline boundary. The method does not apply to copper which is converted to a mesh of interpenetrating twinned crystals by annealing with or without strain.

(ii) Phase change in the solid state. Andrade<sup>10</sup> has developed an ingenious method for growing single crystal iron wires. If cooled slowly iron suffers a phase change at  $906^{\circ}\text{C}$  from a face-centred to a body-centred cubic structure at the lower temperature. A wire in a vacuum was heated by passing an electric current through it. A temperature gradient along it was maintained by a subsidiary furnace. The current on the wire was then slowly diminished so that the point at  $906^{\circ}\text{C}$  travelled along the wire from one end to the other converting it into a single crystal.

Method (c) above, ~~the~~<sup>the</sup> growth from the melt, is probably the surest. The melt is cooled from a point so that the first crystal to form at that point grows  
/outwards



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until it occupies the whole of the charge in the crucible. In some cases it is necessary to take precautions to ensure that growth takes place from a favourably orientated crystal<sup>7b</sup>. Smialowski<sup>11</sup> reports that some metals (Cu, Pb, Sn) show a pronounced tendency to form single crystals whereas others (Zn, Al, Bi, Sb) show a smaller tendency. It will be observed that with the exception of Al, all the latter may be regarded as layered structures.

Many modifications have been used<sup>12</sup> for the growth of single crystals from the melt; but in general the principle has been slowly to lower a crucible with a conical bottom to its cavity through a furnace maintained well above the melting point of the charge. The first crystal to form at the tip of the cone as the crucible emerges, grows upwards through the melt. The maximum rate at which the crucible travels is governed by that at which latent heat of fusion can be dissipated and (presumably) by the mobility of atoms at the liquid/solid interface of the growing crystal, since each layer of atoms must settle into the lattice before the next is deposited. For these reasons a crystal of large diameter must be grown at a much slower rate than a small one.

The modifications are usually aimed at devising methods of heating a charge of metal in a vacuum or inert atmosphere and lowering the crucible or cooling it slowly under these conditions. A typical example is found in the work of Glocker & Graf<sup>13</sup> who used an induction furnace to heat the crucible and suitably orientated "seeds" to give orientated growth. Because induced current stirs the melt vigorously the charge had to be protected either by using a thick graphite crucible or by surrounding it with a tungsten shield. Gwathmey & Benton<sup>14</sup> placed the entire furnace in a

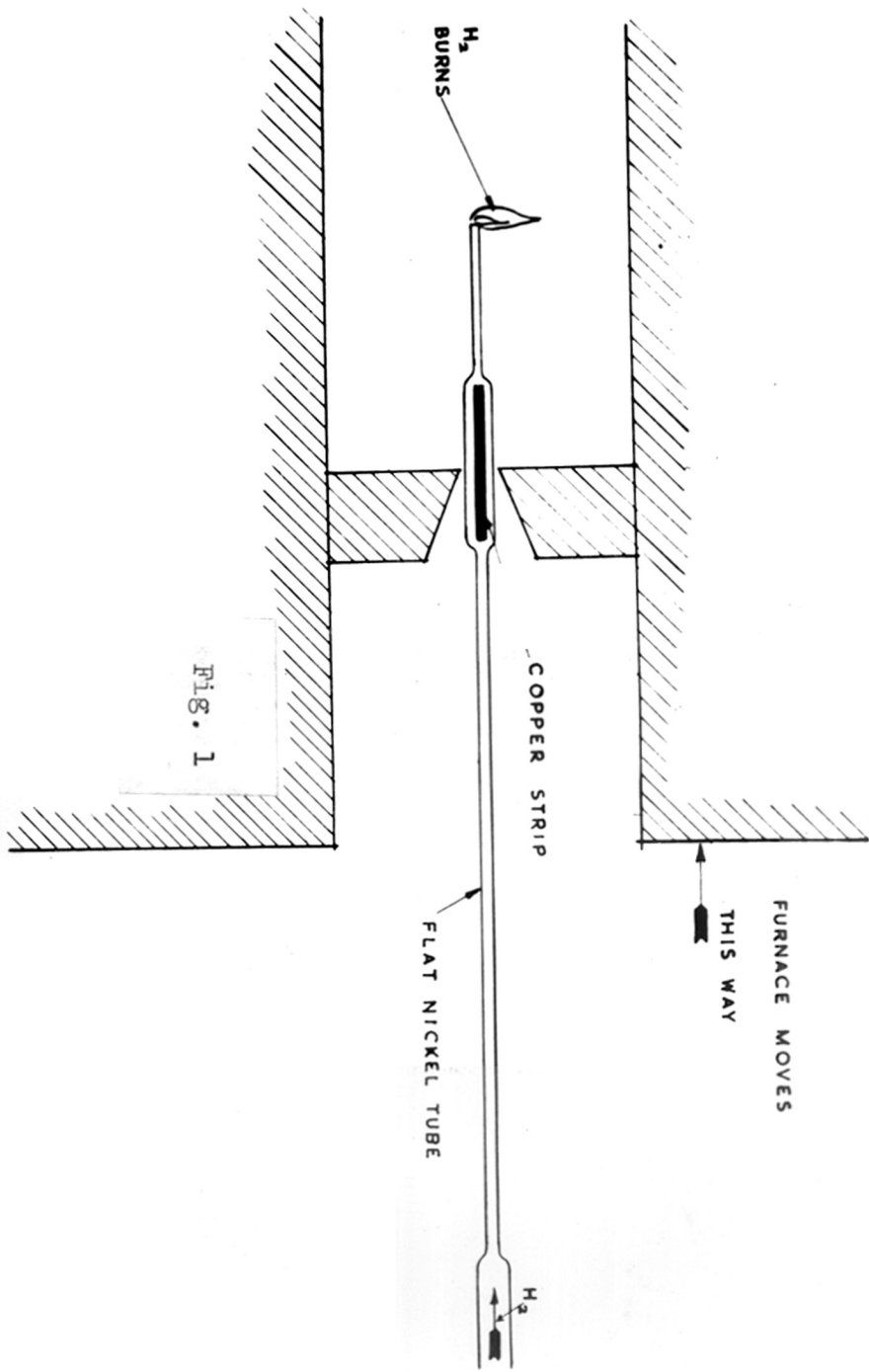
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vacuum and lowered the crucible by means of an iron rod supported on a column of mercury which could be controlled from without. Although a stream of inert gas was allowed to leak into the system near the crucible, the exposure of furnace windings, lagging etc. at white heat, together with a free mercury surface in the same vacuum enclosure with the copper, is open to criticism.

Two interesting methods of obtaining metal crystals with spherical surfaces directly from the melt have been developed. Anderson<sup>15</sup> allowed a single crystal seed to grow along a narrow tube and then into liquid zinc in a wider tube. The solid surface spread radially from the end of the narrow tube and at a suitable point in the process the liquid zinc was poured away leaving a crystal with a brilliantly polished hemispherical surface. The apparatus used enabled the process to be carried out in vacuo.

Stranski<sup>16</sup> and co-workers (p. 115) grew small spherical crystals of zinc and cadmium by slow cooling of droplets.

Because there is a danger that mechanical working of metal crystals may lead to distortion of the lattices it was decided to investigate method (d) (recrystallisation from the solid state) still further. It was thought that it might be possible to use an adaption of Andrade's method<sup>10</sup> using the small difference in energy between a crystal at a high temperature and a neighbour at a slightly lower one. Many experiments were devised in which a piece of

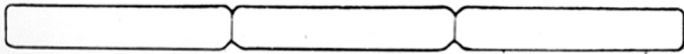


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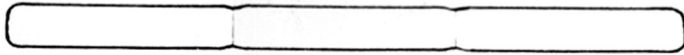
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copper near its melting point was cooled slightly in the region of one small crystal (annealed copper was used so that the crystals were large enough to observe) in the hope that it would grow at the expense of its neighbours. In one case, cooling was by means of a jet of hydrogen and the surface atoms were so mobile at the temperatures used that the small force of the jet created a dimple in the surface of the otherwise solid copper. Even so, the final material was polycrystalline.

Perhaps the best conditions achieved were in the following experiments. The furnace was placed on its side in a trolley which ran on rails. It was very well lagged at one end with a stopper of fireclay about 6 cm. thick. The stopper for the other end was not placed right at the end but inset so that the portion just inside it would be very near the highest temperature of the furnace while that outside would be at a relatively lower temperature but still protected from draughts (fig. 1.). This stopper was about 2 cm. thick and was pierced by a narrow horizontal slot with bevelled edges. The slot was 4 mm. wide and 25 mm. long. The copper was contained in a ribbon like nickel tube made by placing two pieces of 20 gauge x 1" nickel ribbon together, turning the edges over and welding them with a fine oxyacetylene flame.



(a)



(b)

Fig. 2

Sections through annealed sheets of copper  
(a) Crystals randomly oriented  
(b) Crystals twinned

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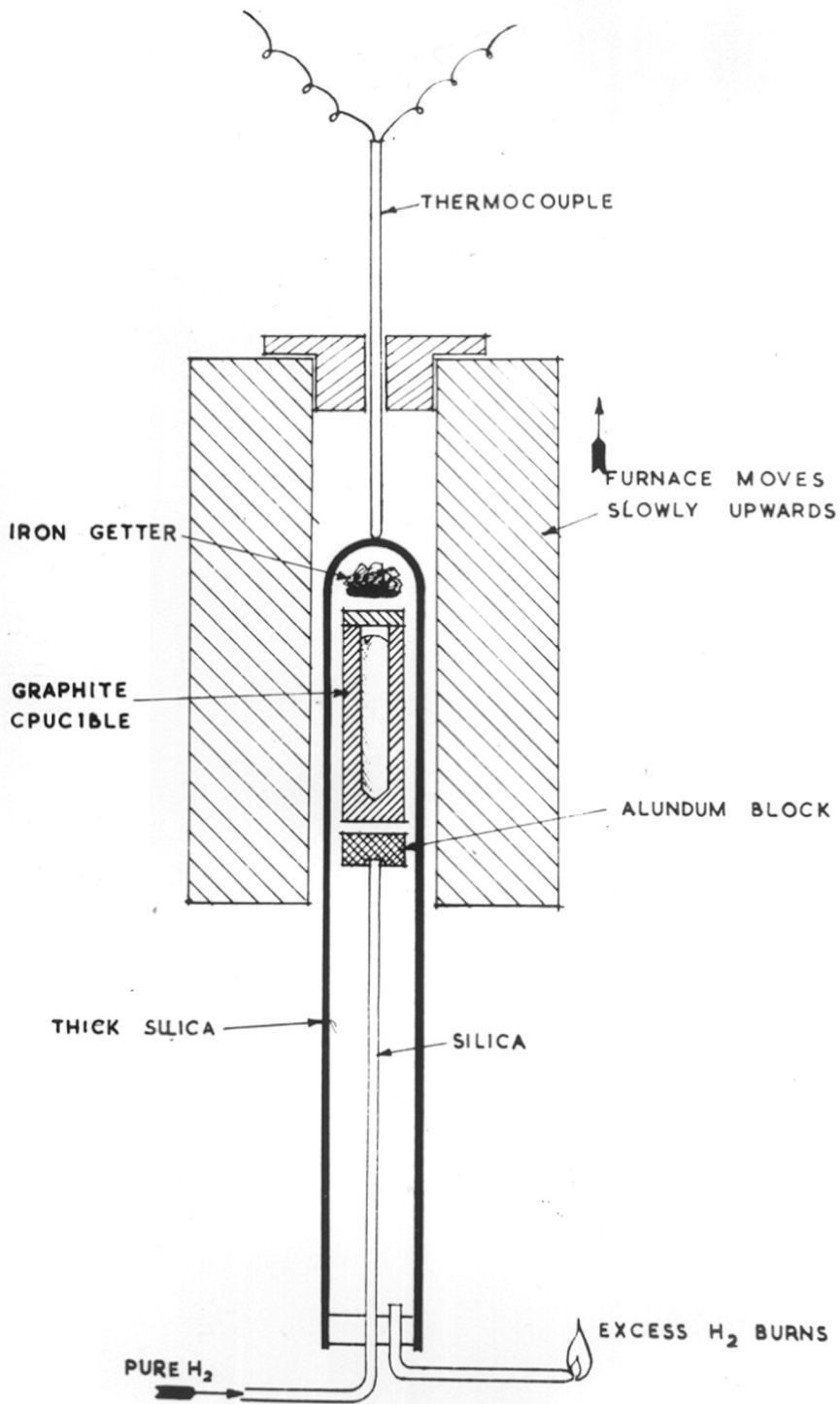
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Hydrogen was introduced at the cold end of the tube and escaped through a small leak at the other end. The rate of flow was such as to making cooling negligible. The copper was placed in the position shown. It was pointed at the end which would first emerge from the furnace and painted with colloidal graphite to prevent contact with the nickel.

It was estimated that these arrangements would allow as high a temperature gradient as possible to be maintained in the copper. Within the furnace, gradients should have been small since at 1000°C heat is transferred principally by radiation.

Needless to say, temperature control had to be very fine in order to be able to approach the melting point of copper as nearly as possible without melting it. The furnace was withdrawn at about 5 mm. per hour in the direction shown.

No single crystals were produced. The best that was achieved was a mesh of interweaving crystals (probably twinned) of very uniform appearance. Similar results were obtained later in growth from the melt on occasions when growth failed to proceed from a single point. The stability of such systems is not surprising in view of the



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low surface energy of the interface of twinned crystals. This is indicated by the lack of tendency of these interfaces to contract on annealing<sup>17</sup> (fig. 2.).

The above experiments demonstrated the practical impossibility of growing copper single crystals by phase change in the solid state and it was decided therefore to grow them from the melt.

The spheres were machined from cylindrical ingots which were grown from rods of "Spectro-pure" copper of the standard used as a reference in spectroscopic analysis and supplied by Messrs. Johnson Matthey. The rods were  $\frac{1}{2}$  inch in diameter and about 4" long. One end of each was turned to a cone of semivertical angle about  $20^\circ$  so that it fitted into the bottom of a graphite crucible as shown in Fig. 3. The crucible was placed in a vertical silica tube in the furnace as shown in fig 3, so that as the furnace was raised slowly (at about 1 cm.



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per hour), the first crystal to form in the tip of the cone grew up through the melt. During growth, a steady stream of pure hydrogen was maintained through the crucible enclosure. The iron getter which was placed on the crucible lid was made by heating domestic "steel wool" in a stream of pure hydrogen for several hours at about 1100°C. Because iron has a much higher affinity for oxygen than copper it not only served to absorb any trace of oxygen which may have diffused in through the walls of the silica tube but also revealed any failure in the hydrogen purification by a tarnished appearance at the end of a run. Contamination by sulphur from the rubber bung at the bottom of the tube was considered extremely improbable with a brisk flow of hydrogen in the direction shown.

The crucibles themselves were machined from the highest purity graphite obtainable, using high speed alloy tools. They were supported as shown on a block of alumina cement which had previously been heated in pure hydrogen at 1100° for several hours.

### II Results

1. Specimens prepared by the method were submitted to Professor G. I. Finch and his collaborators for examination by the method of electron diffraction. Plates were obtained

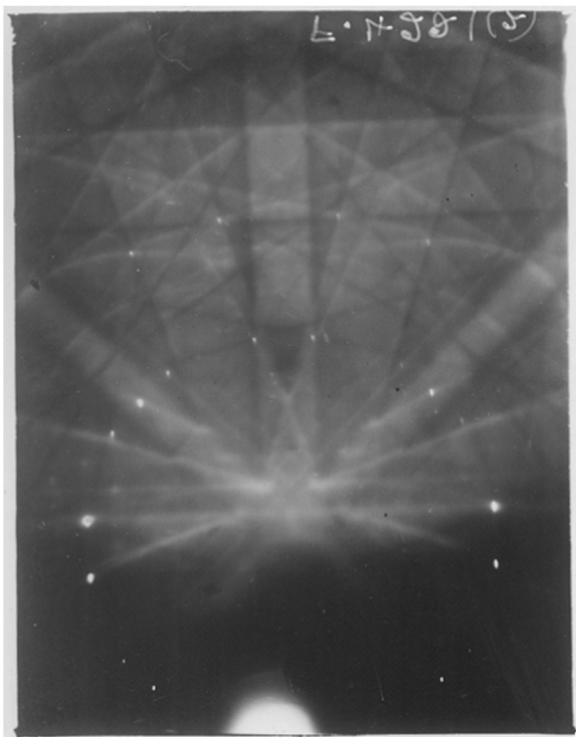
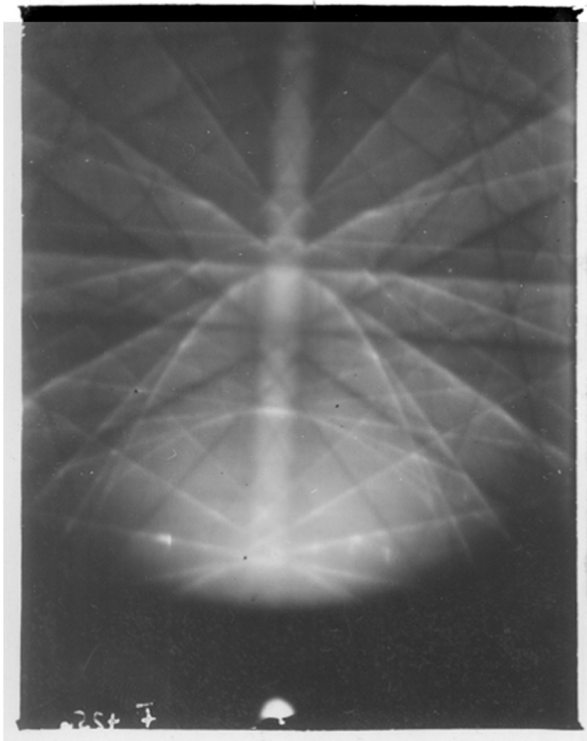


Plate I



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which showed few spots and these well defined with a background of Kikuchi lines (Plate I ). These results indicate a lattice which is relatively perfect over many thousands of atoms and it is probably safe to assume that these crystals are as perfect as can be obtained.

### 2. Analysis

A sample was submitted to Messrs. Johnson, Matthey & Co. Ltd., for analysis. Spectroscopic analysis revealed only those metals known to be present in the original sample supplied by them and these only gave spectroscopic lines marked as "faintly visible", i.e. too little to estimate. A trace of oxygen was detected but estimated as less than .05%. Except for the paper of Glauner and Glocker, no figures of analysis are given by other workers for their metal single crystal and in view of the fact that, with the single exception of a trace of oxygen, the specimen was identical with Johnson, Matthey's "Spectro-Pure" copper, which is claimed to be as pure as any commercially available, it can safely be assumed that these were the purest copper single crystals yet made.

### 3. Freedom from blowholes etc.

Several samples were completely dissolved in pure nitric acid in a white porcelain dish. Control experiments

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were run on the original copper from which they were made. Before dissolving, the outer layers of each specimen were dissolved off in a separate vessel to remove any graphite adhering thereto. The specimens were then thoroughly washed. Each gave about a dozen visible black specks from a gramm of material, but the "controls" gave a similar number. Owing to the impossibility of obtaining a dust free atmosphere in this laboratory (South East London) it is probable that many of the specks in both cases were mainly dust.

Partial dissolution of the original copper often revealed considerable structure and in some cases fissures. Carpenter<sup>7</sup> mentions that Elam found that copper crystals grown in vacuum contained blowholes, whereas those grown in nitrogen did not. It is, of course, most likely that both contained microscopic occlusions originally, but that under reduced pressures some of these grew to visible dimensions. Reports such as these, together with the experiments quoted above create doubts as to the freedom of any piece of metal from microscopic defects of this nature.

#### 4. The question of the tendency of the crystals to orientate.

No marked tendency to orientate was observed.

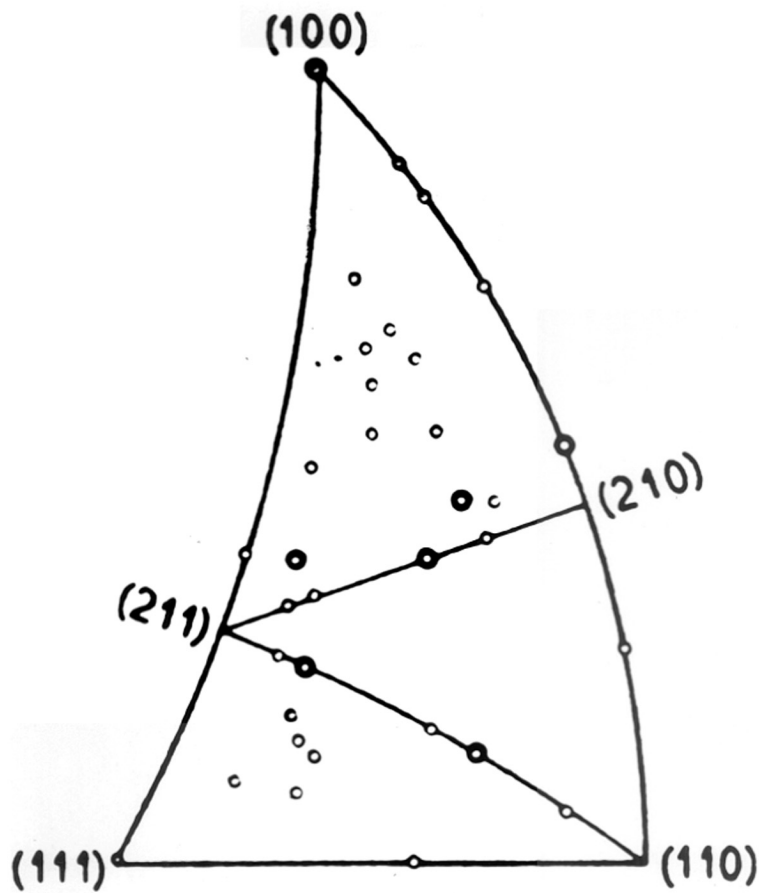


Fig. 4.

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This agrees with the opinion of Elam who based it on work carried out with copper, silver and gold. On the other hand Glocker & Graf<sup>13</sup>, as a result of the orientation of 40 specimens by means of X-rays, show a stereoscopic projection diagram in which the pole of the direction of the thermal gradient lies within the triangles between either the lines joining the (100), (210) and (211) poles or those joining the (211), (111) and (110) poles. Many times this pole lies accurately on one of the following lines:

that joining (100) to (210)

" " (211) " (210)

" " (211) " (110)

Their diagram is reproduced (Fig. 4) and it is seen that the axis of the crystal never lies within the triangle, the corners of which are the (110), (012) and (112) poles. Apart from these two facts, no general tendency can be observed. It is possible that the high frequency currents generated by their induction furnace may have influenced the results.

### III Technical Data

#### 1. Furnace

Several furnaces were constructed in the course of the work. The melting point of copper is 1083°C and a furnace

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temperature of about 1200°C was therefore necessary in order to melt it. This is rather above the temperature at which a long life can be obtained from silica tubes, but at the time silica was the only refractory obtainable in the sizes required within a reasonable time. It is fairly cheap and in any case furnace windings do not last indefinitely at this temperature so that periodic reconstruction is unavoidable. For these reasons furnaces were wound on silica tubing. The conventional design, in which the end pieces of asbestos wood are held in place by four "bus-bars", was not favoured since these bars must pass close to the furnace and rapidly become warped and corroded by the heat. Electrical connections are usually made via these bars, and the high temperature again leads to corrosion difficulties. Furthermore, one of the best lagging materials is light magnesium oxide and this is so fine in texture that it flows almost like a liquid and therefore requires to be held in a well sealed container. A furnace design was therefore evolved to overcome these difficulties.

The outer casing was constructed from a stout tinned sheet steel can of the type used in the commercial handling of liquids. It was 17" x 9" x 9". A circle of 4" in

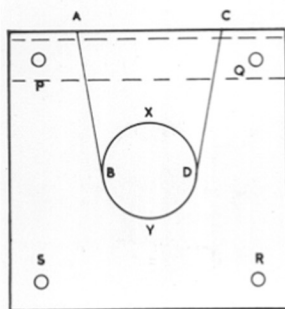
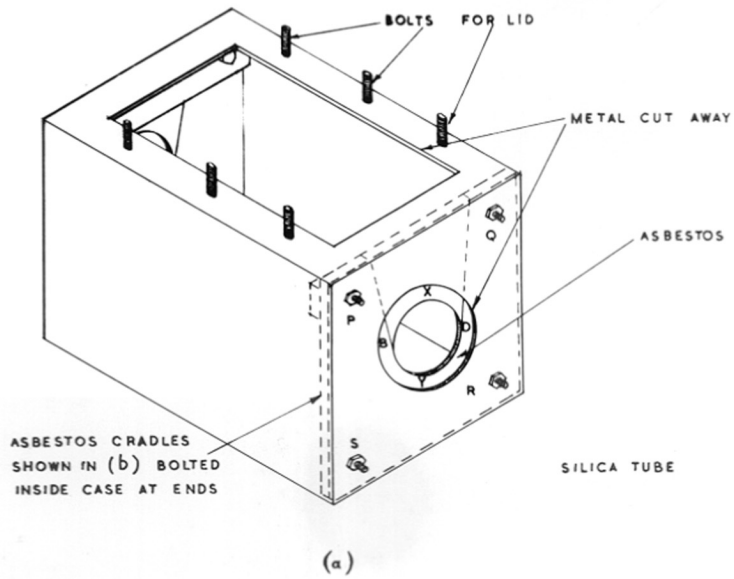


Fig. 5



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diameter was cut from the centre of each square end with an oxyacetylene flame and a rectangle 6" wide and extending to within  $\frac{1}{4}$ " of each end was cut from the centre of one side (Fig. 5a). A lid of asbestos was made to cover the whole of this side and was held in place by bolts and wing nuts. The heads of the bolts were inside and the bolt passed through a piece of steel strip, also on the inside, before emerging through the can itself; the steel strip served to give support to the comparatively weak sheet steel flange which was left after the rectangular hole had been cut. With the lagging used, it was possible to seal the lid on with putty since the outer casing did not get excessively hot.

Asbestos ends were made by cutting a hole to hold the furnace tube from the centre of a piece of asbestos wood, which just fitted into the cross section of the casing (fig. 5b), and then freeing the portion X by cutting along the lines AB, CD. The pieces Y were then placed in position inside the case against each end, and the wound tube put in position with each end cradled in the U shaped cutaway portions. The pieces X were then dropped into position. The whole was then bolted firmly to the end of the case through the holes

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EFGH. A piece of asbestos wood shown in dotted lines in Fig. 5b was placed behind the pieces X to hold them in place. They were unable to move upwards because they were tightly fitted against the end flanges of the top. Small gaps between the tube and ends and between asbestos and metal sheeting were caulked with furnace cement. Electrical connections were passed through the ends by drilling large holes in the metal sheeting, and smaller holes in the asbestos and then plugging the latter with close fitting metal bolts.

It was found that in order to get sufficiently high power dissipation with easy control it was best to use a doubly wound furnace, i.e. two concentric furnaces, the outer uncontrolled and the inner connected to a temperature regulator. The inner tube was  $2\frac{1}{4}$ " bore and  $\frac{1}{8}$ " wall thickness. It was made 17" long so as just to fit inside the case. The outer tube was 2" shorter so that 1" of the inner was left free at each end. It was of such a bore (c 3") so as just to slide easily over the inner tube when the latter was wound. The resistance wire used was 20 s.w.g. "Brightray", and the resistance of each winding was calculated to give 1KW dissipation. The

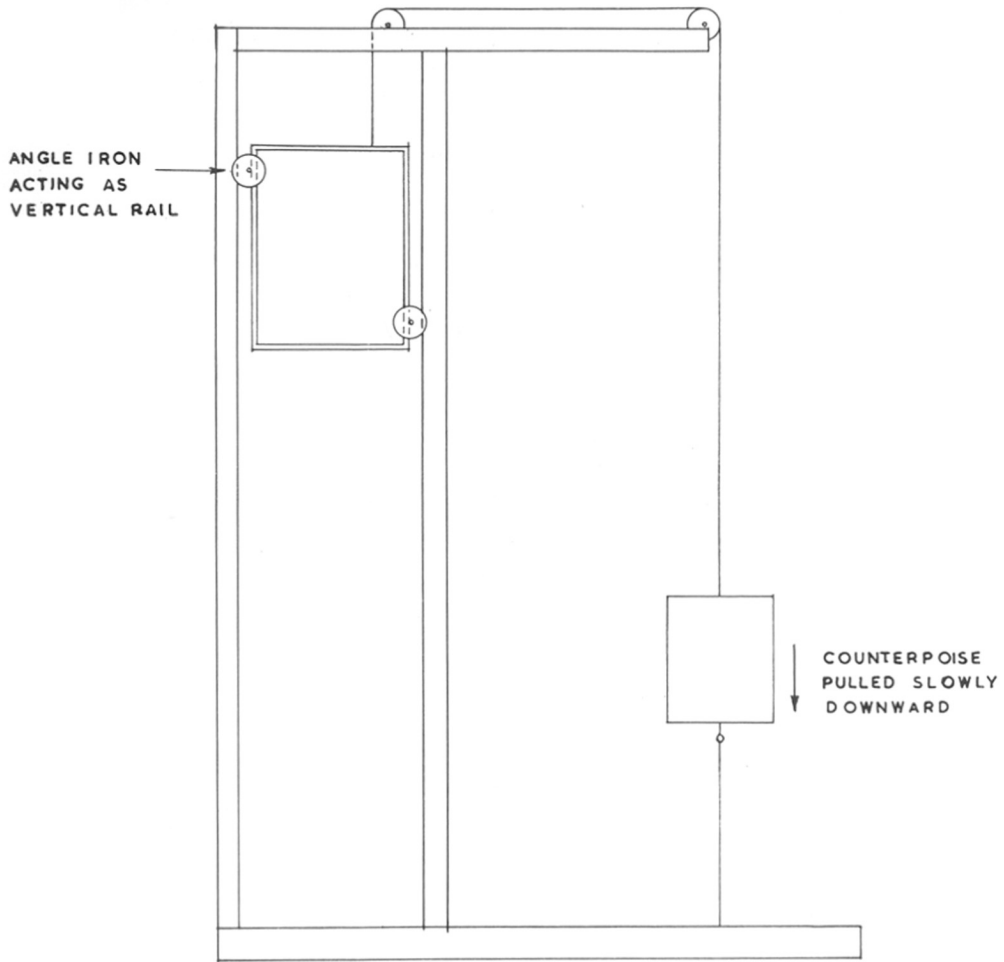


Fig. 6

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pitch of the windings on each was about 20% greater on the centre sections than for the sections within 3" of either end. The windings were encased in a thick layer of "C60" Alumina cement. Each winding was supplied from a separate transformer, but at one end of the furnace both windings were taken to a common lead so as to reduce the chance of large voltages developing between the two at any point along the furnace (the transformers being wired in phase).

The control resistance thermometer was built in next to the outer winding.

The furnace was mounted vertically in a steel "cage" which travelled upwards and downwards in a sort of lift shaft (Fig. 6). By using the assymetric method of support shown, space was left relatively free at the top end of the furnace for the insertion of thermocouples etc., and also the furnace was located firmly within the shaft by the wheels. The furnace was moved slowly upwards by pulling the counterpoise weight downwards with an electric motor working a small winch via a train of pulleys and worm gears. The attachment of the wire from the winch to the weight was made weak, so that, if the apparatus was left too long, damage would not be done by its over running. The lift and shaft etc. were made of welded angle iron.

2. Temperature control

An electronic temperature control unit as described by E. L. Yates<sup>18</sup> was used. The principle of this is to make the two halves of a centre tapped secondary winding of a mains operated transformer act as arms of a Wheatstone net. The third arm consists of a non-inductive fixed resistance, R, and the fourth of a similar resistance, r, plus that of the control resistance thermometer. At balance  $(r + \text{thermometer resistance}) = R$ . If the temperature then rises, a small A.C. voltage is obtained from the bridge and if it falls a similar voltage in opposite phase is produced. This voltage is amplified electronically and fed into a hot-wire vacuum switch which is "floated" at its triggering current by a winding from a mains transformer. If the amplified signal is in phase with this, then the vacuum switch operates the "on" position, if in the opposite phase, it switches off, so that by adjusting the phase connections the furnace can be kept at a constant temperature.

3. Platinum Resistance Thermometer

2 metres of .003" diameter "Thermo-pure" platinum wire were closely wound on a suitably chosen mandrel. Two such coils were made, one with a left hand and the other

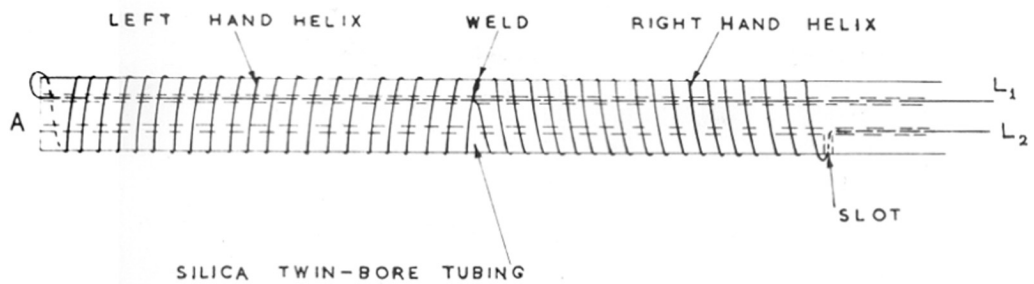


Fig. 7

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with a right hand helix. The mandrel was of such a diameter that when the platinum coil was removed from it, this coil would just slip easily over a piece of circular section twin bore silica thermocouple tubing of 3 mm. diameter. The two coils were put onto the thermocouple tubing and then joined end to end by twisting the wires together to form a single coil of low inductance. Paraffin wax was then melted over them and allowed to set so that they could be handled fairly easily while the twisted ends were welded together. Platinum wire leads were then threaded through the thermocouple tubing, one going right to the end A (Fig. 7) and the other as far as a slot B 6" from A. This slot was made previously by cutting through the silica with a carborundum slitting disc and rounding off the edges with a very fine oxyacetylene flame. The wax was then melted off the coil by placing on a hot plate in contact with filter paper and finally removed by washing with pure benzene. Its ends were then welded to the leads and it was stretched into the position shown in Fig. 7. A suspension of alumina cement in distilled water was applied to it and allowed to dry. This was done in order to prevent the individual turns of wire from making good electrical contact when

the wire sagged at high temperatures. The thermometer was then slipped into a transparent silica sheath of 4 mm. diameter. The thermocouple tube was cemented to the sheath at the "cool" end and an asbestos wood top was also fixed at this end to carry terminals to which contact was made by welding the platinum leads to stouter nickel wires. The resistance at room temp. was about 100 ohms.

The thermometer was inserted through a hole in one end of the furnace casing so that it was in contact with the outer furnace winding with the centre of the thermometer coil near the centre section of the furnace. In one model, the thermometer was actually built into the cement of the outer winding, but at high temperatures silica becomes electrically conducting and the resulting feed-back of mains e.m.f. into the electronic regulator made control impossible. Even with the thermometer just held in contact with the furnace there was considerable feed-back. This was used to good purpose by connecting the thermometer leads so that the feed-back tended to switch the inner winding off. This caused the vacuum switch to "chatter" so that the ratio of "on" to "off" times was dependent on the deviation of the temperature



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from that required, so that a roughly "proportional" connection was applied. It was found by experiment that the best control was obtained by "floating" the outer furnace winding and operating the inner from the temperature regulator. It is possible that some sensitivity was sacrificed by not having the control thermometer inside the furnace but the convenience of the arrangement outweighed this. With the arrangement described regulation to within  $\pm 5^{\circ}\text{C}$  at  $1000^{\circ}\text{C}$  or better was obtained for any given point in the furnace.

### IV Thermocouples

The thermocouple used was of conventional type Pt/Pt-Rh alloy. It was calibrated from time to time by breaking the "hot" junction and bridging it with a piece of silver wire of the same gauge twisted to the two leads so as to form a short length of intermediate metal. The thermocouple was then introduced carefully into the furnace and the galvanometer reading at which the silver melted, thus breaking the connection, noted. The experiment was repeated for gold. The short lengths of thermocouple metal sacrificed made negligible differences to the resistance since a sensitive galvanometer

was used with a high resistance in series. Results obtained were reproducible to within about 1 part in 1000.

V Purification of Hydrogen

Oxygen free hydrogen stored over hydroquinone solution as supplied by the British Oxygen Co. was used. It was passed through two traps at  $-80^{\circ}\text{C}$  to remove moisture and then through a bubbler containing vacuum pump oil to give an estimate of the rate of flow. A manometer also containing pump oil was connected to give an estimate of the pressure of the hydrogen as compared with that of the atmosphere and also to act as a safety valve.

VI Discussion and Further Suggestions

In general, the variations on the method of growth from the melt are as follows:

1. Metal and furnace in same enclosure
2. Metal in enclosure and both surrounded by furnace
  - (a) Enclosure filled with inert gas
  - (b) . . . . . evacuated

There are obvious disadvantages to (1) if fairly large crystals are required. The enclosure must be large enough to hold the entire furnace and yet must be gas tight. The only practicable materials available are opaque so that additional controls or windows must be fitted so

## Crystal Growth

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as to indicate the relative position of furnace and crucible, and provision must be made for moving one of the latter during crystal growth. Convection within the enclosure must be prevented so as not to overheat the materials with which the enclosure is sealed (usually wax). This means an evacuated enclosure and hence the presence of furnace windings and laggings together with the molten metal under circumstances where the former must be continually outgassing (if not actually slowly decomposing in the case of laggings).

If method (2) is adopted the relative merits of (a) and (b) are nearly equal. If an "inert" gas is used, there is risk of contamination by impurities in it. If a vacuum is used, then there will almost certainly be diffusion of oxygen through the walls of the enclosure at a high temperature. The former seems to be the better choice. When the necessity for "gettering" vacuum tubes in the radio industry is considered it seems reasonable to suppose that a good vacuum will not be obtained under the conditions of crystal growth and therefore to use an atmosphere which is not only inert but will "mop up" any impurities likely to diffuse into the system or produced by outgassing of the crucible etc. The question arises

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as to whether hydrogen has any effect upon the crystals produced. Molten copper at its melting point and 1 atmosphere pressure will dissolve .045 atoms of hydrogen per atom of copper<sup>19</sup>. On solidification this drops to .013 H/Cu and on cooling to 400°C becomes negligible. Provided cooling is carried out slowly enough, an atmosphere of hydrogen would not be expected to affect the crystal appreciably. In any case, before copper can be used in a surface reaction it must always be reduced with hydrogen to remove oxide layers. Hydrogen dissolved in copper in this way has been found to have no effect upon X-ray diffraction patterns, although Gwathmey has shown<sup>9</sup> that prolonged annealing of copper in hydrogen affects the electrochemical properties. However this may simply be due to the complete removal of surface oxide.

The final justification for the use of a hydrogen atmosphere lies in the experimental results of analysis and electron diffraction quoted above and the reproducibility of results obtained. The analysis was carried out on a specimen produced before the technique had been fully developed, in a silica tube the end of which had been sealed on by unskilled labour (the author) and may

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therefore be held to represent the maximum amount of contamination to be expected.

As a result of this discussion it would seem that the ideal method for the growth of metal crystals would consist of induction furnace heating of the crucible in a low pressure stream of hydrogen. Similar conditions could be approached in the method here used by using a double walled silica vessel with pure hydrogen circulating in the outer space and the crucible enclosure evacuated.

## Preparation of Crystals

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### The Preparation of Crystals for Reaction

The form of crystal used for reaction was a sphere about  $\frac{1}{2}$ " (12 mm) in diameter at the end of a shank  $\frac{1}{4}$ " in diameter and 1" long. These were prepared by careful turning from rod-shaped ingots. They showed very diffuse patterns on etching due to the destruction of the single crystal structure at the surface. The polycrystalline material was removed by gentle abrasion, with No. 0 emery paper lubricated with benzene and finally by etching until a clear pattern was obtained with no signs of streakiness due to the turning. Crystals were then electrolytically polished.

After a reaction it was usually sufficient simply to repeat the electrolytic polish for the next experiment unless etching had been unusually deep, in which case treatment started again with emery paper.

### Electrolytic Polishing of Metals

At first electrolytic polishing was carried out by the method of Jacquet as described by Benton & Gwathmey<sup>1/4</sup>. In common with other experimenters it was found that very careful adjustment of current density was necessary and that better results were obtained with the bath at about 40°C. Considerable skill and experience were

## Preparation of Crystals

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were required to obtain good results and a further drawback was the difficulty of cleaning the surface after its immersion in 50% v/v phosphoric acid which is fairly viscous. After polishing, a crystal was immediately transferred to another beaker and washed several times in cold boiled distilled water and finally with hot boiled distilled water. It was then transferred to the apparatus which was evacuated as rapidly as possible to remove water. A very slight tarnish appeared to be discernible after this treatment but was removed on subsequent reduction leaving a brilliant polished surface. However, it was found to be very difficult to remove the last trace of phosphoric acid particularly as bubbles adhering to the surface during the polishing appeared to encourage the formation of pits. Precautions were taken to avoid bubbles from the cathode but it was not possible to prevent very small ones from becoming dispersed in the electrolyte within the time required for polishing. If there was considerable pitting it was impossible to obtain a clean crystal.

A further drawback to the method was the scouring of the surface caused by the "tears" of higher density electrolytic solution which flowed downwards over the

surface of the crystals during polishing. This layer of high density solution in contact with the crystal was of course due to the usual Hittorf phenomenon of electrolytic transport. It does not flow downwards in a uniform sheet but tends to coalesce into streams which cut shallow furrows in the copper surface.

Nitric acid polishing was therefore used<sup>20</sup>. The method was to agitate the copper in the concentrated acid, then quench rapidly in a stream of water. It was then washed repeatedly in air free, boiled, distilled water, concentrated hydrochloric acid (which does not etch) and finally distilled water again. It was then transferred to the reaction chamber which was immediately evacuated.

Immediately before using a crystal for reaction surface oxide was reduced by heating in hydrogen to the reaction temperature (usually 445°C) for about 30 min. Preliminary experiments on crystals previously oxidised by heating in a low pressure of air showed that visible layers of oxide were completely reduced in this way within 15 minutes. It was therefore considered safe to assume that this treatment left an



## Preparation of Crystals

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oxide free surface. However, it was found with specimens which had become pitted during the electrolytic polishing that oxy compounds occluded in the pits were not removable by this method. This was understandable in the case of occluded phosphates but also occurred with specimens polished in nitric acid and it was therefore assumed that the common factor was bulk copper oxide or hydroxide. Its presence only became noticeable when the crystal was used in a reaction and manifested itself by destroying the etch pattern, as will be described later. This nuisance was very difficult to eliminate by even the most rigorous washing and must have been due to hydrolysis of copper salts leading to deposition of adherent hydroxide within the pits during the washing process. It was finally avoided, as mentioned, by boiling the specimen in concentrated pure hydrochloric acid after washing. Surprisingly, concentrated hydrochloric acid in the pure state has practically no action (if any) upon the polished copper surface. On subsequent treatment with hydrogen and evacuation at 445°C in the usual way a very slight deposit of copper chloride condensed on the cool parts of the reaction vessel walls where it could take no

further part in the reaction. No difference in the behaviour of crystals so treated and those successfully washed in the ordinary way was detected.

Throughout the entire preparative process the crystals were handled only by a copper wire hooked into a hole in the shank and were never touched by hand or by any surface which might introduce grease etc.

Orientation of Crystals

At first crystals were orientated by the method of Langmuir as described by Bridgeman<sup>7b</sup> followed by Gwathmey & Benton<sup>14</sup>. The crystal is etched with a solvent which exposes known facets, e.g. in this case it was etched with a solution, recommended by Gwathmey & Benton<sup>14</sup>, of 40 gm.  $\text{CuCl}_2$  per litre of conc. HCl. This exposes (001) facets and practically no others. A spherical ball is then attached to one end of the crystal (not necessary, of course, in the case of a spherical crystal). The crystal is then viewed in a room with blackened walls by the light of a small distant light source behind the experimenter's head and rotated carefully with the eye in a fixed position until one of the sets of (001) planes "flashes out". Keeping the crystal steady, a small plane mirror with duplicating ink smeared over its back is then held so that light is also reflected

## Orientation of Crystals

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into the eye by it and is gently touched onto the sphere while so orientated, leaving a spot of ink at the point of contact. This point is, by simple geometric considerations, the pole of the (001) planes concerned. The procedure is then repeated for as many of the six (001) directions as possible.

In practice the method is rather tedious. Because of the manner of preparation of the surface for reaction, permanent recording of the crystal poles is difficult (Gwathmey<sup>21</sup> used pin punched holes). With spheres of small diameter orientation is not very accurate, the degree of accuracy depending upon the skill and concentration of the operator and the elaboration of the apparatus used (e.g. special clamps, high quality thin mirrors etc.). It is simpler to use a reflecting goniometer than to improve upon this method. Further, it is difficult to avoid handling the crystal and this is obviously undesirable when orientating facets which have been produced in a reaction and it is desired to preserve the surface for further examination ("handled" crystals rapidly tarnish).

The obvious requirement is an apparatus into which the shank of the crystal can be fitted in an unique and reproducible position and on which the required crystal directions are marked permanently. This was achieved

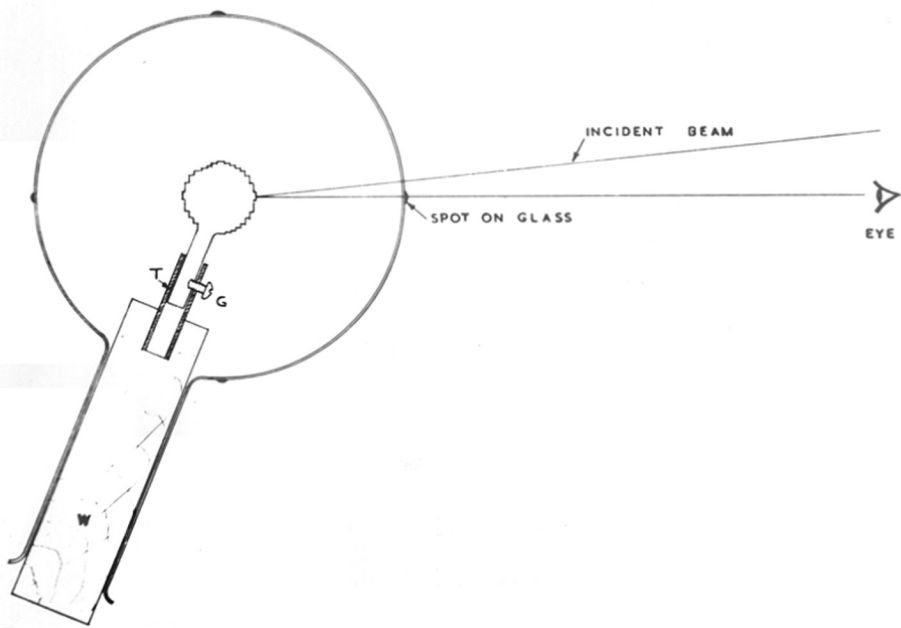


Fig. 8

## Orientation of Crystals

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by surrounding the spherical crystal with a concentric glass sphere which could be locked into a fixed position relative to the crystal (Fig. 8). The sphere was a round-bottomed flask of about 10 cm. diameter. A wooden cylinder<sup>W</sup> was turned so that it just fitted into the neck of the flask and a copper tube T was fixed concentrically in a hole in its end. The tube was of 1/4" bore so that the shank of a crystal would just fit into it, being held in place by a screw G passing through the wall of the copper tube and engaging in a depression in the shank of the crystal. Since the shank was protected during reaction and electrolytic polishing, this depression remained sufficiently well defined to enable the crystal to be located in the same position with sufficient accuracy throughout the useful life of the crystal. The mount was located in the neck of the flask by the superimposition of a mark on the wooden plug and a similar mark on the glass neck.

This globe orientator was used in the following way. It was held at arm's length with a distant source of illumination behind the operator's head which was held so that light falling on the crystal from the source S just

## Orientation of Crystals

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grazed the operator's eye. The author found it possible to get the light actually to pass through the right lens of his spectacles before falling on the centre of the crystal. The orientator was then manipulated until a "flash" was obtained from one of the sets of exposed facets. An ink spot was then put on the globe in direct line with the centre of the crystal and the eye. Within the accuracy expected of such simple apparatus this spot could be taken as the pole of the reflecting etch planes. The angle between the reflected beam and the normal is of the order of  $1-2^{\circ}$  and this is of the order of the semivertical angle of the cone of scattering of reflected light as found by reflecting goniometer. In any case the instrument was used only for locating the main crystal directions, i.e. cubic octahedral and dodecahedral, and for marking the presence of facets of higher indices without assigning more than a provisional set of indices to them.

A separate globe orientator was made for each crystal, so that, once the main poles had been marked, identification of facets produced in a reaction was facilitated by reference to them. Facets of high indices were marked and then identified by reflecting goniometer. Thereafter they could easily be identified by the marks on

## Orientation of Crystals

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the glass sphere. By handling with tweezers or copper wire, it was easy to fix a crystal in place without touching it and the globe then became a useful vessel in which to store the crystal away from dust etc. while yet being able to examine it for the making of sketches etc.

### Identification of Facets by Reflecting Goniometer

When facets of higher indices than (001), (011) and (111) occurred they were identified by measuring the angles between the facets in appropriate crystallographic zones with a reflecting goniometer. A special mount was made so that crystals could be set up in a conventional Wallaston instrument. The mirror was dispensed with, since the surface of the crystal would obviously not give a specular image of a distant illuminated slit which could be aligned with the corresponding image in the mirror, this being the usual way of using the instrument. Instead the eye was always held in the same position to view the crystal. This was done by using a ring sight. Since not one, but millions of facets made up the reflecting surface there was considerable scattering of light and a sharp setting of the instrument was not to be expected. It was estimated

## Orientation of Crystals

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that light of appreciable intensity was scattered through a cone of semivertical angle about  $1-2^{\circ}$  by a given set of facets. Further, the area of the sphere surface containing facets reflecting in any given direction was of several millimetres diameter and judgement had to be used as to when the diffuse "image" of the distant light source (an electric lamp) was in the centre of this area. With experience, it was possible to obtain readings reproducible to within  $\pm 1\frac{1}{2}^{\circ}$ , which was quite sufficient for deciding whether a set of facets were, say, (012) or (013).

### C. Reaction System

1. Vacuum Line
2. Hydrogen Supplies
3. Evolution of the Apparatus
4. Temperature of Reaction
5. Pressure of Halogen
6. Purity of Halogen
7. Effect of a Second Gas
8. Effect of Support on Crystal
9. The Apparatus in Use
10. Details of Experiment for Each Halogen
11. Experiments in the Presence of Hydrogen
12. Experiments at  $570^{\circ}$



## Reaction System

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### 1. Vacuum Line

A conventional vacuum line was built consisting of a mercury diffusion pump backed by a high-speed rotary oil pump and followed by a trap surrounded by alcohol/solid carbon dioxide freezing mixture at  $-80^{\circ}\text{C}$ . The oil pump was protected by a trap containing copper turnings to retain mercury vapour. The rest of the vacuum line was altered from time to time to suit the requirements of various experiments but consisted essentially of a junction separated from the pumping system by a large bore tap. At this point leads to associated parts of the apparatus such as the manometer and hydrogen reservoir were joined to the vacuum line as were also the ground glass cones and sockets by which the reaction vessel side traps etc. were connected. It was not considered that an apparatus such as this would give a really high vacuum in a reasonably short time because of the number of taps, ground glass joints etc. between the diffusion pump and the reaction vessel, but since it was proposed to use halogen vapours in an apparatus containing tap grease, it was improbable in any case that the system could be kept free from traces of grease oxidation products. It is doubtful if a metal such as copper can ever be successfully outgassed (see

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later references) so it was decided that in an exploratory work such as this it was better not to waste time and effort by a really high vacuum technique but to maintain the flexibility of having ground glass joints, taps etc. in the apparatus. Experiment showed that a vacuum of better than  $10^{-3}$  mm.Hg ("black out" with a high tension discharge) was easily attainable. In the final apparatus the halogen was flowed continuously, all joints to the entrance side of the reaction vessel being greased with "Silicone" resin, which reacts more slowly with halogens than "Apiezar L" tap grease. Runs were performed with the halogen (iodine) carried by a stream of hydrogen and gave the same results as those without the hydrogen. The rate of flow of hydrogen through the apparatus must always have been of the order of at least 10 times that of any impurity and in view of the large affinity of the halogens for metals it was improbable that traces of hydrogen halides, hydrocarbons etc. would interfere with the reaction.

In working with halogens, it is advantageous to use mercury in the diffusion pump rather than oil since any failure of traps to hold back either halogen or mercury immediately manifests itself by a deposit of mercury halide.

Because of the sensitivity of copper to mercury vapour<sup>2</sup>,

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the mercury in the nanometer was covered with a film of pump oil<sup>23</sup>. The manometer itself was of the type in which both limbs can be put into connection with the vacuum line for evacuation. It was used for measuring the pressure of hydrogen in the apparatus.

### 2. Hydrogen Supplies

In the early stages of the work oxygen free hydrogen was supplied from a cylinder and led into the apparatus via two taps at  $-80^{\circ}\text{C}$ . This proved inconvenient, so a reservoir was made from two 2 litre round-bottom flasks and sealed to the vacuum line via a tube containing reduced electrolytic copper and a tap. This 4 litre reservoir was filled with pure hydrogen to about 70 cm. Hg. pressure by allowing the hydrogen to flow in slowly over the heated copper. Any serious impurity was immediately shown by tarnishing of the copper. Before filling, the reservoir was evacuated and flushed out with hydrogen twice. One filling was sufficient for several runs.

### 3. Evolution of the Apparatus

For the initial experiments the reaction vessel was a simple test-tube about 1" diameter and 9" long inclined at an angle of about  $45^{\circ}$  and connected to the vacuum line by a ground glass joint. It was heated by a vapour jacket because

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of the easy temperature control obtainable with boiling liquids and also to allow the crystal to be viewed while being heated. This latter advantage was not achieved, since it was subsequently necessary to use sulphur vapour to obtain a high enough temperature.

The halogen was stored in a tube adjacent to the reaction vessel and connected to the apparatus by a ground glass joint. In the initial experiments only iodine and bromine were used. These were in the form of resublimed crystals or packed in glass ampules respectively, the latter being broken into the tube immediately before connection to the vacuum line. During the evacuation of the apparatus and reduction of the surface of the crystal the iodine and bromine were frozen back by solid CO<sub>2</sub> mixture or liquid air respectively. Though, these experiments were designed only to sound the possibilities of the apparatus and precautions were not taken to avoid contamination of the halogen with water vapour, the results agreed with those obtained later under better conditions.

Experimental procedure was as follows. The washed, electrolytically polished crystal was put into the reaction vessel, which was immediately evacuated to remove all moisture. When a hard vacuum had been obtained, the pumping system was cut off, air was let into the apparatus and the halogen

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reservoir filled. The apparatus was then re-evacuated and about 20 cm. Hg. of hydrogen admitted (after flushing with hydrogen). The vapour jacket was then brought up to temperature and reduction of the oxide film allowed to proceed for 30 minutes or more. The apparatus was then evacuated and cut off from the pumps and the halogen brought to a temperature where it would give a suitable vapour pressure by surrounding the container with an appropriate bath. Reaction was allowed to proceed for periods varying between 1 hr. and 3 hr. These experiments yielded information on the following points:

### 4. Temperature of Reaction

The lowest practicable reaction temperature was that of boiling sulphur ( $445^{\circ}\text{C}$ ) below this, e.g. at the b.pt. of benzophenone ( $305^{\circ}\text{C}$ ), the cuprous halide sublimed so slowly that unless halogen vapour pressure was inconveniently small a film built up at the surface. To have worked far above  $445^{\circ}$  would have meant dispensing with vapour jacket heating and would also have necessitated the use of quartz apparatus.

### 5. Pressure of Halogen

At  $445^{\circ}\text{C}$  it was found that if halogen pressure was of the order of centimeters of Hg. a thick coating of

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halide was built up round the crystal. However, if it was of the order of 2 mm.<sup>Hg</sup> clear etching was obtained. The actual pressure did not seem to affect the result in the latter case. It was therefore decided to keep the halogen pressure to 2 mm.Hg. or less.

### 6. Purity of Halogen

At low pressures the halogens give characteristic yellow discharges with a Tesla high tension leak tester coil. At higher pressures of the order of  $10^{-1}$  mm.Hg. a peach colour is obtained with iodine. With the bromine used, however, a colour was obtained which looked suspiciously like that due to oxygen. This disappeared when the bromine was "frozen back" with liquid air but reappeared after a few minutes at say  $-45^{\circ}\text{C}$ . The bromine was therefore distilled in vacuum between a vessel at  $-45^{\circ}\text{C}$  and a trap, which was being continuously evacuated, at  $-80^{\circ}\text{C}$ . The same effect was obtained with the product. After more experience was gained in the handling of bromine vapour at low pressures it was concluded that the phenomenon was simply a pressure effect. Bromine vapour flowing through a constriction will show the purple colour on the high pressure side and yellow on the low pressure side.

By freezing back the halogen after standing in

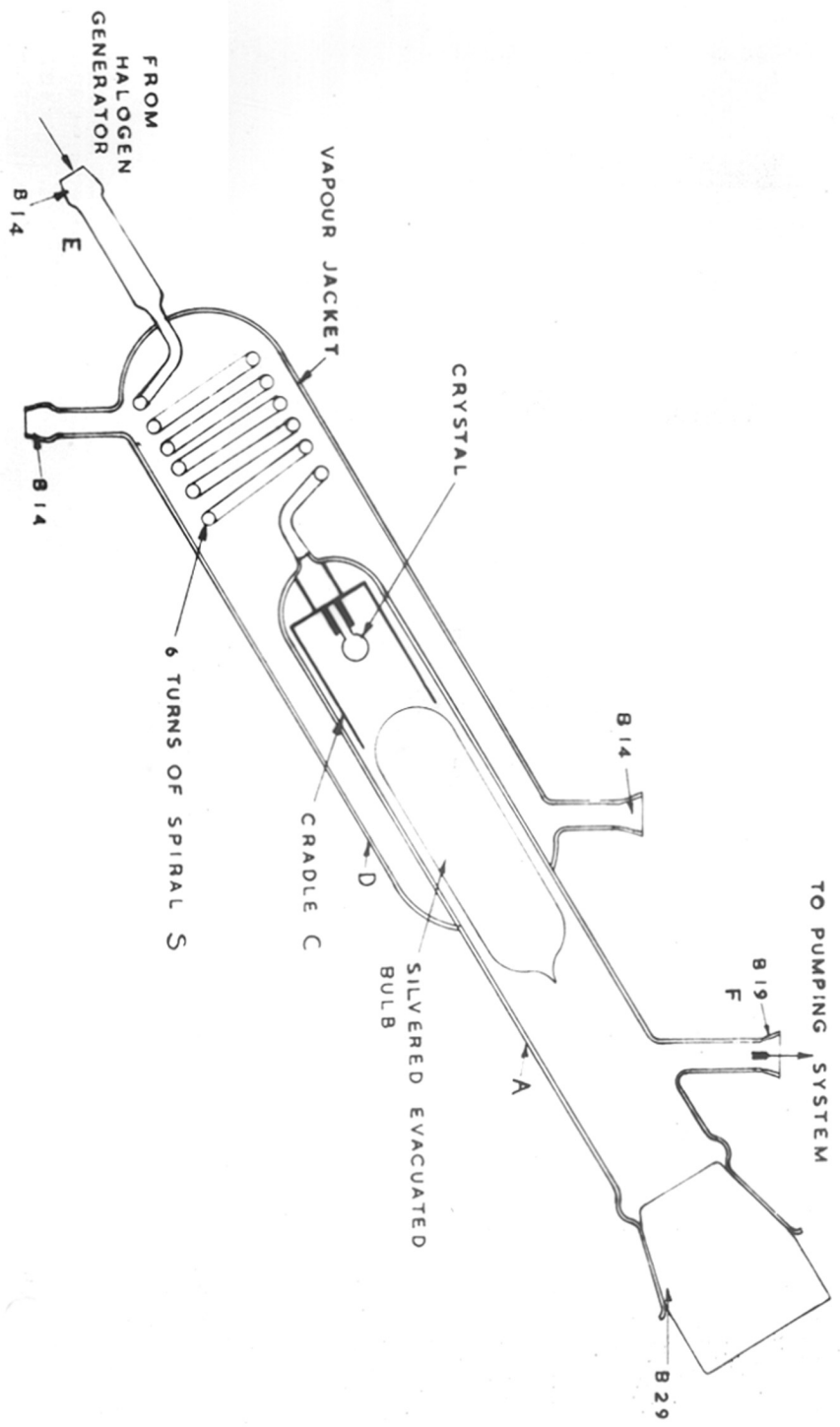


Fig. 9

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contact with greased taps for periods of several minutes a faint blue discharge characteristic of carbon compounds, was obtained.

### 7. Affect of a Second Gas

It was found that the presence of about 4 cm.<sup>H<sub>2</sub></sup> of hydrogen slowed up the diffusion of iodine so that reaction was negligible.

### 8. Affect of Support on Crystal

Etching did not take place on parts of the crystal in contact with the walls or within about 1 mm. of them.

### 9. Reaction Chamber

In the light of the above information, the reaction vessel shown in Fig. 9 was designed, consisting of a tube A surrounded by a vapour jacket D. Halogen vapour was introduced and heated by means of the glass spiral S. The crystal was held by the stem in the cup of the cradle C. This was made from a piece of glass tubing which fitted inside the reaction tube and the cup was held concentrically by a three legged glass "spider". The cradle was held off the bottom of the vessel by a spacer attached to the spider. The upper end of the reaction vessel was effectively lagged by an evacuated glass bulb, silvered on the inside, which rested on top of the cradle and fitted loosely inside the reaction vessel so that there was about 2mm.



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clearance for gases to pass. The upper end of the vessel was sealed with a B 29 stopper and connection was made to the vacuum line by the B 19 cone in the side arm F.

For use with sulphur vapour, the outer jacket had to be heavily lagged.

The apparatus was intended to give a stream of preheated halogen vapour free from molecular -beam or other directorial effects and without appreciable thermal gradients i.e. to provide the crystal with as uniform an atmosphere as possible while maintaining flow.

### 9. The Apparatus in Use

The reaction vessel was connected to the vacuum line by means of the side arm and joint F. With bromine and chlorine, the pumps were protected by an extra trap between them and the reaction vessel. Before use, the vessel was washed with hot concentrated nitric acid and then distilled water and dried by drawing warmed air through it with a Spengel pump.

The washed, polished crystal was introduced into the vessel in its cradle, the silvered bulb placed on tap and the B29 stopper inserted. The lower B14 cone B was blocked with a sealed off socket and the moisture removed from the crystal surface by evacuation. Air was then introduced, the stopper removed from B and the halogen

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generator connected (the details of the latter will be given under the heading of each halogen). The apparatus was evacuated, filled with hydrogen to a pressure of a few cm. Hg. and brought to 445°C. This took about 30 minutes. The hydrogen was then pumped off and the crystal heated for 10 minutes to remove grease or other volatile impurities. Hydrogen was then introduced to a pressure of 20 cm.Hg. and the crystal reduced for 30-45 minutes. The hydrogen was pumped off and the run commenced by allowing the halogen to come to the required temperature.

At first it was thought that care would have to be exercised in not drawing halogen through the apparatus too quickly. However, it was soon found that even when the reaction vessel was isolated from the pumps the pressure of halogen in the upper end of the reaction vessel was hardly detectable by its glow discharge i.e. was of the order  $10^{-3}$  mm.Hg. It was therefore decided always to operate with the pumps connected in order to remove impurities from the system as rapidly as possible. In other words, the copper was acting as a very effective "getter" for the halogen.

### 10. Details of Experiment for Each Halogen

#### I. Iodine

Resublimed iodine was put into a reservoir which was

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in the form of a test tube, bent at its upper end so as to be upright when connected by ground glass joint (sealed with silicone grease) to the entrance E of the reaction vessel. Immediately this connection was made the apparatus was evacuated so that it was swept through by iodine vapour. As soon as the characteristic iodine glow discharge was obtained the iodine was frozen back and the run proceeded with as described in the last section. During reaction the temperature of the iodine was kept at about 20°C, at which its vapour pressure is 0.2 mm.Hg.

Throughout the experiment a thick bloom of white copper halide built up on the cooler parts of the neck of the reaction vessel and on the silvered heat retaining bulb. On examination the deposit was found to consist of columnar crystals with their long axes parallel to that of the reaction tube.

### Bromine

The bromine was obtained pure in capsules from Imperial Chemical Industries Ltd. After careful cleaning a capsule was placed into a tube similar to that used for iodine with a glass sheathed iron rod on top of it. The apparatus was evacuated and the crystal reduced in

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the usual way. The bromine was frozen by placing a liquid air trap round the tube with a small pressure of hydrogen in the apparatus to transmit heat and kept frozen until it was required for use. The capsule was then broken by operating the iron rod magnetically.

During a run, the bromine was maintained at a temperature of about  $-45^{\circ}\text{C}$ , with a bath made by adding solid carbon dioxide "snow" to a nearly saturated solution of calcium chloride. The eutectic at  $-55^{\circ}\text{C}$  mentioned in various chemical handbooks was not observed. The low temperature was maintained by adding more solid carbon dioxide from time to time. The vapour pressure of the bromine was thus about 2mm.Hg.

### Chlorine

This was obtained from a cylinder. A glass trap was set up with a constriction on the in-going lead and a B14 socket on the out-going side. A tube containing caustic soda pellets was fixed into this socket and chlorine passed through the apparatus gently until the caustic soda tube became slightly warm. About 3 cc. of chlorine was then condensed in the trap at  $-80^{\circ}\text{C}$  and the in-going tube sealed off at the constriction. The trap was then placed in liquid air, the caustic soda tube

removed and the B14 socket connected to the cone B of the main reaction vessel, which was immediately evacuated and reduction etc. of the crystal proceeded with.

During the reaction, the chlorine was surrounded by a bath made by pouring liquid air into vigorously stirred alcohol until it was almost solid. This maintains a temperature of from  $-110^{\circ}\text{C}$  to  $-120^{\circ}\text{C}$ . The vapour pressure of the chlorine was therefore about 2 mm.

The chloride which sublimed on to the cool parts of the vessel was yellow to dark brown, but when damp air was admitted, became white. On re-evacuation this became yellow again.

## II. Experiments in the presence of Hydrogen

A needle valve was modified to pass gases into the apparatus slowly. The gases were led into the "packing" side of the valve under pressure greater than atmospheric so that if the packing around the needle leaked, it merely resulted in a loss of gas and not in contamination of the gas by air. A thin flexible copper tube was soldered into the "cone" side of the valve at one end and the other end was sealed into a length of glass tubing and B14 socket by piecein wax. This socket was used for connection to the main apparatus.

Between the reaction vessel and the vacuum line was

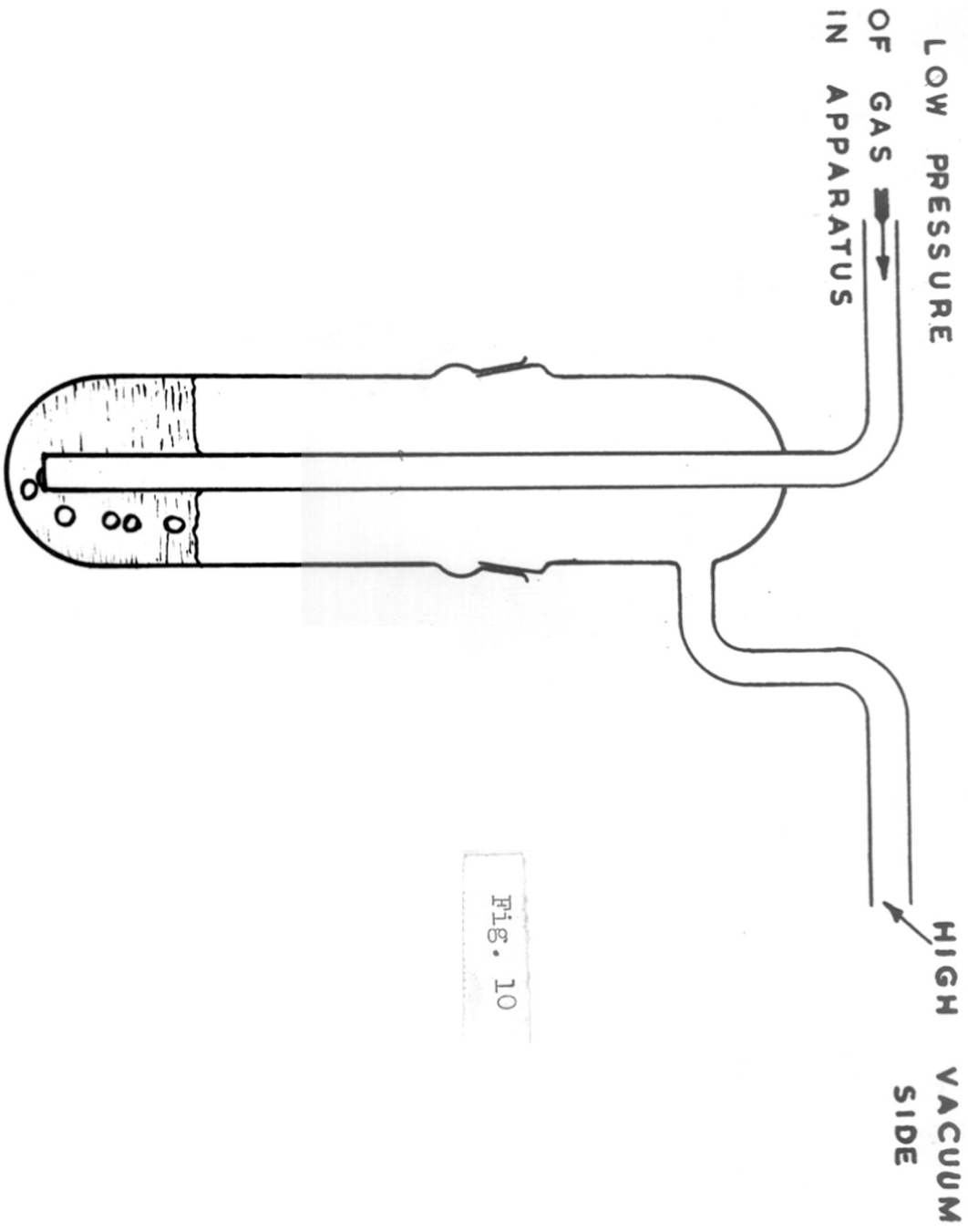


FIG. 10

interposed the bubbler shown in Fig. 10. The height of the silicone oil was adjusted so that when bubbles were passing slowly the pressure difference between the reaction vessel and the vacuum line was about 0.5 mm. mercury.

The apparatus was connected in the sequence:- hydrogen supply - needle valve - trap containing halogen - reaction vessel - bubbler - vacuum line. The needle valve was found to be capable of remarkably fine adjustment. When turned right off it would hold a vacuum of  $10^{-2}$  mm.Hg. easily overnight.

In use, the expansion of the gas on reaching the hot reaction chamber made it a little difficult to adjust the rate of flow, but once adjusted it remained quite steady at about 1 bubble per second.

Experimental Procedure (Iodine only used)

The crystal was dried in the reaction vessel in the usual way and the apparatus assembled as indicated above. The needle valve was closed, the whole apparatus evacuated and the iodine frozen back. Hydrogen was admitted and the crystal surface reduced in the usual way. The hydrogen stream was then adjusted to about 1 bubble per 1 or 2 seconds and the iodine reservoir brought to 20°C.

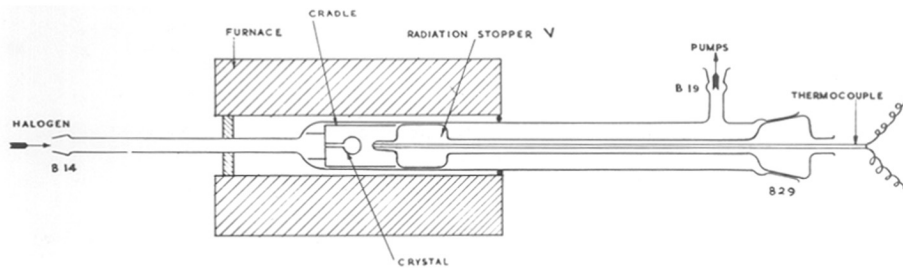


Fig. 11



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### Experiments at 570°C

A furnace of 1½" bore was constructed in two halves, each 6" in length. In place of the usual reaction vessel a simple tube that fitted inside the furnace was used (fig. 11). The bulb V was intended to hinder the radiation of heat etc. in place of the silvered bulb used in the previous apparatus. A thermocouple was carried in its tip and was about 1 cm. from the crystal during reaction. The tube was surrounded by the furnace made in two sections. It was intended to observe the crystal during the reaction by quickly sliding one section to one side, but this was found to disturb the temperature too much so the two units were run as one furnace. The furnace temperature was controlled manually and remained constant to within  $\pm 10^\circ\text{C}$ . The usual experimental procedure was used.

570°C is above the practical limit for Pyrex glass and during the course of a run the walls of the reaction vessel became warped so that it was necessary to break it open to recover the crystal. Two such runs were performed mainly with a view to designing a similar apparatus in quartz.

## Results

### (a) The Copper Halide

In each case, within about 10 minutes of the beginning of reaction, a visible "bloom" appeared on the cool parts of the reaction vessel. With iodine and especially with bromine this usually divided into two bands, one cream in colour, the other dark brown. The lighter band was on the lower, hotter part of the tube, and the darker, which was only a thin mirror unless reaction was prolonged, was in the cooler region. At the end of the reaction the cooler parts of the silvered bulb adjacent to the light band were found to be covered with fibrous crystals with their lengths parallel to the axis of the reaction tube. The darker band was presumably due to a trace of halogen dissolving in the cooler parts of the copper halide film.

The chloride was yellow brown but turned white in damp air emitting a smell of chlorine. It became yellow again on re-evacuation.

The following assumptions fit in with the descriptions of copper halides given in Lange's Handbook<sup>24</sup>.

- (i) Iodine forms cuprous iodide ( $\text{CuI}$ ) on the walls of the tube.
- (ii) Bromine forms cuprous bromide ( $\text{CuBr}$ ) on the walls at moderate temperature, but some cupric bromide ( $\text{CuBr}_2$ ) is formed on the cooler parts possibly by the action of halogen vapour which has escaped reaction with the copper.

## Results

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(iii) Chlorine forms cupric chloride ( $\text{CuCl}_2$ ).

Cupric iodide does not exist at room temperature and its appearance is ruled out. However, Lange describes cuprous iodide as red-brown while we found it to be more nearly "off-white". Colour probably depends on the mode of preparation. The bromide was almost certainly cuprous since cupric bromide is black and deliquescent. Similarly the chloride is assumed to be cupric since the cuprous form is white.

These observations do not, of course, show that the corresponding compounds were formed in the reaction at the surface of the copper. Within the chamber itself, halide molecules and those of the halogen itself must have collided frequently with the chance of reaction. However it is reasonable to assume that halide at the surface of the copper will be hotter and therefore less stable than that deposited on the walls. We should not, therefore, expect cupric bromide or cupric iodide. Evidence is offered later that copper chloride was present on the copper itself during etching.

The copper halides decomposed on the hot parts of the glass walls and crystal holder, depositing copper in the form of a red transparent colouring in the glass. The effect was greatest near the crystal and most intense in the cup of the crystal holder, although the copper stem which fitted into this cup was hardly etched at all. Decomposition of halide on the glass was increased at higher temperatures or by the presence of hydrogen.

(b) Typical Results

Etched crystals show patterns, typical examples of which are drawn in Fig. 1<sub>1</sub>. In these sketches the unshaded portions are those which reflect light back along its own path when it is directed along the axis indicated in each picture i.e. the light is always assumed to be normal to the plane of the page and the pole of the axis concerned is at the centre of the circle. Each of the columns I, II and III corresponds to a single etched crystal thus:-

I Well etched with Br<sub>2</sub>

II Lightly etched with I<sub>2</sub> Compare IIb with Plate II.

III Well etched with Cl<sub>2</sub>

In each case the temperature was 445°C.

The dark spots shown in column II are areas on the sphere which remain highly polished when the etch is light. With deeper etching these too are attacked and the pattern for iodine then resembles that for bromine. Thus the actual appearance depends on the amount of etching, but the microfacets which appear are always the same for a given halogen at the same temperature.

The "flash" varied in intensity according to which particular set of planes was involved and was taken as a rough measure of the extent to which a set of microfacets occurred. It was thus possible to assign an order to them as follows for results at 445°C.

## Results

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Halogen Microfacets	<u>I<sub>2</sub></u>	<u>Br<sub>2</sub></u>	<u>Cl<sub>2</sub></u>
(111)	Very strong	Very strong	Very strong
(011)	Strong	Strong	Strong
(012)	Moderate	Moderate	Hardly discernible
(001)	Very weak	Very weak	Very weak

Whenever a set of facets gives a strong or moderate reflection, the corresponding pole on the sphere is an area only slowly coarsened in the early stages, giving polished spots (See Fig. 11 Column II)

### (c) Effect of Impurities

Badly pitted and inefficiently washed crystals did not give etch patterns but presented a "Matte" etch of uniform intensity. The effect was common to crystals polished by either of the two methods i.e. in the phosphoric acid electrolytic bath or by nitric acid. It was concluded that copper salts became hydrolysed and deposited hydroxide which ignited to oxide in the pits. When such a crystal had been etched, it had a smokey, striated appearance as of cobwebs on the surface, but this material could be removed by wiping. In the first series of experiments an unsuitable crystal was used and it was only when confirming the results for a second crystal which was free from blowholes that the etch pattern was discovered. Comparison of results showed that though oxidized destroyed the pattern, the same microfacets

## Results

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appeared in the same relative intensities as in its absence.

### (d) Effect of Temperature

Below about 400°C it was almost impossible to volatilise the copper halide quickly enough to prevent a layer forming on the surface. Apparently cupric chloride is more volatile than cuprous iodide and cuprous bromide for it was just possible to etch with chlorine at 305°C (the BPT of benzophenone). At this temperature iodine built up a thick crystalline layer. Two runs were also carried out with iodine at 570°C which was the practical limit for glass apparatus. The results for chlorine and iodine at temperatures other than 445°C follow

#### Chlorine 305°C

- (i) The etch pattern was similar to that obtained at 445°C and the same microfacets were obtained in the same order of intensities.
- (ii) There was visible chloride on the surface in the initial stages of reaction, which disappeared later, but when the crystal was exposed to air it tarnished rapidly (within 5hrs). There must have been chloride on the surface.

#### Iodine

##### Room Temperature

A polished, reduced crystal was left with iodine in an evacuated enclosure for 10 days.

- (i) The iodide formed crystallite sheets which started at

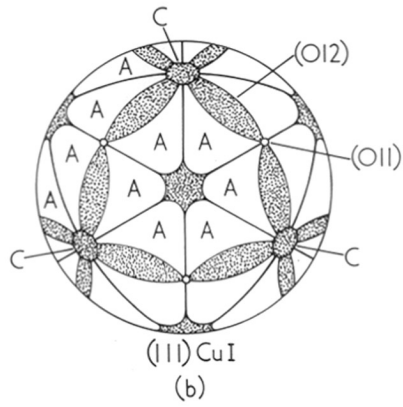
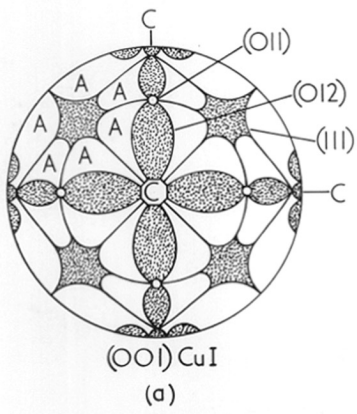


Fig. 13

## Results

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random points and spread over the surface until they met.

The surface then appeared like an "atlas" of the world.

(ii) During reaction the iodide layer was very dark brown and obviously contained dissolved iodine, possibly in the form of the  $I_3^-$  ion. This could be removed by freezing out the iodine vapour into a side tube at  $80^\circ C$  and the pure iodide was then seen to be cream coloured.

(iii) If the iodine was initially admitted while the crystal was at about  $300^\circ C$ , the iodide layer formed a pattern and this was perpetuated by further growth at room temperature for 20 days.

(iv) The iodide layer was loosely bound to the surface and easily removed by picking or gentle abrasion, except at a few randomly located spots. The underlying copper was brightly polished.

### $305^\circ C$ .

(i) A thick iodide layer was formed and appeared to consist of orientated crystallites giving the pattern shown in Fig.13. Under high magnification the iodide was seen to consist of fibrous needles. Strong reflections were obtained from the iodide on the following parts of the sphere:-

(111)region. Dark hexagonal spot and 6 surrounding regions A which reflect in (111) direction. Each of these six regions was centred between a (111) pole and a (012) pole and reflected to some extent in all directions between these two besides giving strong reflections in the (111) and (012) directions themselves.



## Results

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(011) region. Very small spot at (011) pole reflecting in corresponding direction.

(001) region. Small octagonal patch at pole reflecting (001) and with a complicated pattern of diagonals and cross lines.

(012) region. As seen in Fig. 13 there are pairs of regions, marked A which share common\* (012) poles. Each pair makes up a triangle bonded by two (111) poles and a (001) pole. When viewed along the common (012) <sup>direction</sup> pole a strong reflection is obtained from both halves of the triangle at once.

(ii) The iodide was easily removed and the underlying copper was found to be matt with a barely discernible suggestion of etch.\* The dark bars of the pattern shown in Fig. 13 were in the matt copper surface, not the iodide.

(iii) During growth, the iodide was yellow either in vacuum or with iodine vapour present. There was thus no iodine dissolved in it. The iodide became white at room temperature.

### 570°C

Two runs were carried out. In each case there was no pattern and only the (111) microfacets appeared. There was a slight "cobweb" over the surface as when oxide is present at 445°C, but there were no pits

\* Randomly distributed patches reflected in (011) directions.

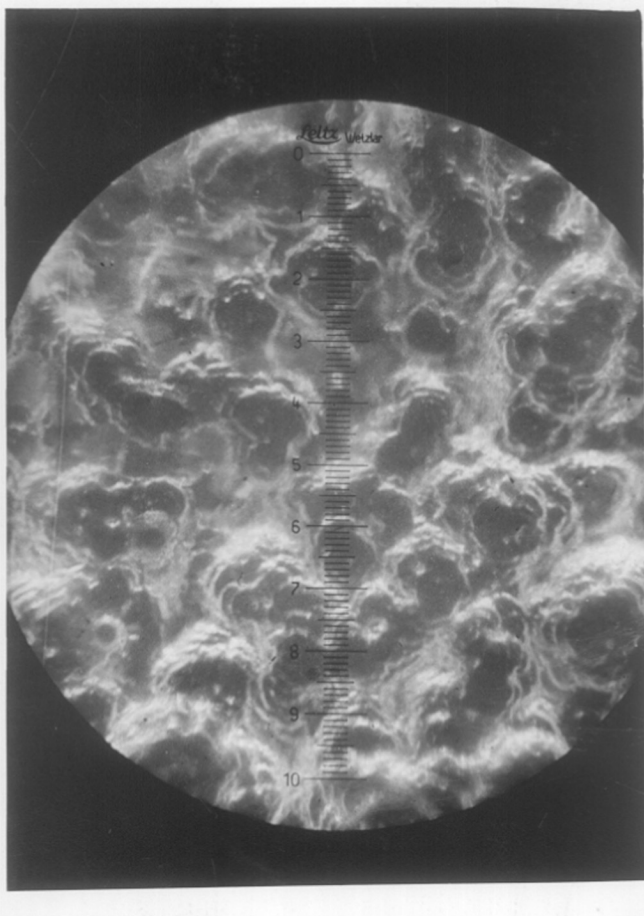


Plate III

## Results

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containing oxide and the crystal was known to be free from this tendency. There was much copper on the walls of the vessel and it is probable that the "cobweb" is due to decomposition of  $\text{Cu}_2\text{I}_2$  on the hot crystal.

The surface was considerably roughened and appeared to have been eaten away much more rapidly than at  $445^\circ\text{C}$ .

A photograph of the etch pits on a (111) pole is shown, Plate III. The dark areas are the centres of the pits which descend in terraces the tops of the terraces and the floors of the pits forming the etch microfacets. It is seen that the pits have an approximately hexagonal symmetry.

This was the only surface texture which could be examined with the apparatus available. All others were too fine.

### (e) Effect of the presence of hydrogen.

When the iodine vapour was carried over the crystal in a slow stream of hydrogen at about 0.5 mm. pressure, the results were identical with those obtained with iodine alone.

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## Theoretical Background

There are, at present, two principal methods of approach to the theory of the structure of metals. The first is that presented in reference 25 in which the binding electrons are regarded as moving in the periodic field of the array of ionised atomic cores occupying the lattice points. The second, due to Pauling, regards the metallic link as due to conventional chemical bonds

resonating among the various positions between an atom and its neighbours. A brief account of each will be given starting with the former.

The simplest form of the theory is that connected with the name of Sommerfeld and may be termed the "electron in a box theory" or "free electron gas theory". The following simplifying approximations are made:

- (i) Electrons are confined to the metal by potential barriers at the metal surface.
- (ii) Electrons move freely through the metal lattice.
- (iii) Electrons do not interact with each other.
- (iv) The number of electrons is equal to the number of positive charges on the ionised cores so that electrical neutrality is maintained.

When the appropriate Schrodinger equation is solved with the boundary conditions given above, a series of solutions is obtained corresponding with stationary electronic states, i.e. for a cubic box of side  $L$ .

$$\psi = \sin \frac{l_1 x}{L} \sin \frac{l_2 y}{L} \sin \frac{l_3 z}{L}$$

where  $l_1$ ,  $l_2$  and  $l_3$  are positive integers and  $x$ ,  $y$  and  $z$  are Cartesian co-ordinates parallel to the sides of the box. This is really the three dimensional analogue of a vibrating stretched string. Each state is associated with an energy  $E$  such that

$$E = W + \frac{h^2}{8mL^2} (l_1^2 + l_2^2 + l_3^2) \dots (2)$$

Where W = potential in the box taking that of a distant point outside the box as zero

h = Planck's constant

m = mass of electron

Behaviour of electrons according to these states only is allowed. The introduction of Pauli's principle limits the number of electrons in each state to two. If the shape of the box departs from a cube, e.g. by elongation of one side, the total number of states for a given energy interval is increased so that the number of states per unit volume in that interval remains constant. Thus, by a succession of limiting approximations, any shape can be accounted for, or in other words the external shape is immaterial provided dimensions are above the order of atomic diameters.

Provided we do not wish to specify the positions of electrons with any accuracy we may represent their states by means of a three dimensional vector diagram. The momentum of each electron is represented by a vector drawn from a fixed origin to a point in three dimensional cartesian space, to correspond with its magnitude and direction. On the simple theory given above, the points corresponding

to a given energy lie on a sphere and the various energy levels are represented by a series of spheres concentric about the origin.

At the absolute zero of temperature the lower energy levels will be filled by electrons in pairs with opposite spins and there will be a spherical surface on the momentum vector diagram sharply dividing filled from unfilled levels. **(Fermi distribution)** Let the corresponding energy be called  $E_0$ . Then as the temperature is raised there is a finite probability, increasing with temperature, that levels just above  $E_0$  will be occupied and some of those just below become vacant. There is no longer a sharp boundary between a region of completely filled states and one of empty states. The number of electrons excited above  $E_0$  by a given rise of temperature is relatively small, so that the contribution of this effect to the specific heat is small particularly as the energy increment for each is low. It is only at relatively high temperatures that the behaviour of electrons approximates to that of a classical gas.

The "free electron" theory accounts for many of the properties of metals such as conductivity, electron emissivity etc. without requiring the electrons to contribute appreciably to specific heat. For instance, electrical conductivity may be explained on the assumption that application of a potential accelerates electrons near the top of the Fermi distribution into higher, unoccupied levels with components of momentum vector in the direction of the field. The momentum

distribution above the filled levels is then no longer symmetrical, but contains more electrons travelling in the direction required by the field than against it. There is nett movement of electrons. The effect is proportional to the field applied and only operates on electrons which are within easy reach (i.e. small energy intervals) of empty levels. At normal temperatures these are a very small proportion of the total number and hence make little contribution to specific heat.

The theory was modified by Bloch to take into account interaction between electrons and the ionised atomic cores. An electron was represented by a plane progressive wave thus:

$$\psi = e^{ikr} \dots \dots (3)$$

Where r is the periodicity of the lattice in the direction concerned

k = the wave number vector given

$$\text{by } k = \frac{2\pi}{\lambda} \dots \dots (4)$$

where  $\lambda$  is given by  $p = mu = \frac{h}{\lambda}$ .

p = mu being the momentum. <sup>^</sup> This probability wave was

This probability wave was assumed to be modulated by a function with the periodicity of the lattice U(r) thus:

$$\psi = e^{ikr} U(r) \dots \dots (5)$$

In the free electron theory, the energy levels correspond with a series of closely spaced values of k so that

$$E \propto k^2 \dots \dots (6)$$

the only limitations on k being that in any given direction an integral number of waves must fit into the "box". In practice this means that k is regarded as

a continuous function since the energy levels are closely spaced. However, analysis shows that when the periodicity of the lattice is taken into account as in equation (5) equations corresponding with conditions where the electron wave would suffer Bragg reflection by the lattice have no real solutions. On account of the Heisenberg principle of indeterminacy neither have equations corresponding to states with energies near these. There are thus regions of forbidden energy in the  $k$  vector diagram. For a given lattice these regions correspond to values of  $k$  determined by the X-ray structure factor and form the surfaces of polygons. States corresponding with points on the surfaces of these polygons are forbidden. Each polygon encloses a space such that points within it correspond with allowed states. The space between any two such polygonal surfaces (or one such and the origin) is called a Brillouin zone. Each Brillouin zone corresponds with a definite number of electronic states per atom.

A further result found by this method of analysis is that the surfaces of constant energy on the  $k$  vector diagram are no longer spherical at any rate in the region of the bounding surface of a Brillouin zone. Surfaces of low energy (i.e. near the origin) are still appreciably spherical, but parts of equi-energy surfaces just below Brillouin zone boundaries are distorted towards the origin. Since the corners and edges of the Brillouin zone polygons are further from the origin



than the centres of the faces, it is possible to have points on both sides of the surface corresponding with the same energy states. Hence it is possible for a Brillouin zone to contain electrons in its lower levels before the next lowest zone is completely filled.

The value of this approach lay principally in that it gave insight into the difference between conductors and insulators of electricity. The conditions for an insulator are:

- (a) All Brillouin zones must be completely full or quite empty.
- (b) The energy gap between the highest level of the filled Brillouin zones and the lowest of the next empty zone must be large.

It is <sup>not</sup> then possible to raise an electron to a higher energy state than those already filled without crossing the large energy gap. There can be no net transport of electrons. A structure which appears to fulfill this condition is diamond for which it can be shown mathematically that the first Brillouin zone contains four electrons per atom which are presumably filled exactly by the valency electrons without overlap into the next zone.

Conversely, a conductor must have incompletely filled zones so that electrons can be accelerated into higher levels with small expenditure of energy. This can occur in two ways:

- (i) There are insufficient valency electrons to fill the occupied zone completely.
- (ii) There are the right number of valency electrons to

fill an integral number of zones but the energy gap between the highest of these zones and the next is so small that electrons "spill over" into the latter before the former is full.

Copper is considered by Mott & Jones to have one valence electron per atom. The lowest zone for a face centred cubic structure will hold two. Hence copper comes into class (i) and is a good conductor. Zinc with two valence electrons and a structure that will hold just two in the first zone is therefore considered to be in class (ii).

Semiconductors are considered to have all occupied zones practically completely full but with an energy gap between the highest almost fully occupied zone and the next zone of such an order that thermal energy will be sufficient at ordinary temperatures to excite some electrons into this next higher zone. The temperature co-efficient of conductivity will therefore be positive unlike that of metals which is negative and due to thermal-vibrational distortion of the lattice.

The analysis which this method entailed showed that for the alkali metals and other monovalent metals there would be, to a good approximation, one electron in the neighbourhood of every core on the average. This led to a third method of approach originally due to Wigner & Seitz. Each atom is considered as surrounded by a polygon constructed by bisecting the lines joining the nucleus to all adjacent nuclei with a normal plane. Only those structures which can be built up of such polygons without gaps can be treated. The principle on which the theory is based is that <sup>the</sup> wave function of

the electron contained in each cell must be the same for all cells, must be centrally symmetrical about the nucleus and must be continuous with those in adjacent cells over the whole of the boundary. The atoms are considered to be brought together slowly from a widely spaced lattice and the modification in the wave function of the valence electrons calculated for various spacings. It is thus shown that the sharp energy levels of the isolated atoms are broadened into bands at interatomic distances of the order of lattice spacings. The energy of the system can be calculated as a function of the lattice spacing and must be a minimum at the actual lattice spacing in the stable crystal.

This method gives a "picture" of the electronic distribution around each atomic core. It has been applied to copper by Krutter<sup>26</sup> and by Tibb<sup>27</sup>. The former modified the Hartree potential field in order to obtain wave functions corresponding to electrons in the 3d shell. He thus showed a strong overlapping of the 3d and 4s bands at the normal interatomic distance. Tibb retained the same Hartree field throughout to obtain the energy bands of the conduction electrons (i.e. those outside of the shell of principle quantum number 3). He also improved on the approximations made so as to fulfill the condition that the wave function must have a node in the (111) direction midway between (111) planes. He concluded that the highest state of the first conduction band is s like while the ~~last~~<sup>lowest</sup> state of the second band is p like.

The Pauling Theory 28.29.25c.

This is based upon a study of the interatomic distances in metallic and other structures. Each atom is considered in relation to adjacent neighbours. Thus, for the body centred cubic structure, bonds are taken as capable of being formed between an atom and its eight near neighbours and also its six next nearest neighbours. In the face centred cubic and close packed hexagonal arrangements, bonds can form between an atom and its twelve neighbours in contact. From a study of the bond shortening effect of  $V$  single electron pair bonds resonating among  $N$  positions in simple non-metallic substances of known structure, an empirical expression is deduced for the correction of the observed bond length to a hypothetical single bond radius corresponding to  $V$  bonds fixed in  $V$  positions. Alternatively, the bond length may be corrected to correspond with any given co-ordination number i.e. any value of  $N$ , keeping the valency fixed.

The empirical equation is

$$R(1) - R(n) = 0.300 \log.n \dots (7)$$

where  $R(1)$  is the single bond radius

$R(n)$  is the observed radius for a given value of  
(n)

$$n = \frac{v}{N}$$

For metals with lower atomic number than chromium, the valence  $v$ , is taken as the number of electrons outside of the inert gas core. The equation (7)

is then found to agree reasonably well with those data for metallic crystals which are suitable for a check on its validity. Additional information is required before the values of  $v$  for higher transition metals can be ascertained. For this, Pauling uses magnetic data, assuming that those electrons which contribute to the paramagnetic moment, though not included in inert gas shells are non-bonding, i.e. unpaired. Iron forms a series of magnetic alloys with the elements preceding it and following it in the periodic table. These alloys have a maximum magnetic moment corresponding to 2.44 unpaired electrons at an average atomic number of  $18 + 8.22$ . If the average atomic number =  $x$  then the fall in magnetic moment on either side of the maximum is given by

(2.44 - Moment in Bohr magnetons)

$$= 1 [(18 + 8.22) - x] \dots \dots (8)$$

e.g. iron itself has atomic number  $(18 + 8)$  and saturation magnetic moment 2.22 Bohr magnetons (i.e. 2.22 unpaired electrons). Pauling assumes that there are 2.44 non-bonding orbitals and that for atomic numbers above  $18 + 8.22$  these begin to be filled by pairs.

Thus we have

<u>A. No. of outer electrons</u>	<u>Fe</u> 8	<u>Co</u> 9	<u>Ni</u> 10
<u>B. Saturation magnetic moment (Bohr magnetons)</u>	2.22	1.71	0.61
<u>C. Difference (A-B)</u>	5.78	7.29	9.39
<u>D. No. of paired electrons</u>	0	$(2.44 - 1.71) \times 2$ = 1.46	$(2.44 - 0.61) \times 2$ = 3.66
<u>E. No. of bonding electrons</u>	5.78	5.83	5.73
<u>= (C-D)</u>			

Pauling therefore assumes that from Cr to Ni the number of valence electrons remains constant at about 5.78. He terms the orbitals contributing to bond formation "bond orbitals" and those outer orbitals which do not take part in bonds "atomic orbitals". In going from nickel to copper the remaining atomic orbitals become filled and pairing in the bond orbitals also commences so that the effective valence begins to drop off rapidly.

Similar assumptions are made in dealing with the fourth and fifth periods of the Mendeleef table and  $R(1)$  is plotted against atomic number for the elements. The curves obtained can then be compared with those for single bond covalent radii, tetrahedral radii etc. and hence, from the observed interatomic distances in a metallic structure, the principle bond types contributing to it may be guessed at. Thus on the evidence cited above Pauling concludes that copper has about 5.4 bonding electrons per atom (as opposed to 1 as favoured by Mott & Jones) and this value when inserted into equation (7) leads to a single bond metallic radius well below that which would be obtained on the assumption of s-p hybridisation. A structure such as  $\underline{d^2} \underline{d^2} \underline{d^2} d d$   $\underline{s} \underline{p} \underline{p} \underline{p}$  is therefore assumed where underlined orbitals are those filled with unshared pairs and the rest can hybridise to form bond orbitals. Statistically any of these may be partially or completely filled with paired or unpaired electrons.

Only a brief discussion of the relative merits of the two methods will be given, since neither appears to the author to give a very clear conception of the state of surface atoms or of how various surface crystal planes may be expected to react with gases. For the discussion of properties such as electrical conductivity, the earlier theory is easier to handle, but in considering <sup>surface</sup> phenomena it is more likely that the Pauling theory will <sup>allow</sup> ~~give~~ the transition of, say, a copper atom from the metallic lattice to a gaseous compound to be followed in terms with which the chemist is familiar. Thus, where bromine vapour is adsorbed on a copper surface, it is to be expected that the halogen molecules will rapidly take electrons from the lattice and split ~~it~~ into adsorbed bromide ions leaving positive holes in the lattice. These will be located in the surface copper atoms and held there by the halide ions in an electrical double layer. This may be visualised as a localising of one of the electrons from each surface copper atom in the Cu-Br bond. At high enough temperatures a propitious thermal vibration allows the system Cu-Br to form and evaporate.

Cu-Br

Presumably, when two of its electrons are so localised, an atom is no longer strongly held in the lattice. It is possible that by a study of the geometry of the hybridised orbitals, the Pauling theory may give insight into the conditions governing the formation of compounds at the surface.

A. Preface

As indicated in the Introduction, previous work on the subject has been spasmodic and isolated and there is as yet no recognised body of literature. The attempt will therefore be made to digest the principal papers in a sequence which welds the subject into a unity. Because of its important implications, papers dealing with work functions (or other potentials) of surfaces have been grouped under the heading of "Electronics", and this group will come first. Papers dealing more closely with the chemistry of surfaces have been grouped under the heading "Vectorial Reactivity".

Where a number of papers all bear upon one subject (e.g. Field Emission) the subject will be treated as a whole but when experiments have been carried out under different circumstances each paper will be dealt with separately. In each case the attempt has been made to elucidate the experimental facts and the conditions under which they were obtained. The development therefore depends upon a procession of papers and topics rather than a theory or point of view. This is unavoidable in the absence of more precise knowledge and it is hoped that the critical survey thus attempted will provide a more solid basis for further discussions.



B. Electronics

Chemical reaction involves transfer of electrons either from one atom to another (electrovalency) or by the sharing of electrons (covalency). In view of this and of the electronic theories of metals which have been outlined, it is manifestly necessary to enquire as to whether the ease with which electrons may be removed from a metal varies with the plane of the surface involved. We will therefore list the studies which might throw light on this subject:

I. Electrochemical potential

II. Photoelectric threshold, contact potentials, work functions, etc.

III. Electronic emission.

None of these give any conclusive proof that it is more difficult to remove electrons from one clean metal face than another. We will discuss each and its drawbacks in turn.

(a) I. The Variation of Electro-Chemical Potential with Crystal Face

This will not be discussed in detail since the evidence is that the effects observed are no more than a manifestation of the fact that chemical reactivity must be a property not of the face alone but of the face together with adsorbed surface layers. It may not give any indication whatsoever of the ease with which electrons are removed from the clean metal surface. Two recent investigations will be discussed both of which indicate that variation of potential with face is slight and dependent on surface conditions.

## Electronics

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In the first of these (which lists references to previous work in the field) C. J. Walton<sup>30</sup> prepared large grained specimens of high purity aluminium by the strain anneal method, cut out individual crystals and measured their solution potentials in concentrated HCl against 0.1N calomel electrode. Solution potentials and the rate of attack (i.e. evolution of H<sub>2</sub>) were measured on several specimens simultaneously.

It is desirable to stress the following points:

1. The potentials measured were not reversible potentials.
2. Electrolytic polishing of surfaces could not be employed since it left a film which upset the reproducibility of the results. Careful metallographic treatment was therefore used.
3. The differences in solution potential between faces of widely differing orientation were extremely small, generally less than 1 m.v. never more than 2 m.v.
4. There were, however, consistent trends. Faces of orientation near (001) tended to have a lower solution potential than those near (111).
5. It was consistently shown that a face which was (111) or nearly so dissolved decidedly more rapidly than a (001) face.

In the subsequent discussion, Dr. D. Harker pointed out that in a strongly etching fluid such as conc. HCl we should expect that all surfaces would be covered with etch pits with sides parallel to certain definite crystal planes and that the rate of

attack may depend on whether the pits exposed a larger or smaller surface area, which would in turn depend on the orientation of the planes bounding the etch pits relative to the face being attacked. Beside this our own work shows that the indices of the planes bounding the etch pits depends on the orientation of the original surface plane i.e. there is a sphere etch pattern effect. This complicates the issue but probably does not prevent Harker's argument being qualitatively correct. Harker also pointed out that the effect he mentioned should lead to all etched surfaces exposing the same crystal planes and hence we should not expect to find different potentials on different faces by Waltons method. The etch pattern effect may invalidate this second argument.

- (b) The second series of experiments in this section 9.31 is described in two papers by Benton, Gwathmey & Leidheiser who prepared single crystal polyhedra (cube and octahedron of copper exposing only (001) and (111) faces respectively and also slices with their edges varnished so as to expose only the above mentioned unvarnished faces. After electrolytic polishing these were immersed in a solution of copper sulphate acidified with sulphuric acid and the potential between them measured. It was found that the (001) face was .006 volts positive to the (111). The experiment was fairly reproducible. When boiled "air free" electrolyte was used in a hydrogen atmosphere the potential dropped to .002 volts but was restored to .006 by bubbling air through the solution.

The electrolyte atomic etched polished spheres most rapidly on (111) faces and least rapidly on (001) in the presence of air. In its absence i.e. with a hydrogen atmosphere the etching rate was greatly diminished. Various treatments of the surface failed to alter this effect with one exception. When a crystal had been previously heated in hydrogen at 550°C for several hours the etch pattern was reversed and so was the direction of the potential between the (001) and (111) faces. The octahedron now became .003 volts positive to the cube.

These experiments taken together with the results for electrolytic etching and deposition (see later) indicate that differences in potential between crystal faces are small and depend strongly upon the nature of the adsorbed layers at the surfaces. There is no evidence to show that they can be directly connected with differences in work function for clean surfaces.

It is probable that there is an equilibrium form for a metal crystal in contact with an electrolyte, but it is equally probable that this form is a property of the system as a whole and not a fundamental property of the crystal itself. The reversible electrode potential is a measure of the "solution pressure" of the surface atoms of the metal. This is most probably dependent on the adsorbed layers, which, as will be shown later, almost certainly exist at the surface.

## II. Photoelectric Threshold and Contact Potential

A series of studies on the electronic properties of single crystal faces were carried out by Farnsworth and

and his co-workers. The metals used were copper and silver. Single crystal faces were cut parallel to (001) and (111) planes and after careful mechanical abrasion and chemical etching to remove debris, were given a final light etch usually with nitric acid. (Thus, from the beginning, the nature of the surface was uncertain. The only way in which a suitable surface might have been prepared would have been by electrolytic polishing, preferably of a crystal grown with the required face in a flat surface). In the vacuum system the crystals were then protected (apart from the required face) by a molybdenum sheath and outgassed by heating to dull red heat in a vacuum of  $10^{-8}$  mm.Hg. for periods as great as 800 hours. Heating was carried out by electronic bombardment of the sheath. After treatment such as this there were definite signs of evaporation of the copper from the surface and that this evaporation etched the surface. Though this may be concluded to invalidate the results, they will be discussed briefly since they emphasize the difficulty of obtaining reliable information by such methods.

The salient features of each paper will be enumerated.

Soft X-rays from (001) and (111) faces of Copper  
Single Crystals <sup>32</sup>

The soft X-ray emission was plotted against incident electron voltage from 90 volts to 220 volts for the two faces indicated. The curves were identical, with fourteen breaks in each. Owing to the complexity of the phenomena involved it would be rash to attempt to draw deep conclusions from this but the experimental facts seem well established.

Contact Potential Differences between the (001) and (111)  
faces of Copper Single Crystals<sup>33,34</sup>

The two faces were cut from the same copper single crystal and prepared by electrolytic etching in acidified  $\text{CuSO}_4$  solution. This latter treatment was found to give a ~~matte~~ <sup>matte</sup> etch i.e. there was no "flash" indicating the presence of specific microfacets. The two crystals were outgassed in high vacuum by electron bombardment of their molybdenum <sup>molybdenum</sup> sheaths as described in the last paper. After several hundred hours outgassing the (111) face was found to be about 0.4 volts positive to the (001). In view of the difficulty of outgassing copper observed in work on autoelectronic emission etc. (see later) it is almost certain that a clean face was not produced. However, it is noteworthy that two pieces of polycrystalline copper similarly treated only gave a difference of about 0.01 volt. <sup>suggesting that</sup> The adsorption of impurities differed in orientation, amount etc. on the two crystal faces.

Photoelectric Properties of the (001) and (111) Faces  
of a Copper Single Crystal<sup>35</sup>.

The treatment of the copper surfaces was similar to that described in the last paper. It was shown that heating to red heat to outgas them resulted in etching due to evaporation of copper and the results seem to have depended on the surface condition at the time of any particular reading. The only definite result is the verification of the sensitivity of photoelectric properties to surface conditions.

Photoelectric Work Functions of (001) and (111) Faces  
of Silver Single Crystals and their Contact Potential  
Difference<sup>36</sup>.

Outgassing was carried out for periods as great as 2,000 hours at  $10^{-8}$  mm. and the evidence indicated that, as gas left the surfaces, the work function increased until a mono-molecular layer of gas remained and that if this could have been removed there would have been a decrease of the order of 0.1 electron volts. This latter conclusion was arrived at from the results of evaporating silver onto the surfaces to produce layers which, although they had complex structures, were assumed to be clean. Such surfaces appeared to contaminate slowly and give a corresponding rise in work function.

Values of the work function believed to be characteristic of the faces when covered by a monomolecular layer of gas are given as:



(111) . . . .4.75 electron volts

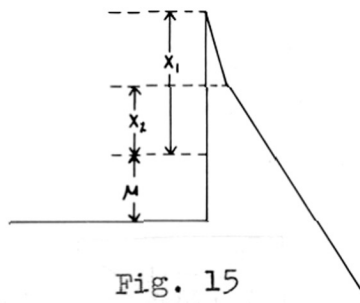
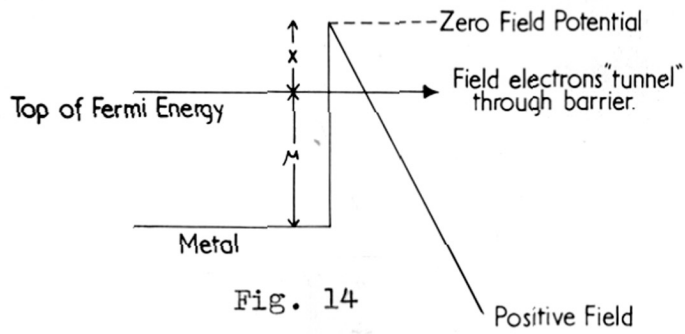
(001) . . . .4.81 " "

Similar work with other metals<sup>37,38</sup> has given similar results i.e. a difference of 0.1-0.2 e. volts for different faces. In none of this work was any attempt made to determine the textures of the surfaces involved and therefore its value is greatly diminished. It seems safe to say, however, that in no case was a clean surface prepared and that different contaminated surfaces appear to have different work functions.

### III. Electron Emission

#### (a) Field Emission of Electrons

The bulk of this discussion is based on an article by R.O.Jenkins<sup>39</sup>. A complete survey of the literature up to 1942 is given therein. The theoretical position at that time was summarised in the Fowler-Nordheim theory. If a fine metallic point is surrounded by a concentric positively charged sphere of comparatively large radius very steep potential gradients of the order of  $10^6$  volts/cm. can be built up at the point by the application of a potential of only a few thousand volts to the sphere.



## Electronics

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In fig. 14, U represent the height of the Fermic distribution of energy of electrons in the metal, X the work function. The greater the applied field, the steeper is the potential gradient CP and the smaller the distance d. When d is small enough electrons can be tunneled through the energy barrier BCD at a reasonable rate. Application of quantum mechanics to the system leads to the equation for the current I:

$$I = 6.2 \times 10^{-6} \frac{U^{3/2}}{(X+U)} X^{1/2} F^2 \frac{6.8 \times 10^7 X^{3/2}}{F}$$

Where F= potential gradient.

Stern, Gossling & Fowler made further calculations to allow for the effect of a contaminating layer. This modifies the potential diagram as in Fig. 15:

$X_1$  = work function of clean metal

$X_2$  = " " " composite layer

From experimental results it was possible to calculate the thickness of a layer of sodium on tungsten and this gave  $2.2 \times 10^{-8}$  cm. in good agreement with the known diameter of sodium atoms.

The theory did not indicate any vectorial property in the emission dependent on crystal direction. The only way in which such a condition could arise was by a

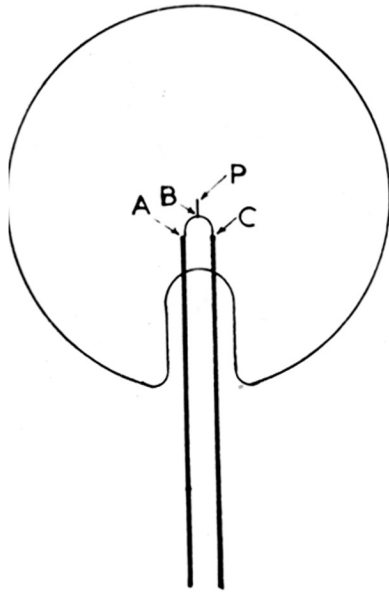


Fig. 16

variation in X with crystal surface plane.

The experimental basis for further work was laid by Muller (1936). He showed that by two experiments that the electrons must come from the top of the Fermic distribution i.e. that emission was not due to a low temperature thermal emission. This he proved by demonstrating that a point was not cooled by taking an autoelectronic current from it. A measurable cooling should have resulted from the emission of thermal electrons. Secondly, he studied the energy distribution of the electrons emitted and showed that the energies were approximately those to be expected of electrons from the top of the Fermic distribution. He next adapted the field emission microscope of Johnson & Shockley until its final form was that shown in Fig. 16.

The wire ABC is a filament. The point P a finely etched metal point which can be heated to any desired temperature by the filament. This is surrounded by a concentric spherical glass envelope covered on the inside by a willemite layer to which the positive potential can be applied. Arrangements were made for applying a high vacuum.

When an autoelectronic current is drawn from the wire an enlarged image of the surface of the metal point is produced on the willemite screen. The magnification is:

$$m = \frac{\text{radius of glass sphere}}{\text{radius of point (}10^{-4}\text{cm)}} \\ \approx 10^5$$

The image which was obtained has a striking resemblance to etch patterns on a spherical single crystal. Thus for tungsten we may summarise the results obtained by Muller and later workers.

1. A point which had been etched in sodium nitrite prior to assembly showed sharp lines in the image. The pattern was ascribed differential emission in different crystallographic directions from the single crystal which made up the fine point. The sharp lines were due to the edges between the main planes etched on the crystal point.
2. On raising the temperature of the point the emission was observed to smooth out and the actual movement of tungsten atoms repositioning themselves could be observed. This was ordered by the underlying lattice into definite lines of flow. After extremely strong heating emission was uniform except for the (110), (211) and (100) directions which gave rise to dark patches.
3. Molybdenum with a similar body centred cubic lattice gave similar results.
4. O<sub>2</sub> gas was found preferentially to poison the (100) faces of the crystal and cause large dark patches in the (100) regions of the image. An 80% increase of voltage was required for image production.

5. By heating an O<sub>2</sub>-poisoned point to progressively higher temperatures the original pattern was reobtained at the original voltage.
6. Muller obtained two pictures of the patterns from nickel and copper points respectively, but found in general that these metals gave unstable patterns. This he put down to the impossibility of outgassing these metals below their melting points. Each metal gave (111) as a non-emitting direction. This is therefore evidence that the (111) planes of these metals will adsorb electronegative impurities very strongly. It is noteworthy that (111) is always a plane obtained in the etching of copper by iodine vapour and is the only plane obtained by etching at higher temperatures.
7. Muller evaporated barium onto the crystal point from one side and was able to make the (110) etc. faces emit on that side. He therefore concluded that non-emission on these faces was not due to cavities since the barium gave no shadow-effect.
8. Benjamin and Jenkins studied the effect of heating the point in the presence of the field. On heating to progressively higher temperatures (though well below the melting point e.g. 1,770° compared with M.pt 2,900°C for Mo) the pattern underwent marked alteration and the required potential dropped to 60% of the original. On heating in the absence of a field, the point reverted to its original state. By the aid of a field plot they showed that the distortion of the point could be caused by the electrostatic field whose force on the

surface was becoming comparable with the strength of the metal and its surface tension at the temperatures concerned. The final "built up" shape would be such as to give the minimum energy with the field applied. They "froze" the point by sudden cooling and examined it with the electron microscope. The published photograph suggests that there were edges and corners to the "crystalline shape" of the point in the directions of greatest emission.

9. Nickel showed the building up effect to a high degree. "Building up occurred principally on (111) planes". Presumably by this they mean that the building up effect tended to make the (111) planes emit more strongly.

10. Muller and later workers showed that Na, Cs, Ba, Th etc. would migrate over tungsten and molybdenum surfaces at high temperatures and that when they did so they settled on certain definite crystal planes sometimes of quite high indices such as (421).

Oxygen inhibited the migration of Ba on tungsten. When barium was evaporated onto a "built up" point the "built up" pattern was obtained but at a lower voltage.

11. Benjamin and Jenkins showed that when a thoriated tungsten wire is used, the thorium diffuses to the surface along preferred directions i.e. (311) and (011). It then spreads from these faces (at which it appears) to cover them and also adjacent faces such as (421). The final pattern is the same whether the thorium is deposited on thoriated tungsten or not.

12. Haefer used an electron microscope to study the size and shape of the point and substituted the values obtained in the Fowler-Nordheim equation. The results were in agreement with the theory. He made further experiments



experiments with Ba, K and Cs layers on the surface and again obtained agreement.

13. Mitchell, J.M. and Ashworth, F.<sup>40</sup> in as yet unpublished work have used a very careful high vacuum technique to study the adsorption of copper on tungsten. In the preliminary work, they observed the adsorption of O<sub>2</sub> and H<sub>2</sub> molecules followed by splitting, rotation of the separate atoms around each other and migration apart. The observation was checked with argon gas which did not give the dissociation effect. The pressure, calculated from the ratio of collision of molecules with the point, was 10<sup>-14</sup> mm.Hg. but the actual pressure was probably 10<sup>-10</sup> mm.Hg., since the collision factor is believed to be 10<sup>-4</sup>. This pressure is that of inert gases not removed by the getter and the authors believe that the tungsten point was completely free from oxygen after flashing under these conditions. The clean point gave a definite emission pattern

(b) Thermionic Emission of Electrons

Martin, S.T.<sup>41</sup> cut a spherical single crystal of tungsten from a coarse grained rod and mounted it at the centre of a spherical, willemite-coated glass sphere to form a low power emission microscope. The phenomena observed were similar to those of field emission but contrast in the image was lower.

Traces of gas such as O<sub>2</sub> entirely altered the relative adsorptive powers of the various faces towards Ba, etc.

In this connection it is interesting to note that Langmuir<sup>63</sup> and later workers<sup>64</sup> used the increase in the work function of tungsten caused by the adsorption of oxygen etc. as a measure of the extent of that adsorption.

Summary of Electron Emission Experiments.

The following phenomena are established by electronic emission experiments:

1. A clean point gives a definite emission pattern even though it is smoothed by heating to near its melting point.
2. Contaminating layers of electropositive elements are mobile at temperatures below those at which they evaporate and are preferentially adsorbed on certain crystal regions where they improve the emission. Electropositive metals diffuse through tungsten crystals in preferred directions.
3. Electronegative elements also may be mobile on the surface and preferentially poison certain crystal planes i.e. lower their electron emission.
4. At temperatures well below the melting point, the surface atoms of a metal will migrate in a strong electric field. This process is governed by the geometry of the underlying metal crystal and leads to "building" upon certain crystal regions so as to lead to a polygonal shape which gives a marked emission pattern. This is almost certainly a manifestation of the effect observed by Johnson (p. ) with electrically heated tungsten filaments. Presumably, due to the emission of electrons, there exists an electron deficiency at the surface, i.e. a positive charge on the surface atoms so that they move in an electric field so as to minimise the energy at the crystal surface.
5. The possibility of observing individual adsorbed atoms etc. has, in a sense, been realised.

(c) Theories of Electron Emission from Crystal Surfaces

This section can be divided into two main parts, i.e.

1. Explanation of the pattern from a clean flashed point.
2. A semi-quantitative treatment of the phenomena of preferential adsorption etc. on the emitting surfaces.

1. The Pattern from a Clean Point

Attempts to correlate the pattern with various aspects of crystal physics have been made by Muller<sup>42</sup>, by Benjamin and Jenkins<sup>43</sup> and by Stranski and Suhrmann<sup>44</sup>. Muller and Jenkins base their ideas upon the electronic theory of metals, while Stranski explores the possibility of relationships between work function and various aspects of interatomic spacing, surface energies etc. Three main theories will be discussed, the first having been put forward simultaneously by Muller and by Benjamin and Jenkins, the second due to Benjamin and Jenkins and the third due to Stranski and Suhrmann.

- (i) Benjamin and Jenkins point out the similarity of the patterns to X-ray diffraction patterns from similar body centred cubic lattices. Both they and Muller independently considered the possibility of connecting the wavelength of electrons having kinetic energy i.e. at the top of the top of the Fermi distribution, with the condition:

$$\frac{q_0}{(h^2 + k^2 + l^2)^{1/2}} = n \frac{\lambda}{2}$$

but they showed that the values of  $\mu$  obtained lay outside of the feasible values except in the cases of one or two non-emitting planes for W, Mo and Ni.

- (ii) Benjamin and Jenkins proceeded to stress the similarity to X-ray diffraction patterns and that the bounding planes of Brillouin zones in k-space are also determined by the X-ray structure amplitude factor. The electrons at the top of the Fermi distribution may be represented as points lying on the surface of constant total energy which would be approximately spherical in k-space. It would only be necessary for this surface to touch or nearly to touch any of the bounding planes of the Brillouin zones in order that the kinetic energy of an electron may be such that it will make a Bragg reflection at a plane with the same indices in the crystal lattice.

However, the two explanations (i) and (ii) are in fact formally identical<sup>45</sup> and therefore if (i) is unacceptable so is (ii) and the latter explanation must therefore be ruled out

- (iii) Stranski and Suhrmann examine the following properties of tungsten crystal faces from a theoretical point of view:

The work of separation of the most loosely bound units of the crystal face.

The shortest distance between atoms in a crystal face.

The specific surface energy.

They investigated the possible relationship of each with the emission pattern, but because the validity of

the available data on work functions is uncertain, no very definite conclusions are obtained as to which property is most important. However, the second is practically ruled out on the evidence considered. Mitchell<sup>48</sup> and Stranski now believe that stepped structures on certain crystal regions are responsible for the pattern from a clean point.

(2) Theoretical Treatment of Adsorption Phenomena

Stranski and Suhrmann<sup>44</sup> examine under what conditions of radius ratio (between adsorbed atoms and those of substrate) the formation of "condensed" (as opposed to "expanded") layers is possible on various crystal faces of tungsten. Their conclusions are fairly well born out by the work of Muller<sup>39</sup>, Martin<sup>41</sup> and Johnson and Shockley<sup>46</sup> but later work of Benjamin and Jenkins<sup>47</sup> does not support their results. There is a possibility that this is because the barium used by Jenkins was contaminated with oxygen. This is part of one of the two main difficulties which occur in interpreting results of this kind. They are:

- (i) The practical impossibility of avoiding contamination of the surface by gases, especially O<sub>2</sub>. Even at 10<sup>-8</sup> mm. Hg. clean evaporated metal surfaces will not remain clean for more than 15 minutes<sup>48</sup>. It is improbable that any alkali metal could remain completely free from oxygen during an experiment. It would require less than a condensed monolayer of oxygen to vitiate the results.
- (ii) The adsorbed atoms will not have the diameters of those in the bulk metal recorded in the literature

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but will be nearer the ionic state. This will be aggravated by the impurities discussed in (a). It is therefore difficult to make predictions on the basis of radius ratios.

C. The Vectorial Reactivities of Crystal Surface Planes

The papers discussed will be grouped under headings I-V as indicated in the analysis on page 97. Early work on the subject was begun in Germany about 1928 principally by the school of Tamman. The single crystal sphere technique appears to have been introduced to the study of metals by this group. Section I includes this work and a paper by Glauner and Glocker who investigated the solution rates of flat surfaces prepared parallel to certain planes. Discussion of one early paper by Tamman is carried out under "Electrochemical Processes" section IIE rather than in its historical sequence.

The German work appears to have lapsed by 1931 and the subject was not pursued seriously until taken up by Benton and Gwathmey in 1939. Gwathmey subsequently explored the field very widely, most of the results being published in the Technical Notes mentioned. However, other papers by Gwathmey's team and work by other authors have been dealt with here under the appropriate headings.

The use of single crystal spheres for studying crystal growth is probably a very old technique and was naturally applied by those investigating the growth of metal crystals from the vapour. The connection between their work and that of Tamman and Gwathmey does not appear to have been appreciated by those working in this field. This work is reviewed in Section III.

Experiments on the etching of metals by vapours have been previously carried out in other connections but neither the necessity for using the sphere techni

## Vectorial Reactivity

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which exposes every plane nor the importance of the method for investigating the chemical properties of surfaces of crystals appear to have been realised. Two papers on this topic comprise Section IV.

A third and related paper, recently published, on the development of facets on silver heated in oxygen is also included.

Section V is a brief discussion of the vectorial nature of diffusion over crystal faces and through crystal lattices. Since such diffusion may be regarded as occurring through the continual breaking and formation of chemical bonds it must be included as a chemical phenomenon.



C. Vectorial Reactivity

I Initial Work

- (a) Hausser and Scholz
- (b) Tamman and Sartorius
- (c) Glauner and Glocker

II The Work of Gwathmey

- (a) Oxidation of Crystals
- (b) Rearrangements due to hot gases
- (c) Corrosion by oils
- (d) Wetting by stearic acid
- (e) Electrochemical Processes

III Reaction of Metal Crystal with its Vapour

- (a) Anderson
- (b) Stranski et al.

IV The Etching of Metals by Vapours

- (a) The etching of copper by oxygen
- (b) The etching of aluminium by hydrogen chloride

V Diffusion Phenomena

I. Initial Work

(a) Hausser, K.W. and Scholz, P.

This classical paper begins with a discussion of the growth of copper single crystals (including orientated crystals) and their faults and continues with a description of their now well known mechanical properties. These authors appear to have been the first to have used single crystal metal spheres to study the properties of surface planes. They showed that when such spheres were etched, a pattern appeared on the surface and that the orientation of crystal planes by reflection from etched surfaces agreed with that given by X-ray diffraction. They showed that oxidation also gave rise to patterns. They noted the fact that with some etching reagents the phenomena were not easily reproducible. They also etched with acids in the presence of  $\text{Ag}^+$  and  $\text{Hg}^{++}$  ions and showed that these metals were deposited preferentially on certain planes to form well marked patterns. These results were reproducible but depended on the conditions e.g. whether  $\text{HCl}$  or  $\text{HNO}_3$  was used as the etching acid.

They also compared ordinary etching with electrolytic etching and demonstrated that whereas the texture of the former was often too fine to see under the microscope the latter gave visible etch pits and grooves which became coarser as the etching proceeded. They suggested that since an etch pattern appears in neutral copper sulphate solution, a potential may exist between different crystal faces. Gwathmey (page 177 has since obtained direct evidence of this).

(b) Tamman, W. and Sartorius, F.<sup>2</sup>

These authors worked with single crystal copper spheres and rods obtained from Hausser. Their work may be dissected under four main headings:

- (i) Etching by oxidation in acid and alkaline media.
- (ii) Deposition of metals from solution onto single crystal spheres.
- (iii) Theory of etching.
- (iv) A study of etch pits etc. from a metallurgical viewpoint.

These will be discussed in the order given.

1. Etching

The following acid oxidising solutions were used:

- (i)  $(\text{NH}_4)_2 \text{S}_2\text{O}_8$
- (ii)  $\text{HNO}_3$  of various concentrations
- (iii) Dilute acetic acid +  $\text{NaNO}_2$
- (iv) 37%  $\text{HCl}$  +  $\text{HNO}_3$
- (v) " " +  $\text{FeCl}_3$
- (vi) " " +  $\text{CuCl}_2$

The authors show a diagram of the pattern obtained from  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and dilute nitric acid which etch similarly to give (011) microfacets on nearly all faces. They also state that results with the other etchants were similar. The author has checked this and finds that it is not so. For instance, mixture (vi) is regularly used by A. T. Gwathmey and by the author as an etch which gives very little pattern but exposes (001) microfacets over most of the surface.

Mixtures of 40%-60%  $\text{HNO}_3$  with  $\text{FeCl}_3$  and with  $\text{CuCl}_2$

are also stated to polish-etch but the author found the polish to be dull and to tarnish very quickly and preferentially on (111).

The alkaline etch used was  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NH}_3$  and this gave (111) microfacets on (111) and (011) areas. Since  $\text{Cu}(\text{OH})_2$  is insoluble, etching in alkaline solution can only occur if accompanied by complex formation.

The authors do not include the action of KCN solution under the heading of alkaline etching. This gives no definite microfacets, but a matt surface. Presumably, however, it only acts in conjunction with oxidation by air. Tamman and Sartorius appear to have assumed that oxidising attack will give one pattern in all acid solutions and another in alkaline solutions. The results obtained with  $\text{CuCl}_2/\text{HC}$  mixtures show, however, that the etch pattern depends on the reagent used, for it is different from that obtained with nitric acid etching. It does seem that all acid oxygen donating reagents give the same pattern in the same conditions of acidity or alkalinity.

## 2. Deposition of Metals from Solution

The authors showed that  $\text{Hg}^{++}$  and  $\text{Ag}^+$  deposited from solution in nitric acid gave different patterns. They attempted to account for this by relating the ease with which Cu atoms lost electrons to the readiness with which  $\text{Hg}^{++}$  and  $\text{Ag}^+$  accepted them, but no definite conclusions were reached.

## 3. Theory

The authors assume that reaction is so rapid at the

of the metal that the concentration of etchant reaches zero at the surface. They then examined the possibility of a correlation between velocity of etching and density of atomic packing on a plane. In the work of Hamberg<sup>49</sup> on the rates of attack of HCl on various faces of a calcite crystal, in that of Becke<sup>50</sup> on the dissolution of fluorspar in acids and alkalis and in their own work on copper, they find none. They therefore conclude that molecules of reaction product are adsorbed with varying strength on various faces and that these adsorbed layers vary either (a) in thickness or (b) in permeability.

In view of the dependence of etch pattern on the surrounding medium the central idea contained in this opinion seems to be unavoidable.

#### 44.) Metallographic Study of Etch Pits

The observation of fundamental importance was that a rod, agitated for 15 hours in  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution became a twelve sided prism and that some of the large etch pits on its faces had exact counterparts reflected, as it were in the opposite face.

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C. Glauner, R. and Glocker, R.

1. Single crystals of copper, each with a principal plane exposed in a flat surface were set up on a special glass stirrer, which was agitated in various etching solutions, and the rates of solution of the faces studied. The solutions usually consisted of  $0.1N.H_2O_2 + 0.3N$  acid (or other reagent).

2. Impurities in the copper appeared to have a marked effect. The reagents fell into two classes:

Class I

Rate of solution not greatly affected by impurities in copper

Class II

Sensitive to impurities in copper

3. Polycrystalline copper always dissolved more rapidly than single crystal.

4. Acetic acid +  $H_2O_2$  (Class I) gave a rate of solution on all faces which were independent of time

i.e.  $\frac{dx}{dt} = a$ . Where  $x = [Cu^{++}]$

HCl +  $H_2O_2$  (Class II) gave a rate which increased with time

i.e.  $\frac{dx}{dt} = a + Kx$

II. The Work of Gwathmey and Co-Workers

The bulk of this work is described in two technical notes<sup>52,53</sup>. It constitutes the nearest approach to an exploration of the whole field yet published. Unfortunately, owing to the (wartime) conditions upon which it was undertaken, much of this work is empirical but a large part of it is of fundamental interest.

Valuable details are given of the growth and preparation of single crystal spheres of several metals. These were subjected to the following reactions:

- (a) Oxidation in air
- (b) Rearrangement of surface layers due to the action of hot gases.
- (c) Corrosion by oils
- (d) Wetting with stearic acid
- (e) Electrochemical processes.

Only the barest details of the methods and results can be given. "Electrochemical Processes" will be treated as a general heading and will include the work of authors other than those cited above.

(a) Oxidation

1. The metals were oxidised in air or oxygen at various temperatures. Most metals showed patterns of interference colours in the oxide layer due to vectorial rates of oxidation. The pattern did not vary greatly with temperature of oxidation although the absolute rates did.

## Vectorial Reactivity

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2. Metals which form adherent protective films, not easily reduced in hydrogen, do not form very well defined oxidation patterns. This applied also to silver and gold which do not oxidise to any extent. The results may be summarised:

### Well defined patterns

\* Cu (fcc) } Patterns rather  
Ni (fcc) } similar  
Fe (bcc)  
Zn (hex) (exception?)

### Diffuse patterns or none at all

Au (fcc)	None
Ag (fcc)	"
Al (fcc)	Diffuse
Cd (hex)	"
Bi ( graphite)	"
Sn (tetragonal)	None
Cr (fcc)	"
In (fc tetragonal)	"

3. Sharp patterns were only obtained with Ni and Fe if the crystals were preheated in dry hydrogen for 24 hours at 550°C. It is noteworthy that these metals are easily passivated.

4. Ni, which has about the same size and weight of atoms as copper and immediately precedes it in the periodic table, gives a pattern which is rather similar, although the order of rates on the various faces is not quite the same.

f.c.c. = face centred cubic

b.c.c. = body centred cubic

hex = modification of close packed  
hexagonal



Vectorial Reactivity

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5. With copper, sunlight hastened atmospheric tarnishing and accentuated the variation in rate with plane. If the ultra violet band was filtered from the light it no longer had this effect. This emphasises the importance of electronic processes in the oxidation
6. More detailed work with copper<sup>54</sup> showed that heating in vacuum would not cause rearrangement. Heating above 550° in hydrogen would polish a previously roughened sphere.
7. Previous etching etc. of the surface altered the rates of reaction, but not the ratio of the rates.
8. When heating in air at 300°C specular reflections were ~~obtained~~ obtained from the oxide on the <sup>(112)</sup>poles to which the oxide adhered firmly while on all other regions it was easily rubbed off to reveal brightly polished copper.

(b) Rearrangements due to Hot Gases

The most detailed work, carried out on copper single crystal spheres, was published in a separate paper<sup>21</sup>.

1. Mixtures of hydrogen and oxygen of from 1-20% O<sub>2</sub> were passed over the spheres at 1 atmosphere and 360-440C. After a few minutes the surface became "foggy" and after 15 minutes a pattern was obtained. In general  
(111) remained smooth and (111) microfacets appeared on adjacent areas,  
(001) became rough and showed (011) microfacets (weak)
2. From 0.6 to 2.5% O<sub>2</sub> the rate of reaction on (111) was about twice that on (001) as shown by experiments on large flat planes prepared from the same crystal.
3. A (111) face, previously roughened by etching, tended to become smooth.
4. Considerable metal was deposited on the walls of the reaction vessel.
5. The presence of a small amount of another metal such as zinc, electrolytically deposited on the sphere had a profound influence on the pattern. This may have some connection with the action of promoters.
6. Beside the reaction of H<sub>2</sub> and O<sub>2</sub> on copper, other reactions catalysed by a crystal produced rearrangement in its surface to give either roughening or microfacets. Results are summarised below. Total pressure is 1 atmosphere in each case.

<u>Metal</u>	<u>Reaction</u>	<u>Remarks</u>
(a) Cu	$H_2 + 1\% - 20\% O_2$ at 360°C - 440°C	(111) microfacets (strong) in (111) regions (011) " (weak) " (001) " Roughening on (001) areas with complicated structure
(b) Cu	$NH_3 + O_2$ at 500°C	Striking pattern
(c) Cu	$NH_3$ decomposed at 500°C	Striking pattern
(d) Ag	$4O_2 + 3H_2S$ at 200°C	Roughening on (111) regions
(e) Ag	$20 H_2 + 1 Cl_2$ at 250°C	Preferential roughening of (001) areas
(f) Ni	$8H_2 + O_2$	(001) microfacets (strong) on (001) regions with complicated fine pattern (111) areas smooth but (111) microfacets (strong) on areas between (012) poles.

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7. With Cu (reaction (a)) the (001) faces which roughened most are regions of high oxidation rate. Similarly with Ni (reaction f) the regions which showed marked rearrangement were those of high oxidation rate.

8. In a further work Gwathmey and Leidheiser heated an electrolytically polished nickel sphere in carbon monoxide at 550°C. After 10 hours, carbon deposited on the (111) poles and finally, after several days only (001) poles and bands running from them through (011) remained free. In the presence of a large excess of hydrogen (90%) there was no deposit but the (111) poles were roughened.

### C. Corrosion by Oils

This work was almost entirely empirical and was carried out under conditions similar to those obtaining in internal combustion engines. The crystal spheres were alternately dipped in hot oil and exposed to an atmosphere of gas ( $O_2$ ,  $H_2$  etc.) several times per minute. This produces two distinct effects

- (a) the amount of metal removed varies with plane.
- (b) Some regions are roughened and others remain smooth.

### D. Wetting of the Surface by Stearic Acid

1. When spheres of certain metals are immersed in liquids such as stearic acid for several hours at elevated temperatures and then raised above the surface, the

film of adhering liquid breaks first at certain poles and then rolls back so that adhering drops are left only at certain other poles. The effect was only detectable with Cu, Ni and Fe. Other metals remained completely wetted. Thus, with the exception of Zn, metals which give good oxidation patterns also give good stearic acid wetting patterns.

2. Even Cu, Ni and Fe spheres remained completely wetted when the atmosphere above the stearic acid was  $H_2$ . It thus appears that the phenomena are connected in some way with surface oxide layers.

#### E. Electrochemical Processes

##### 1. Electrodeposition

##### (i) Cu on Cu single crystal from $Cu^{++}$

Gwathmey<sup>9.31.52</sup> appears to have overlooked a paper by Tamman and Straunainis<sup>8</sup> and to have repeated some of the work therein. It is interesting to compare the two methods of approach. Both worked with copper single crystal spheres. Tamman and Straunainis showed that it was necessary to etch them (with  $HNO_3$ ,  $(NH_4)_2S_2O_8$  or ammonia +  $H_2O_2$ ) to obtain orientated deposits. These they obtained on flat surfaces worked on the spheres parallel to cubic, octahedral, dodecahedral etc. faces. The orientation of the deposit was verified by etching followed by reflection of light and also by sectioning to show that the deposit was metallographically indistinguishable from the substrate. Gwathmey started with electrolytically polished spheres and although he used lower current densities was unable to obtain orientated

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overgrowths at (001) poles but did so on other faces. <sup>Using</sup> ~~Using~~ electrolytically polished and polish etched spheres respectively, both Gwathmey and Tamman report that the deposit showed microfacets on certain poles. Gwathmey continued deposition for long periods (c. 50 days) and obtained a polyhedron with flat moderately rough (111) faces flat smooth (012) faces and rough (011) regions containing (111) and (012) microfacets. When a deposit was obtained on (001) by raising the current density it was polycrystalline. When hydrogen was bubbled through the solution, the product was a roughened sphere but each pole had the same characteristics as in air saturated solution.

Gwathmey's results appear to be the more valuable since the various poles of Tamman's sphere would expose not the plane of each pole but the microfacets due to the etch (e.g. (001) microfacets do not appear with any of the etchants used by Tamman). Furthermore, it illustrates the persistence of surface character with increasing thickness of deposit. Unfortunately neither Tamman nor Gwathmey investigated the deposit by X-ray or electron diffraction techniques which might have given information on the micro textures and structure, e.g. the extent to which lineage occurred.

### (ii) Cu on Cu from Cu (CN)<sub>4</sub><sup>-</sup> solution

Tamman showed that orientated deposits are only obtained when the Cu<sup>++</sup> (hydrated) ion itself is reduced and not from complex ions. The author suggests that an

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agent such as the CN group might co-ordinate so strongly onto the metal surfaces as to prevent continuation of growth except by unconnected crystallites; as Tamman and Straumain's suggest for deposition from  $\text{Cu}^{++}$  at high current densities, the process may be analogous to crystallisation from a super-saturated solution.

### (iii) Zn on Zn from $\text{Zn}(\text{CN})_4^{--}$ solution

Gwathmey<sup>52</sup> showed that at first (0001) and (1100) microfacets appeared at the corresponding poles but that after several hours the deposit became random.

(All further abstracts in this section are taken from the paper by Gwathmey<sup>52</sup>).

### (iv) Metal on a similar metal

#### (a) Cu on Ag from $\text{Cu}^{++}$ solution.

A deposit was obtained over the whole surface which behaved very much as Cu deposited on Cu single crystals. The deposit was shown to be single crystal by polishing and etching it.

#### (b) Ni on Cu

Suitable conditions for obtaining an oriented deposit were not found, though there was slight orientation on (113). Deposition was preferential on (111).

The following general results were noted:-

### (v) Metal on another metal - general case

Usually the metal deposits preferentially on and

around one set of poles at first and then spreads. Specular reflections from certain areas at low current densities indicate that these deposits are orientated with respect to the substrate.

(vi) Sometimes deposits adhered more strongly at certain poles than on the rest of the crystal.

(vii) Comparison of a metal on metals similar to each other

Nickel behaved similarly on both Cu and Ag as did lead on Cu and Ag.

(viii) Effect of Alternating Electrolytic Current

When subjected to 60 cycle a.c. in an electrolytic bath, specular relations were obtained from certain areas with some metals, e.g. Ni, Cu. The pattern produced is the one usually obtained by exposure to the electrolyte alone but appears much more rapidly. The authors suggest that it may be a good method of determining equilibrium faces in electrolytic solutions.



III. Reaction of Metal Crystal with its Vapour

These processes do not differ formally from reactions at crystal surfaces. However, owing to the homogeneity of the systems involved, theoretical treatment is simplified to the extent of being feasible. The foundation of this was laid by Stranski<sup>55</sup> who makes the following approximations and assumptions<sup>16.44</sup>:

- (i) Each atom may be considered as a neutral particle.
- (ii) Between an atom and each of its neighbours there is an interaction energy dependent on their distance apart.
- (iii) The interaction between an atom and any given neighbour is independent of the presence or absence of other neighbours.

Thus, by considering the number of atoms which are first nearest neighbours (1st shell atoms), 2nd nearest neighbours (2nd shell atoms) etc. it is possible to calculate the energy of separation,  $\psi$ , of an atom at any given position in a crystal surface. The average energy,  $\bar{\psi}$ , corresponding with the pressure of vapour surrounding the crystal is then calculated. Then, starting from any single crystal form, all crystal units with work of separation less than  $\bar{\psi}$  are eliminated, one after another from its surface. Lastly the areas of all surfaces are varied with the final mean work of separation reaches the value  $\bar{\psi}$ . In this way it is possible to calculate the equilibrium, forms of crystal at given vapour pressures, i.e. at given temperatures. Reasonable assumption have to be made concerning the interactions between an atom and its neighbours in successive shells.

Obviously metals which sublime easily, such as Zn or Cd, offer the most suitable material for testing this theory. Two papers will be discussed:

(a) Anderson, P.A.<sup>15</sup>.

1. Hemispherical crystals about 1 cm. in diameter were formed as described on page 10
2. The temperature of the metal surface was not stated but the degree of supersaturation was about  $5^{\circ}\text{C}$ , i.e. the vapour was in equilibrium with a mass of metal about  $5^{\circ}\text{C}$  above the temperature of the hemisphere.
3. Absolute cleanliness could not have been achieved, e.g. greased joints were used for connection to the vacuum line. An improvement of vacuum from  $10^{-3}$  to  $10^{-6}$  mm.Hg. produced no change in the results.
4. The initial surface was of a brilliant polished appearance. It rapidly became foggy and finally a visible structure appeared. The ultimate form was step like as if a roughly spherical shape had been built up from different sized hexagonal plates parallel to the (0001) planes.

Using a model similar to Stranski's and taking into account neighbouring shells up to the fourth, Anderson showed that the results were more or less in accord with Stranski's theory.

(b) Kaishew, R., Keremidtschiew, L. and Stranski, N.<sup>16</sup>

These authors prepared spherical single crystals in vacuum in sealed off glass apparatus by evaporating the metal from one end of a glass tube and carefully cooling the spherical droplets which formed at the other end. Growth from the vapour was then continued by maintaining a very small temperature gradient from the former end to the other.

Results and notes:

Cd

1. The spheres, grown from the melt, showed steps parallel to the (0001) plane.
2. Temperature of growing crystal about 300°C; m.pt. of Cd 320°C.
3. The final form was similar to that obtained by Anderson for Zn, i.e. a coarsened structure was formed.
4. In general the faces produced were (001), (10T0), (10T1). Below a certain supersaturation, about 1°C or less, other faces appeared such as (10T2), (1120). The first set belong to equilibrium forms owing their existence to interaction between nearest neighbours only, the second set are due to interactions between second nearest neighbours only.

Zn

1. It was fairly easy to produce perfectly rounded surfaces from the melt.
2. Zn crystals do not coarsen but the faces appear as small flat areas on the sphere. The faces which always appear are (0001), (1010), (1011), (1120) and (1012).
3. Vicinal faces usually appeared at one stage but disappeared finally.
4. In the final form (1120) and (1012) disappeared and only (0001), (1010) and (1011) remained.
5. The faces, when suitably illuminated, had a finely striped appearance indicating a stepped structure.

Discussion

The theory of Stranski appears to account satisfactorially for the main facets which appear. The possibility of contamination by oxygen, which may have been expected to invalidate Anderson's results is probably obviated by the gettering effect of a relatively high concentration of zinc vapour.

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### IV The Etching of Metals by Vapours

#### (a) The Etching of Copper and Oxygen<sup>56</sup>

1. The following facts established in this paper are considered to bear upon the etching of metals.

Freshly precipitated or dried cuprous oxide when heated at  $900^{\circ}\text{C}$  in vacuo in a silica tube will volatilise and collect on the cooler parts of the tube.

2. Clear copper was oxidised and then heated at  $900-950^{\circ}\text{C}$  in vacuo from 1 to 20 hr. (according to thickness of oxide) to remove oxide. The copper was left bright and etched.

3. Copper melted in graphite crucibles in vacuo tended to become de-oxidised.

4. Treatment as in (2) produced striations (which were sometimes curved).

5. X-ray investigations showed a double fibre structure for the oxide with preferred orientations.

(i) Sharing a (110) direction in common with the copper with orientation the same as the copper.

(ii) Rotated about a common (110) direction  $54^{\circ} 44'$  from the copper lattice.

6. Repeated treatment of the same surface always produced striations in the same places.

7. The striations were oriented in the directions of (001) and (011) faces.

Two of these points seem to require further discussion. The first is that Gwathmey found that heating an etched crystal in hydrogen at  $550^{\circ}\text{C}$  tended to polish the surface. It is therefore rather surprising that Ela<sup>n</sup> never "overshot" and obliterated the etching to give a final polished surface. In

our attempts to produce single crystals by annealing copper in an atmosphere of hydrogen it was often possible to observe a faint etch pattern on the surface by which the outlines of the large crystals produced the annealing could be clearly seen. The finish was brilliant with no sign of oxidation. Elam could not obtain striations on single crystals but put this down to de-oxidation brought about by the method of preparation. We therefore suggest that the effect is in some way connected with strains set up at the boundaries of the crystals. This would account for the reproducibility observed in (6). Another possibility is that a trace of copper evaporated in Elam's vacuum and thus maintained an evaporation etch. Yet another is that there was a continuous but minute diffusion of air through the silica walls at  $900^{\circ}\text{C}$  and that the experiment was therefore effectively analogous to ours but with oxygen in place of halogen.

These results (i.e. exposure of (001) and (011) faces) do not entirely agree with those obtained by Benton & Gwathmey<sup>54</sup>, who heated an electro-polished copper sphere in oxygen at 0.3 mm. pressure to  $1000^{\circ}\text{C}$  and obtained specular reflections from the (111) and (011) poles, but not from (001).

The Etching of Aluminium by HCl Gas<sup>5</sup>

In the preliminary experiments pure and impure polycrystalline specimens of aluminium were etched with HCl (aq) and with HCl/HF (aq) mixture and then examined in the electron microscope by the oxide film technique.

In general, cubic faces were revealed. However, the authors concluded that the etch figures were not due to the reaction with solvent of the aluminium itself on various faces. They were simply the dissolution forms of a reaction product.

They therefore etched aluminium foil with dry HCl gas at 250°C and 100 mm.Hg. pressure. It was assumed that the oxide played no part.

When deeply etched, the surface did not appear very regular or "crystalline" but there were rounded masses with occasional sharp corners and edges. The masses had a terraced appearance similar to that of copper etched by iodine vapour at 570°C (Plate 2). When less deeply etched, quite sharp etch pits were produced with sides parallel to (001) and (111) which is in accordance with Stranski's theory for interactions between first nearest neighbours only.

Here again the effect of adsorbed substances which must be present at the surface, seems to have been left out of account. Furthermore, a face centred cubic structure should, according to the theory, always give the same dissolution forms, yet the etching of copper with the halogens exposes mainly (111), (011) and (012) facets rather than those calculated. There are thus two discrepancies (a) the facets exposed are not in general those calculated. (b) All crystals with the same structure do not give the same results. Which particular planes are exposed seems to be a vector sum, as it were, of metal and etching agent.

The Thermal Etching of Silver<sup>63</sup>

The development of boundary grooves and striations on the crystals of polycrystalline silver was studied at temperatures between 300 and 950°C in atmospheres of air, oxygen, pure nitrogen and in vacuum.

1. Striations on the crystals only appear in atmospheres containing oxygen. They could be made to disappear again by heating the specimen in nitrogen.
2. It was shown that the striations lay in the same directions as slip planes produced by deformation of the specimen and were therefore consistent with their being due to the development of (111) faces.

Discussion

The authors discuss the causes of the appearance of the (111) faces and consider three mechanisms:

- (a) Preferential attack of oxygen on silver with evaporation of silver oxide.
- (b) Modification of the surface energies of the surface planes by adsorption of oxygen, together with migration of silver atoms over the surface so as to build up steps with faces parallel to (111).
- (c) Redistribution of silver atoms by migration through the vapour phase in the form of silver oxide or atomic silver.

The authors consider that it is not possible to ascertain whether any one of these is predominantly responsible for the striations. It should be noted that Gwathmey, Leidheiser and Smith<sup>53</sup> obtained reflections from the (111) and (001) regions of an electro-polished single crystal of silver after



heating in hydrogen or in vacuum, but that these were much stronger when the sphere was heated in an oxygen containing atmosphere. Faint reflections such as these would be most difficult to detect in a polycrystalline specimen examined under the microscope by a fixed source of illumination, which probably accounts for the failure of Chalmers, King and Shuttleworth to observe them. The thermal etch pattern of silver is therefore similar whether produced in oxygen or in vacuum, but the former gives a more intense etch.

#### V Diffusion Phenomena

There is ample evidence that diffusion within a crystal or over its surface may be governed by crystal direction. Thus Banks, Day and Miller<sup>57</sup> studying the self diffusion of zinc by the use of a radioactive isotope showed that diffusion followed the equation

$$\text{Diffusion coefficient} = A e^{-Q/RT}$$

$$Q_1 \text{ (parallel to } c \text{ axis)} \approx 28600 \text{ cal/mol}$$

$$Q_2 \text{ (perpendicular " " ")} \approx 19600 \text{ " "}$$

But 
$$\frac{A_1}{A_2} \approx \frac{1}{10^3}$$

On the other hand, Maier and Nelson<sup>58</sup> using the same method for copper, find no detectable anisotropy. It is quite probable that such an effect would exist in a hexagonal lattice but not a cubic one.

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The conclusions of the section on Electron Emission show that in general, diffusion of adsorbed particles over the surfaces of metals and of dissolved substances within them are markedly dependant on crystallographic direction. R. P. Johnson<sup>59</sup> has also shown that the migration of the surface atoms of an electron emitting tungsten filament under the influence of a potential gradient is a vectorial property tending to build up facets parallel to certain crystal planes.

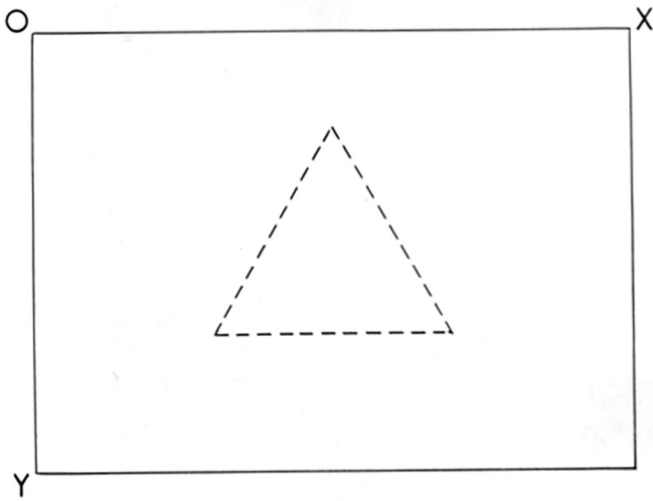
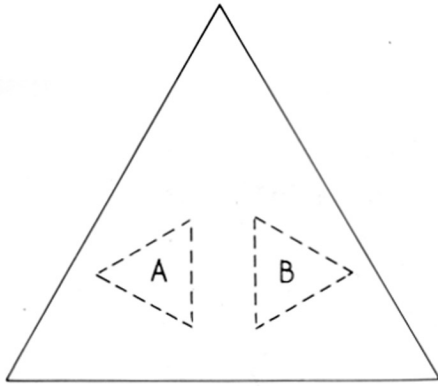


Fig. 17

## Conclusions

A. Summary of Results

Since this chapter is naturally based on the author's results, these will be briefly summarised for each halogen in turn.

Iodine

All pressures about 0.3 mm.Hg.

Product CuI (crystals) or cuprous iodide vapour.

1. Room Temperature

- (a) Stable form of iodide  $\beta$
- (b) Random growth of CuI on copper.
- (c) The underlying copper is polished
- (d) The CuI layer is saturated with iodine during reaction at this temperature and appears black.

2. 305°C

- (a) Stable form of CuI is  $\alpha$
- (b) When iodine vapour is first admitted, an interference pattern is observed on the copper surface. This soon disappears and a pattern formed by CuI crystallites is observed. Reflections are obtained from this on the following poles of the copper (in the corresponding directions): (001), (011), (111) and (012).
- (c) The underlying copper is matt with a faint etch, (011) reflections being obtained in randomly distributed patches.

Further work, carried out since the main experimental section was completed, has shown by the electron diffraction method that the iodide is orientated in the following manner:

(111) Pole: The closest packed planes of the iodide,

Conclusions

i.e. the (111) planes, are parallel to the (111) plane of the copper, so that the copper and the halide share a common (111) axis normal to these planes. The halide cube is rotated  $30^\circ$  from the "twin" position so that the two cubes do not share a common cube face diagonal, i.e. the orientation corresponds with putting two cubes corner to corner so as to appear as mirror images, then rotating one of them  $30^\circ$  about the common axis. This is the same arrangement as that found by Usmani<sup>64</sup> for cuprous iodide formed electrolytically on the (111) face of a copper single crystal. Usmani also reported twinning of the CuI on the (111) plane of the CuI i.e. the (110) plane of the copper which is normal to the common (111) plane, i.e. crystals appear which correspond to rotation of the CuI by  $30^\circ$  in either direction about the common axis. This is represented in Fig. 17a. The heavy lines represent the cube face diagonals which bound the (111) face formed by cutting off the corner of a copper cube. The dotted lines represent similarly the cubeface diagonals of the iodide. The two possible orientations are represented by the triangles A and B.

(011) Pole: The (111) planes of the iodide are parallel to the (011) plane of the copper. One of the cube face diagonals of the iodide in this plane is parallel to the cube face diagonal of the copper which is also in this plane. This is shown in Fig. 17b. Again the heavy lines represent the outlines of the (011) face of a copper crystal which is formed by cutting off the corner of a crystal cube. OX is a cube face diagonal and OY is a cube edge. The dotted lines are cube face diagonals of the iodide.

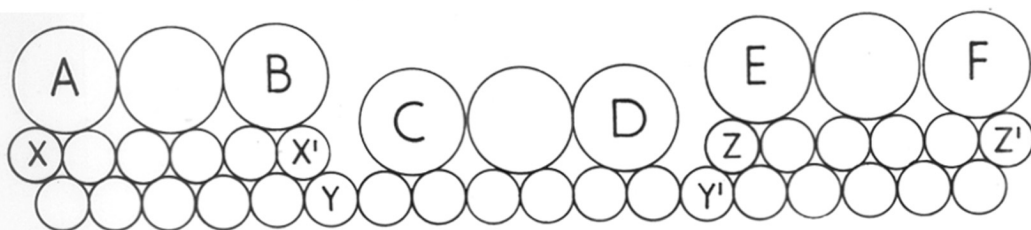


Fig. 18

Conclusions3. 445°C.

- (a) Stable form of CuI is  $\alpha$
- (b) CuI evaporates away as fast as it forms and a pattern of etch micro-facets is obtained on the copper itself giving reflections in the same directions as does the iodide at 305°C.
- (c) The effect of impurities such as those due to inefficient washing is to destroy the pattern but not the micro-facets, which appear in the same relative intensities as in (b).
- (d) A given reflecting (hkl) region reflects in nearly all possible (hkl) directions. (See Fig. 12).

4. 570°C.

- (a) Stable form of CuI is  $\alpha$
- (b) CuI evaporates as it forms. Only (111) micro-facets produced on the copper.

Bromine

Product CuBr (crystals) or  $\text{Cu}_2\text{Br}_2$  (vapour).

1. 445°C.

- (a) Stable form of CuBr is  $\beta$
- (b) Results at c 2 mm.Hg. pressure practically identical with those of  $\text{I}_2$ , 3 (b) above.
- (c) At 170 mm.Hg. pressure a thick layer of bromide was formed consisting of large crystals which did not appear to have any particular orientation. The underlying copper showed the same reflections as in (b).

ConclusionsChlorine

Product cupric ~~chloride~~ <sup>chloride</sup> vapour: structures of stable forms at various temperatures unknown. All pressures about 1 mm.Hg.

1. 305°C.

- (a) The same micro-facets were obtained on the copper as at 445°C but arranged in a slightly different pattern.  
 (b) There was a detectable deposit of  $\text{CuCl}_2$  on the copper.

2. 445°C.

- (a) Copper chloride evaporates away. Etch pattern with the following microfacets:  
 (111), (011), (001) and very weakly (012). Compare with (111), (011), (001) and (012) strong for  $\text{I}_2$  and  $\text{Br}_2$ .

The following general observations are noted:

- I. The crystal structures of the stable forms of the bulk halides ( $\alpha, \beta$  etc.) at various temperatures do not bear any relation to the mode of attack on the copper.
- II. Iodine and bromine give practically identical results, while the pattern given by chlorine differs by giving only a very faint (012) reflection.



Discussion

The main experimental facts which must be accounted for are:

- (a) the reflections in the directions (001), (011), (012) and (111) both from the etched copper and from orientated iodide films.
- (b) The relationship between the surface condition of the copper, i.e. polished, matt or etched, and the temperature at which reaction was carried out.
- (c) The simplification of the etch pattern when the temperature is raised from 445°C to 570°C.
- (d) The difference in the results obtained with chlorine as compared with the other two halogens used.

The latter point emphasises the fact that when a crystal is etched, the particular facets exposed depend not on the crystal alone, but on both crystal and environment. The effect is most marked in solution so that, for example, copper etched by  $(\text{NH}_4)_2 \text{S}_2\text{O}_8$  in acid solution exposes mainly (011) microfacets, while in ammoniacal solution the same reagent leads to (111) facets<sup>2</sup>, from which it is inferred that there is strong chemical interaction between the metal and one or more of the constituents of the etching solution, which determines the direction of etching. Similarly, when a metal is etched by a gas, it must be assumed that reaction does not take place at a bare metal surface but on one that is modified by adsorption, since for every collision which the reacting gas makes with a reaction site (a repeatable step) in the surface, there must be, on the average, a collision with every other surface atom and it is unlikely

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that halogens or their products will fail to be adsorbed. In any case, the experiments with chlorine at 305°C and bromine at 445°C show that the result is practically the same whether detectable amounts of halide are present or not: the layer in contact with the surface, therefore, consists of either halogen or copper halide in the adsorbed state or of crystalline copper halide. In the former case the adsorbed layer will conform to the adsorption sites in the copper faces while in the latter case the metal lattice is in direct contact with the halide lattice.

Since the interaction between copper and halide is sufficiently strong to cause orientation of the halide at 305°C and since etching only occurs where the mobility of ions, atoms or molecules in the medium surrounding the crystal is high (such as in aqueous solution or in copper halides at temperatures at which they are volatile) so that the forces holding adsorbed atoms to the surface are comparable with those exerted on them by the environment, it is concluded that, in general, the surface is covered by an adsorbed layer during etching and that this is responsible for the influence on etch forms of the constituents of the etching fluid. This assumption is made in the following discussion and leads to a consistent interpretation, not only of the results described in the experimental section of this paper, but of polish attack, etching and dissolution phenomena in general.

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The assumptions made are:

- I. The metal surface is covered by a practically complete adsorbed layer during etching.
- II. The properties of the adsorbed layers are different on different crystal faces and, in particular, the presence of the layer alters the binding energies of the metal atoms to different extents on different faces.
- III. The etch pits in the surface under attack will have the appropriate dissolution forms, i.e. may be regarded as "concave crystals" with well defined shapes, which are all orientated in the same way with respect to the dissolving crystal. Adjacent pits will tend to run into each other so that if (hkl) is one of the sets of facets bounding the etch pits, the (hkl) poles and other suitably orientated regions will contain mainly (hkl) microfacets, thus giving rise to the etch pattern.
- IV. When a crystal is etched, crystal units are removed through the adsorbed layer at repeatable steps in the metal surface. This is illustrated for an idealised two dimensional case in Fig. 18. As units such as B and E become undermined by removal of crystal units they (or others from the fluid phase) migrate to the adsorption sites left bare by the removal of units such as X' and Z.

The structure of the adsorbed layer, together with that of all metal atoms at or near the surface, must be regarded as a whole, i.e. as an adsorption complex. Such a structure is stable from our point of view when

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metal atoms cannot easily be removed from it and the energy of adsorption is not important, except in so far as it is related to the stability of the complex in this sense. In fact, faces on which weak adsorption occurs may be more stable as etch planes than those on which adsorption is strong, since the probability of the complex breaking up in such a way as to remove metal atoms from the face is low. The energy of a metal atom in an adsorption complex will depend on the electronic configurations which exist between the atom pairs, metal-metal, halogen-halogen (or other adsorbed groups) and metal-halogen. These in turn will depend to some extent on the relative sizes of the atoms, the geometry of the crystal face, the mode and amplitude of thermal vibrations etc. The energy cannot therefore be predicted simply.

(a) The appearance of reflections in the directions (001), (011), (012) and (111)

A step in a face of an "infinite" crystal not only exposes a row of atoms with fewer metal neighbours than have those on the face in general, but also creates a dislocation in the adsorption complex (see Fig. 18). Stepped structures are therefore expected to be readily attacked. The only faces in a close-packed cubic crystal which cannot be regarded as stepped are (001) and (111). In these, the atoms exhibit quadratic and triangular close-packing respectively and all the surface atoms lie in a plane, a surface atom being regarded as any atom which can make contact with adsorbed atoms. Two other faces, (011) and (012) are homogeneous in their adsorption sites, i.e. there is only one kind of adsorption site in the surface, so that every site is geometrically equivalent to every other

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site. Such faces, on which the sites are identical, will be termed "homogeneous faces". Adsorbed layers on these faces are planar and not stepped. On all other faces there is more than one kind of adsorption site and, in some cases, occupation of one kind of site sterically prevents occupation of the others. Thus the adsorbed layers on faces other than homogeneous faces are either very sparsely packed or are stepped and the adsorption complexes are not expected to be stable unless some special geometrical or dimensional relationship exists between the adsorbed atoms and those of the crystal. This is supported by the fact that in various studies on the etching of metals, the faces which appear as microfacets on face-centred crystals are limited to one or more of the homogeneous faces.

Since essentially the same etch results are obtained whether the halide layer is thick or invisibly thin it appears, that, in general, we are dealing with solution of copper into copper halide. The high volatility of the halides at etching temperatures suggests that the dissolution of the metal takes place into halide that is sufficiently mobile to be regarded as effectively a liquid and is thus analogous to etching in solution. However, when metals are etched in aqueous media, usually only one or two of the homogeneous faces appear as microfacets. Presumably the appearance of all four in our experiments is due to the simplicity of the etching agent. The adsorption of molecular halogen at the metal surface is considered improbable<sup>63</sup> and the layer at the surface therefore consists of either halogen atoms or adsorbed copper halide, i.e. halogen atoms with further copper atoms adsorbed on them. The probability that adsorption complexes can be formed on all four homogeneous faces is much greater with small, simple units such as these than with the relatively large and

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complicated units which occur in aqueous solution.

At 305°C the cuprous iodide is orientated on the (111) and (011) arêas of the copper with its most closely packed planes parallel to the surface. The observed reflections come from steps (in the surface of the iodide) parallel to these planes caused by surface migration or evaporation-etching of the iodide. Similar reflections from the iodide are obtained on the (001) and (012) regions of the copper and it will therefore be assumed that on these regions also the (111) or some other plane of high packing density, likely to form an evaporation-etch plane of the iodide, is parallel to the interface. Even after only a slight amount of attack the copper surface will become etched or rearranged on the atomic scale so as to expose mainly etch planes and orientation is most probably due to the transformation of layers adsorbed on the etch planes of the metal into halide crystallite nuclei as they thicken. The most stable orientations of the halide nuclei will be those in which the best fit is obtained at the interface. If the spacings of the two lattices were such that one was approximately an integral number of times that of the other it would be expected that the axis normal to the interface would have the same symmetry for both the copper and the halide. This is not the case, however, for the (011) plane of the copper. It is therefore concluded that, in cases such as this, orientation is determined mainly by the tendency for adsorption to build up densely packed layers of halide units parallel to the etch plane surfaces and that these subsequently transform into crystallites with one of the more densely packed planes parallel to these layers. Such planes are also the evaporation-etch planes of the halide so that the reflections from the iodide are closely related to those from the etch planes of the metal.

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### (b) The condition of the surface of the copper

Two distinct states of the copper surface after attack may be distinguished, the etch pattern obtained at about  $450^{\circ}\text{C}$  and the polish produced by attack at room temperature. The imperfect matt etch produced by iodine at  $305^{\circ}\text{C}$  would appear to be an intermediate phenomenon.

In the last section, etching was interpreted by supposing solution of copper into mobile solid halide to be analogous to etching in aqueous solution, the etch pattern being determined mainly by the formation of adsorbed layers which modify the stabilities of the crystal faces.

Polish attack on the other hand must be due to a process on which the geometry of the crystal lattice has little effect and in which diffusion predominates. This makes any fit between the crystal and the layers in contact with it improbable. The absence of an adsorbed layer on the copper at room temperature is also to be expected on the ground that, under these conditions, the halide is a brittle solid of negligible vapour pressure so that the layer at the interface is much more likely to conform to the halide than be adsorbed on the copper. The system is therefore presumed to consist of the halide and copper lattices in direct contact so that the dissolution of metal atoms is determined by chance configurations rather than by the geometry of the metal lattice.

The conclusion that the absence of adsorbed layers is favourable to random attack is supported by the closely related phenomenon of electro-polishing. This generally takes place at high current density or at moderate current density in the presence of a substance such as

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phosphoric acid which is unfavourable to the deposition of ordered layers. At low current density under similar conditions electro-etching usually occurs. From this it is inferred that under polishing conditions the adsorbed layers are either swept from the surface or become disordered so that the process is similar to the polishing effect which is obtained by dissolving crystals rapidly in a non-reacting solvent (e.g. salts in water). In the absence of ordered adsorbed layers (of reagents or solvent) the dissolution process is governed mainly by the laws of diffusion and will therefore tend to produce a smooth interface. The solution of copper into non-fitting halide which occurs at room temperature is considered to be an analogous process, being influenced more by diffusion within the halide than by conditions at the copper surface.

The slight roughening of the underlying copper after attack at  $305^{\circ}\text{C}$  and the faint etch reflections which it gives imply that the mechanism is similar to that which operates at  $445^{\circ}\text{C}$ , but that, owing to the lower mobility of the halide atoms, the etch is very imperfect. The lower mobility may manifest itself in two ways, the one mechanical and the other chemical. In the first case, since there is an increase in volume when copper is converted into halide, close contact cannot be maintained between a diminishing copper surface and growing halide if the interface is indented by etch pits. Etching can only occur by continual breakdown of the halide and reformation of new crystallites and presumably this occurs to some extent at  $305^{\circ}\text{C}$ . Secondly, the vapour pressure of the halide is much lower than at  $445^{\circ}\text{C}$  so that the halide will now compete more strongly for the layer at the interface between it and the copper and the chances that it will conform to one or the



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other at any point will be more nearly of the same order. There is therefore a much greater likelihood of random attack and this leads to the formation of imperfect microfacets, and matt appearance. The relative importance of the two effects may be judged from an experiment of Benton and Gwathmey<sup>54</sup> in which an electro-polished single crystal copper sphere was oxidised in air at 300°C. Reflections from the oxide indicated that it was orientated on the (311) poles to which it adhered firmly, while on all other regions it could easily be rubbed off to reveal a bright copper surface. It is inferred from this that on those regions where the layer at the interface can conform to the copper, the tendency is to etch and the oxide is firmly bound to the interface layer which it shares with the copper while on those where this does not occur, polish attack takes place and the non-fitting oxide is only loosely bound to the surface. The absence of the adsorbed layer therefore appears to be more important than the mechanical effect in bringing about polish attack.

An alternative explanation of the polish obtained at room temperature, i.e. that reaction occurs via a thin film of oxide, must also be considered, for, under the conditions used, the removal of the last trace of oxygen from the surface of the copper is improbable. Benton and Gwathmey<sup>53</sup> obtained a well defined interference pattern by exposing an electro-polished single crystal sphere of silver to iodine vapour or to iodine dissolved in an organic solvent at room temperature. A faint interference pattern is obtained when iodine vapour is first admitted to the copper sphere at 305°C and, as already mentioned<sup>54</sup>, the interference pattern produced by oxygen

on copper above  $200^{\circ}\text{C}$  appears to be connected with orientated oxide. This suggests that orientation of halide does not occur on copper at room temperature because the metal is protected by a film of oxide. However, this assumption would lead to the expectation that the dissolution of copper in, say, dilute ammonium persulphate solution would be somewhat similar to the reaction with gaseous halogen at  $20^{\circ}\text{C}$ , whereas the former etches while the latter polishes. In any case, this argument simply transfers the discussion from the halide to the oxide. Unless further investigations show that it has an important influence it will be assumed that the effect of a trace of oxygen is negligible.

(c) The simplification of the etch pattern at  $570^{\circ}\text{C}$

The result at  $570^{\circ}\text{C}$  may be compared with previous work of a similar nature. Elam<sup>56</sup> obtained striations on copper by first oxidising the surface then evaporating the oxide in vacuum at  $950^{\circ}\text{C}$  and identified them as being due to (001) and (011) faces. Benton and Gwathmey<sup>54</sup> heated an electro-polished single crystal of copper sphere in oxygen at 0.3 mm.Hg. pressure and  $1000^{\circ}\text{C}$  and obtained striations around the (111) and (011) poles. Chalmers, King and Shuttleworth<sup>63</sup> found that polycrystalline silver heated in air at  $500^{\circ}\text{C}$  gave striations which were identified as having (111) faces while Gwathmey, Leidheiser and Smith<sup>53</sup> showed that an electro-polished single crystal of silver heated at  $500^{\circ}\text{C}$  in air, oxygen, hydrogen or in vacuum gave specular reflections from the (111) regions and weaker reflections from the (001) regions. Preferential evaporation of silver appeared to be the predominating cause but that fact that the patterns were more intense

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in air and oxygen suggested that the presence of silver oxide enhanced the preferential evaporation.

The simplification in the etch pattern of iodine on copper at 570°C as compared with that obtained at 445°C may be due to a preferential decrease in the binding energies of metal atoms on faces other than (111). Such a change may be associated with either a difference in the mode of thermal vibration of atoms on various faces or to a general decrease in the interaction between the copper and halogen atoms so that the interactions between the metal atoms alone become relatively more important. The surface may then be regarded as effectively bare and the most stable faces will be those on which each metal atom is shielded by the largest number of neighbours. The stabilities would then be expected to parallel those for a face-centred metal in equilibrium with its vapour. Calculations by Stranski and Mahl<sup>3</sup> lead to the prediction that, if interactions between nearest neighbours only are taken into account, the most stable faces are (111) and (001) while if second nearest neighbours also are included, the stable faces are (111), (001) and (011).

Alternatively, the high rate of reaction and the imperfection of the etch pits indicate that, in the reaction between copper and iodine at 570°C, equilibrium is not approached, i.e. that the etch form is a dissolution form and not an equilibrium form. If the rates of reaction on various faces of the equilibrium form differ widely so that for instance,

$$\frac{\text{Rate (011)}}{\text{Rate (111)}} > \sqrt{\frac{2}{3}}, \quad \frac{\text{Rate (001)}}{\text{Rate (111)}} > \sqrt{\frac{2}{3}}, \quad \frac{\text{Rate (012)}}{\text{Rate (111)}} > \sqrt{\frac{4}{15}}$$

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all faces other than (111) will tend to disappear in the dissolution form.\* The simplification in the etch pattern may therefore be mainly due to an increase in the rate of diffusion in the vapour phase relative to the rates of reaction, resulting in a change from a practically reversible reaction at 445°C to one in which only the forward reaction is important.

It is therefore concluded that, while the evidence is compatible with a lessening of interaction between the copper surface and adsorbed layers, other effects also may be responsible for the change in etch pattern.

### (d) The "anomalous" behaviour of chlorine

The weakness of the (012) reflections obtained by etching with chlorine as compared with bromine or iodine may be due either to dimensional effects or to the high electronegativity of chlorine, for, although electronegativity and atomic dimensions are interdependent, it is sometimes convenient to consider them separately in cases such as this where geometrical aspects are determined mainly by the metal crystal. The (tetrahedral) covalent radii of the halogens at room temperature are, in Angstrom units:- Cl, 0.99; Br, 1.17; I, 1.33; and the ionic radii:- Cl<sup>-</sup>, 1.80; Br<sup>-</sup>, 1.96; I<sup>-</sup>, 2.20; while that of copper in the metal is 1.27. The parameters of the copper halides correspond with almost pure covalent bonding, but an

\* These ratios are obtained by comparing the lengths of vectors drawn from the centre of a cubic crystal normal to the appropriate crystal faces, the length from the centre of the crystal to the point at which the plane of the face is intersected representing the rate of growth of that face. The values given are those for which the faces concerned just become edges or corners of an octahedron.

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adsorbed halogen atom in a complete monolayer will be in a rather different situation from one in a copper halide crystal and, in particular, the metal crystal will act as a large effective excess of electropositive atoms which can donate electrons to the adsorbed layer. The adsorbed atoms may therefore have considerable ionic character with radii lying between the covalent and ionic values. Bromine and iodine give similar etch results and the covalent radius of iodine is greater than that of crystal copper so that, if the effect is a steric one, it must be presumed that both of them have larger effective radii than copper while that of chlorine is smaller. However, such an effect should be most pronounced on, say the (111) planes where the smaller diameter would permit much higher packing density on the surface by occupation of every adsorption site as opposed to occupation of alternate sites. The effect is attributed therefore to a difference in the electronic structures of the adsorption complexes brought about by the higher electronegativity of chlorine.

### Summary

The general conclusion reached is that a crystal tends to impress the geometry of its surface lattice planes on its immediate surroundings by forming an adsorbed surface layer: the etch form of the crystal is due to the modified surface thus produced. If, on the other hand, the configuration at the surface is determined by the surroundings (i.e. by potential gradients etc.) so that there is a complete misfit, reaction is more likely to be governed by the laws of diffusion and polish-attack

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then takes place. An intermediate state, in which the adsorbed layer is replaced by an orientated overgrowth accompanied by imperfect etching of the crystal surface, is also possible.

## ACKNOWLEDGEMENTS

The author wishes to place on record the thanks he would have expressed to the late Professor C. S. Gibson, F.R.S. under whose liberal direction this work was carried out. Thanks are also due to Professor G. I. Finch, F.R.S. and Professor E.N. da C. Andrade, F.R.S. for generous and helpful advice in overcoming difficulties, the gift of reprints and papers not available in libraries, examination of crystal material and expert opinion thereon. The Royal Society is thanked for a grant which enabled valuable materials and apparatus to be purchased. The diagrams were drawn by Mr. K. J. Fereday from the author's sketches and notes and the author wishes to thank him for his elegant work. The electron diffraction experiments were carried out in the laboratory of the Department of Applied Physical Chemistry, Imperial College, London with the permission of Professor G. I. Finch, F.R.S. and with the generous help of Dr. H. Wilman.

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