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AN ELECTRON DIFFRACTION STUDY
OF CHEMICAL REACTIONS
WITH SPECIAL REFERENCE TO
REACTIONS ON SINGLE CRYSTAL SURFACES,

COMPUTERISED

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C O N T E N T S .

<u>Subject</u>	<u>Page</u>
I. INTRODUCTION 	1
II. LITERATURE ON CRYSTAL GROWTH AND CHEMICAL REACTIONS IN RELATION TO THE CRYSTALLINE STRUCTURE OF SOLID SURFACES.	
(1) Crystal Growth on Solid Surfaces	8
(2) Preferential Adsorption of Substances	10
(3) Epitaxy in Minerals and Metals ...	13
(4) Surface films on Metals ...	15
(5) X-ray Studies of Surface Films...	17
(6) Electron diffraction Studies of Chemically Formed Surface Films...	19
(7) Chemical Reactions on Single Crystals: Minerals 	24
(8) Chemical Reactions on Single Crystals: Metal Single Crystals	25
III. EXPERIMENTAL PROCEDURE AND METHOD OF ANALYSIS.	
(1) Existing methods of Preparing Single Crystals of Metals 	30
(2) Method of Preparation of Single Crystals used in the present investi- gation	32

Subject	Page.
(3) The preparation of a Plane Metallic Single Crystal Surface ...	34
(4) Methods for Preparing Surface Films by Chemical Reactions ...	36
(a) Oxidation ...	36
(b) Formation of Halides and Sulphides	36
(c) Etching of the Single Crystals	36
(5) Experimental Technique: Surface Structure Analysis by Electron Diffraction	36
(6) Interpretation of the Electron Diffraction Photographs ...	37

IV. RESULTS WITH ZINC SINGLE CRYSTALS.

(1) The Surface Structure of the Cleavage Face of Zinc Single Crystals.	46
(2) Oxidation of the basal plane of the Zinc Single Crystals.	
(i) Oxidation at 200°C. ...	48
(ii) Oxidation at 400°C. ...	49
(3) Oxidation after treatment with Benzene	50
(4) Oxidation after treatment with Hydrogen Sulphide Gas ...	52
(5) Surface Structure and Oxidation of (001) Faces of (1012)-twins formed by Mechanical Fracture ...	53

V.. RESULTS WITH ANTIMONY SINGLE CRYSTALS.

(1) The Surface Structure of the Cleavage Face of Antimony Single Crystals	55
(2) Oxidation of Cleavage Faces of Antimony Single Crystals ...	55

SubjectPage

VI. RESULTS WITH BISMUTH SINGLE CRYSTALS.

(1) The Structure of the (111) and (100) Faces of Bismuth Single Crystals.		
(i) Cleavage Face fill) ...	1	61
(ii) Cast Surface (100) relative to the pseudo cube axes ...		62
(2) Thermal Oxidation in Air of the (100) and (111) Faces of Bismuth Single Crystals		63
(3) The Reaction of Dry Iodine Vapour with the (111) and (100) faces of Bismuth Single Crystals		67
(4) The Reaction of Moist Halogen Vapours on the (100) Face of Bismuth Single Crystals		69
(5) The Reaction of Bismuth Crystal (100) Faces with Iodine Vapour from various solutions		73
(6) Effect of Dipping the (100) Face of Bismuth Single Crystals in Iodine Solution in Benzene		76
(7) Effect of Carbon Di-Sulphide Vapour on the (100) Face of Bismuth Single Crystals		76
(8) Effect of Etching on the (100) Face of Bismuth Single Crystals.		
(i) Dilute hydrochloric acid and bromine water		79
(ii) Nitric and acetic acids ...		82
(iii) Yellow ammonium sulphide ...		83

VII. RESULTS WITH TIN SINGLE CRYSTALS.

(1) The Structure of the Natural Face of Tin Single Crystals		84
(2) The Effect of Etching of the (100) Face of Tin Single Crystals		85
(3) Oxidation of the (100) Face of Tin Single Crystals		85
(4) The Reaction of Iodine Vapour on (100) Faces of Tin Single Crystals		92

Subjectpage

VIII. GENERAL DISCUSSION

(1) Views on the Mechanism of Formation of Oxide Films on Metal Surfaces ...	95
(2) Nature of Oxidation of Cleavage Faces of Zinc Single Crystals ...	101
(3) Nature of Oxidation of Cleavage Faces of Zinc Single Crystals which have been exposed to Sulphur ...	109
(4) Nature of Oxidation of (001) Faces of (1012) Twins of Zinc Cleavage Surfaces	110
(5) Nature of Oxidation of Antimony and Bismuth Single Crystal Surfaces ...	111
(6) The Rate of Oxidation of (111) and (100) Faces of Bismuth Single Crystals ...	112
(7) Nature of Oxidation of (100) Faces of Tin Single Crystals ...	114
(8) Other Chemical Reactions with Bismuth and Tin Single Crystal Surfaces ...	115
(9) Nature of the Epitaxial Orientations Observed ...	116
IX. SUMMARY ...	119
X. REFERENCES ...	126

AN ELECTRON DIFFRACTION STUDY OF CHEMICAL REACTIONS
WITH SPECIAL REFERENCE TO
REACTIONS ON SINGLE CRYSTAL SURFACES.

I. I N T R O D U C T I O N.

The chemical properties of a solid material vary according to the nature of its surface, not only in respect of atoms or molecules of which it is composed, but also to a considerable extent according to the spacial arrangement of these chemical units, as exemplified by the crystal structure, orientation and lattice perfection; and by the surface texture (habit, crystal growth) surface roughness, etc. which comprise the physical structure of the surface.

The first direct means of determining this atomic arrangement in solids was provided by the method of X-ray diffraction in 1912, but owing to the weak interaction of X-rays with matter, this method can only yield information about the average structure in comparatively thick layers. In electron diffraction, however, first demonstrated in 1927, there is a comparatively intense interaction with atoms so that clear diffraction patterns are readily available from exceedingly thin films, even only a few atoms thick, and hence also even 50 KV electrons have low penetrating power and the patterns obtained from relatively smooth solid surfaces yield information only about the structure of the immediate surface regions.

As there are already a number of reviews describing the experimental and interpretative techniques of electron diffraction as applied to the study of surface structure (Kirchner, 1932; Finch, Quarrell and Wilman, 1935; Finch and Wilman, 1937; Finch, 1938; Thomson and Cochrane, 1939), it is not necessary to go into such details. Since 1927 electron diffraction has been applied to a wide variety of surface structure investigations in this laboratory especially those of catalysis, wear and lubrication, corrosion and chemical reactions, electrodeposition, anodic processes, photo-electric properties, molecular structure, properties of plastics etc. and crystal growth in general. The results of such electron diffraction investigations have already provided a much clearer insight into the physics and the chemistry of surfaces than had previously been possible. The experiments described below were designed to investigate further the nature of chemical reactions in their relation to the structural form of surfaces, especially in the fundamental case of the single metallic crystal surface.

The general nature of chemical reactions on solid surfaces as already revealed by electron diffraction is briefly as follows.

When the atoms or molecules of a gas come into collision with those of a solid surface and form a solid reaction product, then, if the rate of liberation of energy in the reaction is slow enough, crystal nuclei

of the reaction product tend to be built up in a definite spacial relationship relative to the atomic arrangement in the substrate surface. This relationship may be one of pseudomorphism combined with crystal orientation or crystal orientation alone - usually the latter. The orientations taken up by crystals of the reaction products and of deposits generally relative to a substrate of either amorphous or crystalline nature, appear to be usually those in which the potential energy of the atomic packing of the deposit and substrate atoms is a minimum. In general this means in effect that crystals grow on those of a different substrate material in the way or ways which most nearly continue the atomic pattern in the substrate crystal. The way in which atoms or molecules become arranged into a lattice during crystal growth is determined by the nature and distribution of the field of force surrounding each atom or molecule and by the way in which this field is modified by the neighbouring atoms in the growing crystal. Since the atomic net planes in different directions in crystal have different densities and distribution of atomic population, it follows that the rate of a reaction should also depend on the crystallographic nature of the boundary surface of a crystal. Usually it is found that adsorbed gas atoms or deposit atoms have considerable mobility over the solid surface before losing most of the free energy and becoming more or less fixed in position as part of a growing crystal in the deposit (Volmer, 1932).

This mobility increases with increase of temperature, as also does the amplitude of oscillation of the atoms of the solid substrate about their mean position.

A satisfactory understanding of the properties of a polycrystalline metal is dependent on a knowledge of the properties of the individual crystals. Especially is this true of the important surface phenomena such as photo-electric and thermionic emissions, work function, auto-electronic emission, adsorption of gases, corrosion and contact catalysis. Some of these properties have been shown to vary with the nature of the exposed crystal plane, and others are supposed to be similarly affected.

When a polycrystalline material is brought into contact with a reacting substance and is allowed to undergo a chemical reaction, the reaction starts on all the different exposed faces of the crystallites, the net result of the reaction being the sum total of the different reactions on these faces. The reaction, however, may proceed on one face rapidly, on another face slowly, or even not at all. Also there is the possibility that one type of reaction may occur on one face and a different one on another. Also, in cases where the final reaction product is a mixture of two or more compounds the particular product formed may depend on the crystallographic direction of the crystal surface. It has already been observed that the same reaction proceeds on different faces of the same crystal at different rates (cf. Gwathmey and Benton, 1939, 1940, 1942).

Single crystals clearly provide a means of studying chemical reactions and crystal growth in their simplest form eliminating the influence of varying orientation and grain boundaries. One of the most important steps in metallographic research in recent years has been the invention of methods for the preparation of metals in the form of single crystals as such.

In the present investigation single crystals were prepared from some of the more fusible metals, namely, zinc, bismuth, antimony and tin, and the crystallographic direction and structural nature of the different crystal faces prepared were determined by electron diffraction. The nature and progress of chemical reactions such as thermal oxidation and the formation of halides and sulphides were studied, using different faces of these crystals with correspondingly different atomic population density.

The results, described below, define the chemical nature and crystalline form of the products in the above reactions, and show the dependence of reaction rate and crystal size and orientation of the reaction product on the structure, roughness and temperature of the surface. In the case of relatively perfect (001) zinc cleavage surfaces the important result was established that even when examined in vacuo within a few minutes after cleavage, they were invariably covered with an extremely thin, optically invisible layer of highly oriented zinc oxide crystals having an exceedingly

smooth surface. On the other hand no such oxide layers were detected on antimony, bismuth and tin surfaces when freshly cleaved or prepared in the way described below. The results on thermal oxidation of zinc cleavage faces showed that the initially spontaneously formed oxide layer remained almost unchanged even after two hours' heating at 400°C. , and only after long further heating at this temperature did growth of unoriented zinc oxide crystals become appreciable. On the other hand, zinc cleavage faces exposed for a short time to mild attack by sulphur vapour gave rise rapidly at 400°C. to a layer of zinc oxide partly in (001) and partly in (101) orientation. Clear evidence of the increased rate of oxidation with roughness of the zinc surface was found by comparison of observations with the cleavage plane and with the much rougher (001) faces of the (10 $\bar{1}$ 2) twinned crystal. The cleavage faces (111) and pseudo cube (100) faces of bismuth were nearly atomically smooth but differed strikingly in their chemical reactivities, the (100) face being more reactive than the (111) face.

Thermal oxidation of bismuth crystals gave unoriented Bi_2O_3 ring patterns. Very smooth antimony (111) cleavage faces, however, when heated at 400°C. in air for a short time yielded patterns showing Sb_2O_3 in strong two degree (111) orientation.

In the case of the (100) faces of tin heated in air at 100°C. for five hours an arced ring pattern corresponding to

the normal SnO_2 was obtained while a similar face, when heated at 200°C . for one hour, gave a ring pattern which corresponded to cubic structure with $a = 5.30 \text{ \AA}$.

Reaction of (100) faces of tin and (111) and (100) faces of bismuth with halogens and H_2S gas yielded halide and sulphide surface layers which were strongly oriented when the rate of reaction was comparatively slow.

Besides throwing light on the nature of these chemical reactions, these results have also shown several new examples of epitaxial orientations developed in reaction products on metal single crystals, which provide further evidence of the determining factors involved in such a controlled type of crystal growth.

II. LITERATURE ON CRYSTAL GROWTH AND CHEMICAL REACTIONS IN RELATION TO THE CRYSTALLINE STRUCTURE OF SOLID SURFACES.

(1). Crystal Growth on Solid Surfaces.

Chemical reactions at crystalline solid surfaces are essentially similar in nature and related to crystal growth of deposits on such surfaces; thus it is a phenomenon of crystal growth, and as such is helpful to a study of chemical reactions. In particular, many of the general relationships of epitaxy, followed in crystal growth, are also obeyed in the growth of chemically-formed deposits. The chemical formation of a crystalline film on a solid surface, for example, by thermal oxidation in air, is accompanied by the formation of crystal nuclei which grow eventually into a visible continuous film of the compound.

An important group of researches thus concerns the growth of crystals on different substrates. It is found that in many cases the crystals formed are oriented with some particular crystal plane parallel to the surface of the substrate. When the substrate is a crystal having some similarity of structure to that of the deposited or chemically produced substance the crystals of the latter

often grow in a special orientation closely related to the structure of the substrate, which determines not only the crystallographic plane which is built up parallel to the substrate surface, but also the directions of the lines of atoms in the plane, and thus leads to the complete orientation of the deposited crystals.

The evidence of the formation of a surface film due to chemical reaction and the nature of crystal growth which takes place on solid surfaces have been followed by a number of methods.

Of those methods of investigation in which the microscope is used as a means of observing some property of the surface, one of the most important is that depending upon the specific orientation by many crystal surfaces of certain crystals grown thereon. This phenomenon has been known for many years and was the subject of experiments by Wakkernagel in 1825, when it was found that lead nitrate crystals occupy regular positions when deposited on alum and also alun on boracite, and by Frankenheim in 1836. Since that time investigations have been made by de Senarmont, Sadebeck, Barker, Wallerant, Miigge and Friedel, and in more recent years by Buckley (1930), Bunn (1933), Sloat and Menzies (1931), France and co-workers (1942) and especially by Royer (1936). Many of the known examples are due to Royer, who has carried out a systematic investigation of this phenomenon, called by him "Epitaxy", since 1924.

Royer mainly directed his work towards determining the conditions necessary for the oriented growth of crystals of one substance upon the surface of another. Similarity in atomic pattern in the two parallel junction planes evidently plays an important and probably a predominant role in determining the orientation relationships.

Recently, Willems (1943) observed similar orientation relationships when organic substances crystallise from organic solvents on single crystal faces of antimony, ionic crystals, and also mica and other minerals. According to Willems oriented growth of organic substances takes place when molecular linkings connect the lattice of the crystallising compound with that of the substrate.

The study of mutual orientation or "Epitaxy" in thin layer overgrowths has been especially applied in this laboratory using electron diffraction to ascertain the epitaxial relationships, and to the study of specific problems of surface structure, in particular the demonstration of the recrystallization of the Beilby layer of flowed material on polished surfaces (Finch and Whitmore, (1938), Beukers (1939)).

(2). Preferential Adsorption of Substances.

An affinity of different adsorbates for particular crystal faces and for other adsorbents has been observed in the phenomenon of adsorption of dyes on crystal surfaces and also of gaseous substances on different adsorbents.

Even on perfectly formed crystals some faces adsorb dyes while others do not. This was known to Lehman (1894) and was extensively studied by Gaubert (1911). A crystal will sometimes adsorb one dye on one set of faces and another on a different set, no adsorption of the first dye occurring on the second set of faces, and vice versa. Thus, lead nitrate adsorbs methylene blue on its cube face; urea nitrate adsorbs this dye on the (110) faces, another set of faces adsorbing none of this dye, but easily adsorbing picric acid. If the crystals are grown in a solution coloured with both dyes, one set of faces develops with a blue colour, the other with a yellow. These different adsorptions are of great importance in determining the growth of the crystals, for if a substance, coloured or uncoloured, is adsorbed on a set of faces, growth of the crystals perpendicular to these faces is retarded, because deposition on them is slowed down. These faces often appear finally as the only faces of the crystal, for the others grow freely and therefore much faster, and so the faces on which deposition is impeded by, say, an adsorbed dyestuff, are prolonged parallel to themselves until their mutually inclined faces finally meet at an edge. Desch (1928) has drawn attention to the effect of differential adsorption of urea on the growth of sodium chloride crystals; urea is deposited preferentially on the cube faces, so that it is the octahedral faces which grow in urea; and finally determine the habit of the crystals. Numerous similar

cases of preferential adsorption on certain crystal faces are given by Saylor (1927) and France and co-workers (1928).

The differences in activity of various crystal faces, i.e., the influence of atomic distribution on crystal surfaces, have also been observed in adsorption of gases by solids and in catalysis. Thus two kinds of adsorption have been recognised on charcoal surfaces such as physical adsorption and chemisorption (McBain, 1932). Rideal and Wright (1925) found that charcoal can adsorb oxygen in at least three different forms: one of these can only be removed as oxides of carbon, at very high temperatures; another can be removed as oxides by evacuation at ordinary temperatures; and another can be pumped off as oxygen. It is probable that the partial graphitic structure of such carbons is the cause.

Afanasier, Talmud and Talmud (1926) found that orientation of molecules in the surface layer of the adsorbent has a large effect on the adsorption of gases; thus, if molten palmitic acid is sprayed and the droplets are allowed to cool, the surface of the particles so formed consists of methyl groups. If, however, molten palmitic acid is emulsified with water at 80° and the emulsion poured into cold water, the solidified droplets have the COOH group in the surface. Palmitic acid in this form adsorbs more ammonia than does palmitic acid with the end methyl groups exposed.

Heterogeneity of solid surfaces has also been observed in the catalytic properties of surfaces. Vayon and Husson

(1922) found that there are, on platinum black, at least three different levels of catalytic activity: a clean catalyst ^{ll} ~~with~~ hydrogenate propyl ketone; after poisoning with a small amount of carbon disulphide, propyl ketone cannot be reduced, but piperonal is hydrogenated; a further addition of carbon disulphide prevents the reduction of piperonal but leaves the power of catalysing the reduction of nitrobenzene. A number of other examples showing heterogeneous character of solid surfaces has been given by Adam (1941)

(3). Epitaxy in Minerals and Metals.

Oriented overgrowths and intergrowths among both metallic and non-metallic substances have been recognised and studied for well over a century. The work of Widmanstätten in 1808 on the geometrical structure in meteorites, a structure known by his name, demonstrated that oriented intergrowths can occur in purely metallic systems. This fact led to much of the early microscopic study of alloys, contributing greatly to the advance of physical metallurgy. The problem has been attacked again in recent years in a comprehensive fashion with the object of discovering what atomic movements may occur during phase changes in alloy systems by a number of workers (Mehl and co-workers, 1934, 1937; Preston, 1940, 1946; Bragg, 1940). Although many

aspects of this general problem remain unsolved, it may be said that the orientation of a new phase forming under favourable conditions by precipitation from solid solution, or by transformation, invariably bears a unique relationship to the orientation of the phase from which it was formed, and that similarity in atomic patterns in the junction planes in the two phases plays an important part in determining the orientation relationships. The body-centred cubic phase referred to as kamacite, which forms the well defined lamellae in meteorites, has been shown by Young (1926) to lie parallel to the octahedral (111) planes of the face-centred cubic taenite, which may be regarded as the undecomposed residue of the high temperature phase. The (110) planes in kamacite and the (111) planes of taenite are the most densely packed planes in their respective lattices. The (111) plane in the face-centred cubic phase becomes the (110) plane in the body-centred cubic phase by a slight shift or rearrangement in atomic position, for measurement shows that the interatomic distances in the two planes differ by only 2 per cent, and the atomic composition by only 4 per cent. There is thus a definite relation in orientation between the lattice of the precipitate and the lattice of the parent solid solution. This is a general rule which applies to a large number of alloy systems; the lattice of the precipitated phase always orients itself to give a best fit on the parent lattice. The

crystallographic planes which meet in the surface of separation need not necessarily be the planes of closest atomic packing of either lattice.

Analogous orientation relationships exist in oriented intergrowth in non-metallic systems - mineral or inorganic. In 1827 Haidinger discovered natural intergrowths of haematite and magnetite, and demonstrated that the rough form of the magnetite octahedrons was delineated by small crystals of haematite, of which the basal (001) planes lay parallel to the octahedral cleavage planes of the magnetite. The description of this orientation relationship was later completed by Von Rath, who showed that the edge (001):(101) in haematite lies normal to the (111) direction in the (111) match plane of magnetite. Similar orientation relationships have been found in more recent years for other non-metallic systems (Mehl and McCandless, 1937).

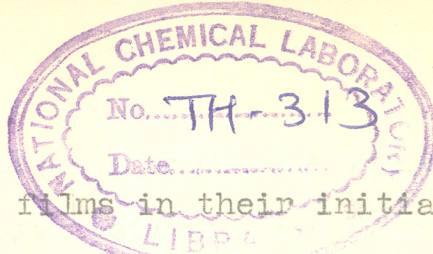
(4). Surface Films on Metals.

Reaction films or layers present an especially interesting case. It was suggested by Tammann (1922), that reaction layers, such as oxides, formed directly on metal crystals, for example silver reacting with gaseous oxygen, are oriented with respect to the metal crystal, presumably owing to some crystallographic mechanism operating during the formation of the reaction layer. The work of Elam (1930) on the

formation of γ -brass on β -brass by reaction in zinc vapour offered qualitative support for this idea.

The formation of oxides on metals has great general interest. If it can be shown that oxides are oriented, and if the complete orientation relationships can be determined, the atomic crystallographic mechanism of oxidation may to some extent be inferred. Furthermore, the existence of such orientation relationships will imply the presence of atomic bonds between the oxides and the base metal, and a study of these in relation to the crystal orientation, together with a study of the degree of strain induced by imperfection in the lattice registration at the interface, should contribute much to the study of the adhesion and stability of films on metals and thus to an understanding of the conditions under which some films afford protection against oxidation (passivation) whereas others do not interfere with corrosive attack. One of the early applications of electron diffraction by Finch and Quarrell (1934) showed the existence of a two-dimensional pseudomorphism between deposits and substrate crystals in certain cases.

In general, the methods used for the study of the formation of films on metals as described above have been of doubtful validity and have often given ambiguous results. It is true that information concerning these films can be obtained by means of the microscope, but for a fundamental understanding of such growth it is necessary to know



the nature and structure of the films in their initial stages of formation. Specially it has been generally agreed that the initial film formed during a corrosion process is of the greatest importance in determining the subsequent progress of corrosion. This information can now be given directly by the electron diffraction method. Broadly speaking, it may be said that electron diffraction can be applied with almost certain hope of successful results to any type of surface film arising in connection with metals.

(5). X-ray Studies of Surface Films.

X-rays penetrate much deeper than electron rays, but nevertheless they have been used in a few cases to provide information regarding the structural relationship between oxide films and the metallic base. Mehl, McCandless and Rhines (1934) found that the atoms in a ferrous oxide film grown on iron usually stand in a simple crystalline relation to those of the basic metal, whilst if the ferrous oxide decomposes, giving magnetite, the orientation relation is continued in the latter. Studies by Goldschmidt (1942) bring out a simple crystalline connection between iron, ferrous oxide and magnetite, thus explaining why an easy transition is possible. The transition from iron to ferrous oxide is a true oxidation, while the change from ferrous oxide to magnetite consists not in the addition of oxygen but in the abstraction of iron.

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The relations of halide, sulphide and oxide films to their metallic single crystal bases (silver, copper and lead) and also of one halide to another (e.g., silver chloride formed on silver bromide) have been studied by Schwab (1942), who concluded rather surprisingly that orientation only occurs if the film has a larger molecular volume and if the two lattices contain phases with nearly the same spacings (within 5%). Thus, silver chloride on silver bromide is oriented but silver bromide on silver chloride is not. A recent study of Schwab (1947a) shows that silver iodide films are formed by exchange of a coating of silver bromide in iodide solutions with a lattice orientation. As long as they do not undergo recrystallisation or polymorphous change they belong to the hexagonal modification and grow upon the lattice of the substrate bromide crystal so that the hexagonal bases (001) plane coincides with the octahedral plane (111) of the bromide. Both planes have the same closest hexagonal arrangement of atom and contain ions of one sign only. Because of this the phenomenon differs from the formation of the other silver halides on each other or on silver. In the coating plane the distances of nearest neighbours differ by as much as 13%.

Schwab (1947 b) also finds, on thallous chloride, that films of thallous bromide grow up in an isomorphously oriented arrangement, forming intermediate mixed crystals. Thorium iodide does not do so, and silver chloride is

oriented. On thorium bromide an isomorphous oriented mixed crystal, rich in thorium iodide is formed. Silver bromide is also oriented. On (110) plane of thorium bromide the (110) of silver bromide builds up, the crystallographic axes within these planes being perpendicular to each other. This orientation of a sodium chloride lattice on a caesium chloride lattice is energetically much more favoured than the (100) on (100).

These findings, by X-rays, are contrary to the true facts as since revealed by electron diffraction, and represent merely an averaging over a very considerable film thickness, usually of at least several thousand Angstroms. Electron diffraction gives a very different picture, showing that in the initial stages epitaxial relationships are followed and are only gradually departed from with increasing film thickness.

(6) Electron diffraction Studies of Chemically Formed Surface Films.

In many thin surface tarnish or corrosion films the arrangement of the atoms is identical with that in the oxides as met with in the massive state. Preston and Bircumshaw (1935, 1936) have found that the cuprous oxide (Cu_2O) formed on copper polished in air at ordinary temperatures, the

nickel oxide (NiO) present on oxidised nickel, and the stannic oxide (SnO_2) produced on molten globules of tin, all show their normal structures. On some metals, the nature of the oxide depends on the temperature. The film formed on aluminium exposed to air was found by them to be amorphous, although it crystallised slowly when heated to 580°C . forming aluminium oxide (Al_2O_3). On α -brass (80% zinc) the film formed at 100°C . was cuprous oxide, whilst that formed at 400°C . was zinc oxide.

The same authors also examined films after their removal from the metal. Oxide films from molten lead were found to be rhombic lead oxide (PbO) although some evidence was obtained that at low temperatures and pressures the first formed oxide was tetragonal PbO . Darbyshire (1931, 1934) found that the oxide films taken from copper, nickel, cadmium, magnesium and aluminium corresponded with the structure as known from X-ray work, although there were discrepancies between the calculated and the observed intensities for certain rings.

Jenkins (1935) obtained electron diffraction patterns by reflexion from molten lead, zinc, bismuth and tin which showed that the surfaces are covered with thin oxide films consisting of small flat crystals resting on their (001) faces. The films can be removed by nickel gauze, and give by transmission patterns which show that after removal

the chemical composition is unchanged but the orientation is disturbed.

Very interesting researches have been carried out on zinc. According to Finch and Quarrell (1933, 1934) the oxide film formed on zinc at room temperature is pseudomorphic relative to the metal, being in a sense a continuation outwards of the crystal structure of the metallic base. It differs from the structure of ordinary zinc oxide in being compressed in the direction parallel to the surface and correspondingly extended in the direction normal to the surface, so that the volume of the unit cell is almost the same as in normal zinc oxide. At higher temperatures, or in growths exceeding a certain thickness, this distorted cell of zinc oxide changes to the normal form, and the protective character, which is almost certainly favoured by the lateral compression, vanishes: consequently fresh pseudomorphic oxide appears below it on the metal, which in turn passes into the ordinary form, so that the oxidation continues. Finch and Quarrell used for their research thin films of zinc condensed from the vapour in vacuo.

The work of Dobinski (1936, 1938) provides additional information about the oxidation of metals at ordinary temperatures. Copper polished with wet rouge in air yielded a different pattern from copper polished under benzene or pent^aone; when the latter was exposed to air, the original

pattern gradually decayed, being replaced by the pattern characteristic of polishing in air. A series of pictures taken every few hours showed the gradual appearance of this new pattern, which was clearly due to oxide. His results also demonstrate that polishing often causes one constituent of an alloy to accumulate in the surface layers, so that the oxide formed on the surface contains this constituent in a proportion far exceeding that of the metal itself; as a result, the film is sometimes far more protective than might have been expected. Like Vernon, he attributes the improvement produced by polishing in the resistance of stainless steel, to the fact that chromium atoms are brought to the surface. According to Tokumitsu (1940) the films formed by polishing on iron-chromium alloys below 600°C . consist of hexagonal mixed crystals, probably $\alpha(\text{FeCr})_2\text{O}_3$ whilst above 1000° the films possess a cubic spinel structure similar to magnetite and are probably FeCr_2O_4 .

The films formed on alkali metals exposed to air have been studied by Yamaguchi (1940) who states that lithium shows the pattern of Li_2O with a small amount of LiOH ; sodium and potassium become coated with bi-carbonates; whilst calcium develops the oxide CaO .

Much interesting work has been carried out on iron. Nelson (1938) finds that the magnetite pattern is always obtained immediately after abrasion and becomes stronger after gentle heating, but that if time be permitted the

pattern characteristic of α -Fe₂O₃ appears; this needs one hour at 180°C. and 1000 hours at 130°. The magnetite pattern had been observed previously by many other workers, but some of these ascribed it to γ -Fe₂O₃, which gives practically the same pattern as magnetite. Perhaps the most satisfactory explanation of Nelson's results is to attribute the pattern to magnetite formed at the elevated temperatures which are certainly reached during abrasion as indicated by the work of Bowden and his colleagues.

Jackson and Quarrell (1939) have studied oxides formed at elevated temperatures at very low oxygen pressures, using a camera which allows the structure to be examined on the specimens at the high temperatures instead of after they have been cooled down. The film formed was magnetite below 440°C. and ferrous oxide above that limit, possibly because the decomposition pressure of magnetite reaches the pressure commonly met with in the camera about that temperatures. On Armco iron a new hexagonal structure was met with when the films were very thin, although they passed into normal FeO when the thickness was increased, or reverted to magnetite when cooled to ordinary temperatures. The film formed on γ -iron above about 900°C. was always found to be magnetite, accompanied perhaps by some γ -Fe₂O₃.

(7). Chemical Reactions on Single Crystals:
Minerals.

It will be noticed from the above accounts of the literature on the studies of surface films on metals that most of the studies have been made on polycrystalline surfaces, and that consequently the formation of surface films on such material is subject to many uncertainties and difficulties in interpretation. Only a few studies have been made on films on single crystals, which eliminate many of these difficulties.

The formation of a compound on the surface of single crystals of minerals has been investigated by some investigators by electron diffraction, and these have found that when the conditions are suitably chosen crystals of the compound are formed which are completely oriented with respect to the substrate. Thus, Yamaguti (1935) studied the effects of oxidation of cleaved surfaces of zinc blende and found that the oxidised product ZnO was so oriented that the (103) plane of ZnO is resting on the cleaved face of ZnS and the (101) axis of the former is parallel to the (110) axis of the latter. Aminoff and Broome (1936) found that when (111) and (110) faces of a crystal of sphalerite (ZnS) are heated in air, an oxide layer is formed which shows orientation relative to the ZnS structure. In 1938 they also stated that when a crystal of zinc blende (ZnS) is heated

in air a film of ZnO is formed in which the c and a -axes of the ZnO crystals are perpendicular to the tetrahedral faces and parallel to the tetrahedral edges, respectively, of the ZnS crystal.

The formation of antimony oxide on a cleavage face of stibnite (Sb_2S_3) upon heating in air has been studied by Miyake (1938) who found that the orientation of Sb_2O_3 with respect to the stibnite cleavage was such that the (110) plane of Sb_2O_3 lay parallel to the cleavage (010) and the a -axis 001 of the Sb_2S_3 was in a direction parallel to a cube edge (010) of the Sb_2O_3 .

Uyeda (1938) studied the thin layer of oxidation product formed at high temperatures on a cleavage face of molybdenite and found the oxide was MoO_3 which had two types of orientation. The (111) plane of MoO_3 is parallel to the cleavage plane of molybdenite and the direction normal to it is a fibre axis. The (010) plane of MoO_3 is parallel to the cleavage plane of molybdenite and the (101) plane of the former is parallel to the $(10\bar{1}0)$ plane of the latter.

(8). Chemical Reaction on Single Crystals.
Metal single crystals.

Thomson (1931) found that the oxide (Cu_2O) layer on a copper single crystal is oriented as a single crystal in such a way that the copper atoms in the oxide lattice are

similarly place to those in the copper lattice but farther apart. While Yam^aguti (1938) who heated a copper single crystal up to very high temperature (1000°C) found two other types of orientation of the oxide lattice on the copper.

(1936)

Burgers and Van Amstel^a volatilized barium on copper and found a preferential orientation of the crystallite with 111 direction perpendicular to the surface. Oxidation of such oriented layers gave BaO layers with 110 direction nearly normal to the surface. The direction of closest packing of barium atoms in the two structures are thus approximately parallel.

Wilman (1940) investigated the reaction of halogen vapours with the (111) twinned silver films prepared by condensation on hot rocksalt cleavage faces and with similar films reduced to single crystal structure by heat treatment. The persistence of the Ag twin spots and lines indicated that both types of diffraction are probably due to twinning alone and not to the presence of crystal surfaces parallel to the individual planes.

Cochrane (1936) deposited electrolytically Ni, Cu, Zn, Cd, Ag, Cr and CO on etched copper single crystals and found that at small current density the layers are oriented except in the case of Zn and Cd. Irregularities (lines and spots) in the Ni and Cu patterns obtained were accounted for by

assuming repeated twinning on (111) plane.

Finch and Sun (1936) have shown that metals electrolytically deposited on a neutral lease, such as a polished disc of the same or of a different metal, give as a rule a random arrangement in thin films, but an orientation with a plane parallel to the surface if the deposit is thick. The plane chosen for orientation depends on the current density (and other bath conditions), which was of the order of 0.01 amp. per sq.cm. and on the composition of the bath as well as on the metal.

Finch, Wilman and Yang (1947) deposited copper on electropolished cube face of copper single crystals and silver on different faces of etched copper single crystals, and observed single crystal orientation of silver, gold, copper, nickel and cadmium, Chromium, however, did not give any orientation owing probably to the intense hydrogen evolution and the high current densities called for in this case.

Usmani (1941) deposited thin films of Cu_2I_2 , Cu_2Br_2 , Cu_2S and Cu_2O electrolytically at low current density on an etched copper single crystal surface and found that the layers possessed definite orientation relationships with the copper base. The most densely packed (111) planes in each case are parallel to the (111) plane of the copper.

Thirsk and Whitmore (1940) working in this laboratory,

found that Ni vapour condensed on the surface of corundum gave rise to unoriented crystals, as does also the NiO formed by heating the condensed film on the corundum. The crystals assume special orientations depending on the crystallographic direction of the surface. NiO reacts slowly with corundum at 900° to form Ni spinel, which takes up orientations similar to those of the NiO. The most perfect orientation occurs on the prism face $11\bar{2},0$. Some of the observations suggest that diffusion of metal ions only can occur in the spinel lattice.

Thirsk and Whitmore also found that Fe_2O_3 vapour condensed on to heated crystalline MgO gives rise to a compound, apparently $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ having a spinel structure oriented parallel to the MgO lattice and exhibiting slight twinning on octahedral plane.

It will be noticed from the above literature that there exists a large load of evidence regarding epitaxial arrangement of atoms or molecules when they come in contact with a solid surface. It will also be apparent that the incoming atoms or molecules should follow definite laws as modified by the existing field of forces on the substrate surface. Although a few empirical formulae have been put forward to explain such phenomenon, specially in crystal growth from solution, there exists no complete explanation to co-ordinate the different aspects of epitaxial growth.

Such general explanation would demand results from the most simple cases to eliminate the complicating factors. Such simplification of the problem has been obtained in the present investigation by using single crystal substrates and atoms or molecules in the gaseous state as reactants.

III. EXPERIMENTAL PROCEDURE AND METHOD OF ANALYSIS.

(1) Existing methods of preparing single crystals of Metals.

Single crystals of typical metals were first prepared in 1914 by Andrade by the process of slowly cooling wires which had been heated to the melting point (Andrade and Roscoe, 1937).

Single crystals of metals are now prepared by a number of methods which fall under four main categories.

(a) - According to the method developed in 1917 by Czochralski, a crucible containing the metal is maintained at a temperature a few degrees above the melting point. A sheet of mica perforated in the centre is floated on the surface. The diameter of the hole determines the diameter of the crystal rod. A seed crystal having the required orientation is used to touch the melt exposed through the hole in the mica and then withdrawn at a regular rate. The withdrawal is effected by some mechanical arrangement either driven by clock-work or an electric motor. The rate of growth varies with the size of the rod but may be as great as 1 cm. per minute. The diameters of the rod vary from 0.5 to 5.0 mm. The length of the single crystal wire produced by this method is limited only by the distance the rod can be withdrawn and it has further the advantage that almost any orientation may be obtained although crystals of zinc with

certain definite orientations are difficult to prepare by this method.

(1921)

(b) - Carpenter and Elam, annealed a polycrystalline rod of the metal by heating to relieve all strain. It is then stretched a small amount - usually from $\frac{1}{2}$ to 4 per cent, so that the grains are plastically deformed. The crystal is then heated for several days at an increasing temperature, finally being heated for a short time just below the melting point. The cooling is carried out carefully in order to avoid strains being set up. The whole rod, under this treatment, becomes monocrystalline. The disadvantage of this method lies in the fact that the orientation cannot be predetermined.

(c) - A method, of which there exist a number of versions, consists in crystallisation from a point in tubes or other containing vessels. According to the procedure described by Bridgman, (1925) a tube containing the molten metal is carefully cooled, the cooling being made to proceed regularly along the length of the containing tube by the use of a gradient furnace. Provided the temperature gradient exceeds a certain critical value and the rate of advance of the crystallisation front is sufficiently slow, it is generally possible to cause the whole contents of the tube to grow as a single crystal.

(d) - A method particularly useful for the conversion

polycrystalline wires of zinc and cadmium into single crystals is due to Kapitza(1928). A length of wire is touched on a hot plate, so that the end melts into a little pool. On lifting up the wire an 'appendix' is formed. The wire is placed in a glass tube in such an atmosphere that the oxide coating which holds the molten metal in cylindrical form is neither destroyed nor grows excessively thick. A furnace maintained at a temperature above the melting point of the metal is slowly drawn over the wire, the end with the 'appendix' entering the furnace first. The rate of growth for a wire about a millimetre in diameter may be arranged to be 1 mm. per minute.

(2). Method of Preparation of single crystals used in the present investigation.

In the present investigation single crystals of zinc, antimony, bismuth and tin have been prepared by two different methods.

- (i). Single crystals of zinc, antimony and bismuth were prepared by a modified Bridgman method.
- (ii). A method has been developed for the preparation of single crystal surfaces of tin and bismuth by casting the molten metal on clean plane glass surfaces and allowing the melt to cool slowly.

Method (i).

The single crystals of zinc, antimony and bismuth were prepared by lowering a glass tube containing the molten metal slowly through a vertical tubular furnace. If the rate of lowering is at least as slow as the velocity of crystallisation the solidification starts at the bottom of the tube and proceeds along its axis. The pyrex glass moulds 8-10 mm. in diameter were tapered to a capillary end, so that when the melt begins to solidify there would be room for only a few crystal nuclei to form, thus increasing the probability of obtaining a single crystal through the whole length of the tube.

To prepare the crystal, the glass tube was heated to about 50°C. above the melting point of the metal and molten metal of high purity was slowly poured into it. When the metal had solidified the tube was transferred to the vertical furnace, where the metal was remelted and the glass tube was slowly lowered. The lowering was effected by means of a water float and the speed could be adjusted within fine limits by regulating the flow of water into the tank. The speed of lowering was about 1 cm. an hour.

The furnace was run in general about 100°C. above the melting point of the metal. Large castings, about 8-10 mm. diameter, could be obtained fairly readily from zinc,

antimony and bismuth.

(3). The preparation of a plane metallic single crystal surface.

A particularly useful method, previously used in this laboratory for a wide range of metals, for preparing a plane single crystal metallic surface, was as follows:-

Method (ii)

A microscope slide about 1" x 1" was first cleaned with benzene followed by fuming HNO_3 and distilled water. The process was repeated several times till the whole glass surface was completely wetted by water. The glass plate was then dried with filter paper and placed on one end of a cylindrical brass slab about 4" in diameter and 5" in height, the cylindrical wall of which was lagged with asbestos. The brass slab was heated to about 75° above the melting point of the metal, measured by a thermometer in a hole drilled about 3 mm. below the top surface and reaching to the middle of the slab. Pure tin or bismuth was melted and the oxide layer was skimmed off. The skimmed, silverwhite tin or bismuth was now poured on the hot glass plate so as to form a globule of about 1 cm. in diameter. The glass plate with the molten metal was now covered with another brass slab of the same diameter and height as the first but with a cylindrical hollow $1\frac{1}{2}$ " in diameter and 1" deep in

the centre so as to fit on the first without disturbing the molten metal. The second brass slab, which was also similarly covered with thick asbestos was heated to a temperature about 100° above the melting point of the metal and was covered on top with asbestos. The whole system was now allowed to cool slowly at about one degree per minute. It will be noticed from the description given above that cooling starts from the flat bottom of the lower slab.

After cooling, the metal surface, in contact with the glass, had a very smooth and mirror-like appearance and yielded beautiful Kikuchi band patterns when examined by electron diffraction. The Kikuchi bands indicated the perfection of the crystals and allowed their orientation to be defined with high accuracy.

The metals, zinc, antimony, bismuth and tin from which single crystals were prepared, were 99.99% pure analar quality supplied by Hopkins and Williams Co. London.

(4) Methods for Preparing Surface Films by Chemical Reactions.

Formation of Surface Films on the Single Crystals.

(a) Oxidation - In order to oxidise the cleave face the crystal was heated in air in an electrical furnace made by winding Nichrome (22 gauge) wire around a vertical tubular Pyrex glass furnace 25 cms. long by 6 cms. diameter, closed at its upper end. The temperature was measured by a thermocouple inserted in the furnace.

(b) Formation of halides and sulphides - Halides and sulphides of the metals were allowed to form by exposing the faces of the crystals to the corresponding gases in a partially evacuated dessicator for a known time.

(c) Etching of the single crystals - The different crystal faces were etched by dipping the crystal in dilute solutions of the reagent.

(5) Experimental Technique: Surface Structure Analysis by Electron Diffraction.

The design and mode of operation of the electron diffraction camera (Fig. 1) and the constant-current high tension circuit have been described in detail by Finch and Wilman (1937).

The Kikuchi band patterns described in the following pages

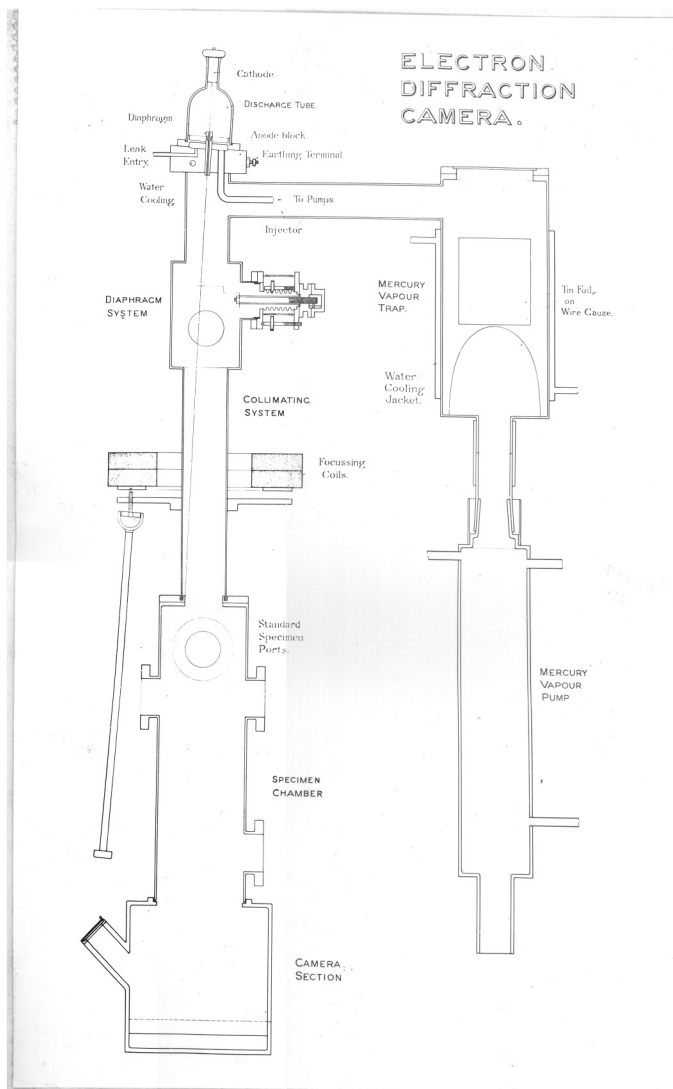


Fig. 1

were taken by the method of reflection at grazing incidence with a camera length of about 25 cms. The accelerating voltage was in all cases between about 50 - 65 kV. The grazing angle was of the order of one or two degrees and sometimes less.

(6) Interpretation of the Electron Diffraction Photographs.

The effects observed with the diffraction of electrons by crystals are similar to that obtained with X-rays, and their interpretation also follows along somewhat similar lines. This subject has been described in detail in a number of reviews on electron diffraction (Finch, Quarrel and Wilman, 1935; Beeching, 1935; Finch and Wilman, 1937; Thomson and Cochrane, 1939). The salient points helpful in interpreting the results of the present investigation have been outlined below:

The various types of electron diffraction pattern may be considered on the basis of the pattern yielded by a single crystal.

Electron waves scattered from a row of atoms of spacing 'a' in a direction making an angle α with the atom row will be in phase if -

$$a(\cos \alpha - \cos \alpha_0) = n\lambda$$

where h is an integer and α_0 the angle between the incident waves and row of atoms and λ the wavelength of the electron beam.

If there are M_1 atoms of scattering power ψ in the row the intensity 'I' of the scattered radiation at a screen distance 'R' is given by -

$$I = \frac{\psi^2}{R} \cdot \frac{\sin^2 M_1 h \pi}{\sin^2 h \pi}$$

Similarly the waves scattered from two other rows of spacing 'b' and 'c' in a diffracting crystal containing M_2 and M_3 atoms respectively reinforce at the screen

$$\text{if } b(\cos \beta - \cos \beta_0) = k\lambda$$

$$\text{and } c(\cos \gamma - \cos \gamma_0) = l\lambda$$

where k and l are also integers; and the intensity of the diffracted beam from the whole crystal is

$$I = \frac{\psi^2}{R} \cdot \frac{\sin^2 M_1 h \pi}{\sin^2 h \pi} \cdot \frac{\sin^2 M_2 k \pi}{\sin^2 k \pi} \cdot \frac{\sin^2 M_3 l \pi}{\sin^2 l \pi}$$

h , k and l are the so-called Laue integers or indices.

Maxima of diffracted intensity are obtained in directions such that h , k and l are all integers. The intensities of diffracted beams having integral values of h , k and l are further modified by the structure factor corresponding to the atomic positions in the unit cell.

The positions and form of the diffraction spots in the pattern given by a crystal in a definite azimuth (e.g., as

in Fig. 2) can be worked out from a consideration of the Laue "zones". It is only necessary to consider the zones for three conveniently situated axes in the crystal. The convenient axes are not always the crystal axes. They are usually the atom row in the direction of the beam and the two other important rows, all three rows being mutually positive or nearly so. Since any three atom rows define a lattice and since it is always possible to find an atom row in the beam direction and two steeply inclined to it, a solution of the problem in this manner is possible. An atom row of spacing a' inclined at α'_0 to a beam of radiation will give rise to diffracted beams which lie on cones with the atom row as axis, each cone being defined by an integral value of the Laue index h' . The cones will intersect the screen or photographic plate in hyperbolae, ellipses or circles according to the value of α'_0 . For an atom row at right angles to the beam the zones of intersection are hyperbolae, but for fast electrons and in the region of pattern near the central spot they may be considered as straight equidistant lines of separation $\lambda L/a'$. The breadth of a zone is inversely proportional to the number of atoms in the row so that the zone due to a long row is sharper than that due to a short row. The zone breadth on a screen 4 cms. away is $2\lambda L/11a'$. As the atom row is inclined the zones become more and more curved and when it is in the direction of the beam the zones are circles. This is sensibly true for the

practical case when an atom row is inclined at not more than about 5° to the beam. The radius of the h' 'th order circular zone is given by R_h where

$$R_{h'}^2 = R_0^2 + L^2 \cdot 2h'\lambda/a'$$

where R_0 is the radius of zero order zone. The shape and position of the spot pattern is obtained from the areas of intersection of the three sets of Laue zones.

The limitations imposed on the use of electron diffraction for the study of surface layers by the necessity of using thin films was removed when Kikuchi and Nishikawa (1928) and later Thomson (1930) and Shinohara (1930) discovered the grazing incidence method of electron diffraction whereby the examination of the surfaces of single crystals and of films on surfaces can be carried out without disturbing the relationship between the film and substrate. In the case of a reflexion specimen the Laue zones on a screen are of the form shown in Fig. 2.

With a smooth surface the depth of penetration below the surface is small, and the horizontal zones become broad bands. The spots are consequently much drawn out, as in Fig. 2. The spots in the 1st and higher orders of the circular zones are, however, sharper, due to the increased penetration effective in contributing diffracted beams which emerge more steeply from the crystal towards these zones. The effective limit of penetration of 50-60 kV electrons for coherent diffraction is

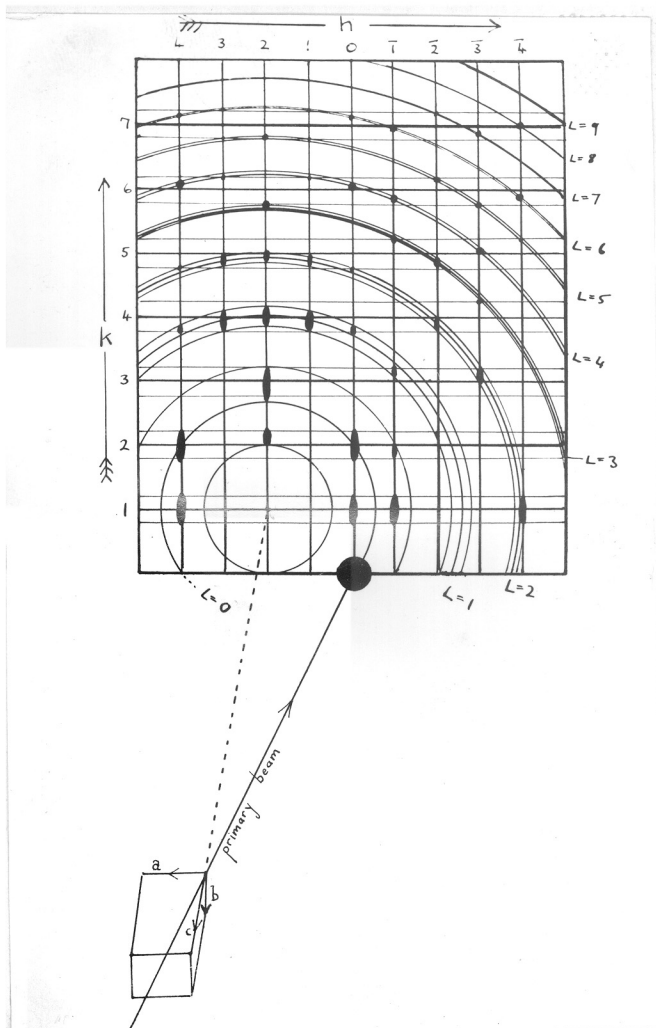


Fig. 2

about 500 Å. in the case of materials like mica made up of light atoms, and correspondingly less with increasing atomic weight, down to only a few hundred angstroms for heavy elements such as gold. Correspondingly, in the case of reflection patterns obtained with an electron beam grazing an atomically smooth surface the coherent (spots or rings) near the primary beam is only contributed to effectively by the surface region of the crystal to a depth of about 20 Å. even when it consists of a material of light atoms like hydrocarbons and their derivatives (Kikuchi, 1935; Finch and Wilman, 1937; Schoon, 1938).

A characteristic feature of the pattern from a smooth surface is the way in which it changes as the angle of incidence of the electron beam is varied. The horizontal zone being broad a variation of incidence causes the spots to move up or down with a waxing and waning of intensity. If the number of atoms in the direction of the beam be also small, the circular zones become broad bands and the spots are drawn out very much. This is in striking contrast to what is observed with a rough single crystal surface. The penetration here is larger and the horizontal zones are sharp. Change in the incidence causes the spots to wax and wane in intensity but they remain fixed in position.

In the case of a very thin transmission specimen there is a relaxation of one diffraction condition and an extended cross grating pattern representative of the

lattice arrangement in the cleavage plane is obtained. With thicker specimens spots on circular zones and also effects due to secondary scattering (K lines) make their appearance. With thick specimens (3000 A.) only these secondary effects are observed.

The secondary scattering effects first discovered by Kikuchi in 1928, and now known after him, take the form of black and white lines and white bands on a print. As Kikuchi pointed out they may be considered in principle to be due to selective Bragg reflection of scattered electrons from crystal planes, as Rutherford and Andrade (1914) suggested to account for their results on γ -ray scattering. The lattice-plane spacing 'd' can be calculated from the line pair separation D and is given approximately by

$$d = \frac{\lambda L}{D}$$

where L is the camera length.

Single crystal diffraction patterns provide much more complete though usually also more complex information than is yielded by the ring patterns obtained from polycrystalline material, with respect to the structure of the material, i.e., lattice type, symmetry and atomic arrangement. The Kikuchi bands given by single crystals have been made use of in a general way, by inferring from their presence that there are relatively large thicknesses (several hundred A or more) of coherently diffracting crystals in the specimen.

and from their diffuseness or displacement the degree of fine-scale surface roughness, mosaic structure and distortion of the crystal. It is generally agreed that Kikuchi bands are due to multiple scattering. The methods of interpretation of these bands have already been developed by a number of investigators (Finch, Quarrell and Wilman, 1935; Finch and Wilman, 1937; Wilman, 1948.).

Although the pattern from a polycrystalline specimen may be worked out from the rotation of a single crystal pattern it is more conveniently considered as Bragg reflection from the various planes in a crystallite. A set of planes of spacing 'd' inclined at the correct Bragg angle would reflect electron waves in the same manner as X-rays according to the equation

$$2d\sin\theta = n\lambda$$

In a specimen with tiny crystallites sets of planes inclined at the correct angle may be found all round the normal to the surface, resulting in the familiar ring diffraction. Furthermore, in a randomly oriented specimen most sets of planes in the crystal lattice occur at the appropriate Bragg angles and other rings are obtained.

For a cubic lattice, the interplanar distances are given by definite values of the integers h, k and l in the equation

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

so that the ring radii become equal to

$$\frac{\lambda L}{a_0} \sqrt{h^2 + k^2 + l^2}$$

In random polycrystalline reflection specimens nearly half the rings appear above the shadow edge but the rings are limited to shorter arcs if some or all of the crystallites are oriented with a particular plane parallel to the substrate. The arcs whose centres lie on the plane of incidence correspond to the orders of Bragg reflection from the planes which are parallel to the surface. The remaining arc positions lie at positions characteristic of the orientation and the crystal system.

A simple way of defining the positions of these diffractions is as follows:-

The hkl diffraction must lie at the intersection of the hkl ring with the corresponding orders of the l' layer lines due to the lattice row normal to the plane parallel to the substrate. If this row is $[uvw]$, then

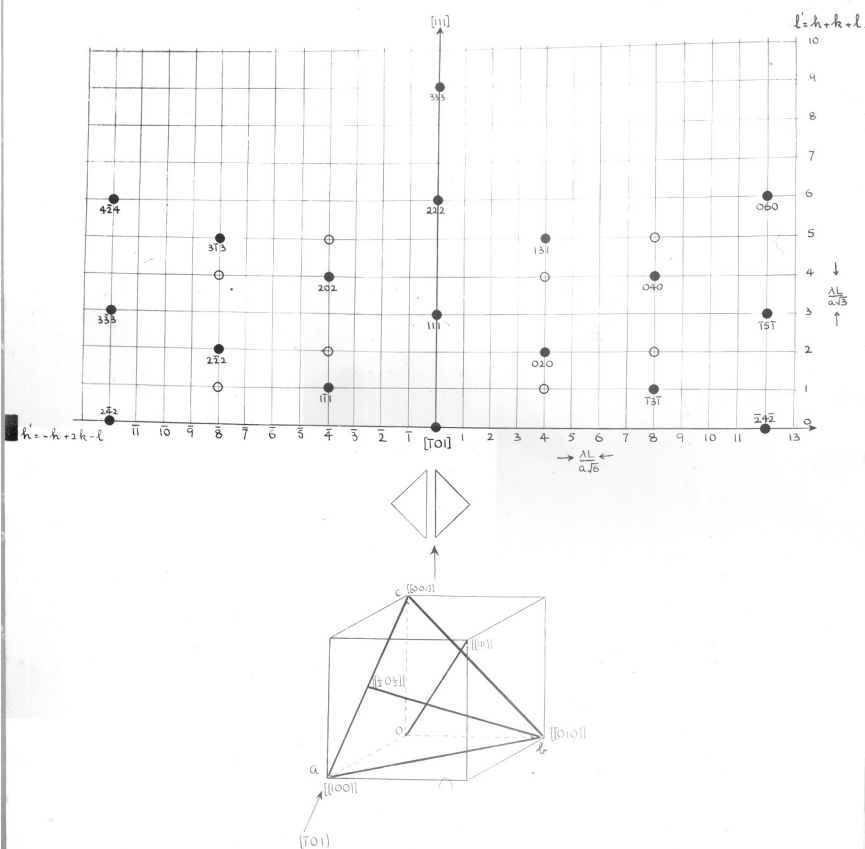
$$l' = uh + vk + wl$$

The l' layer lines are practically straight with spacing $\lambda L/a' \cos \theta$ where a' is the lattice translation in the direction $[uvw]$ and θ is the angle which it makes with the setting normal to the beam.

Thus, for a (111) orientation in the face centred cubic system $a'^2 = 3a^2$ and the layer line separation becomes equal

to $\lambda L/a\sqrt{3}$ which is $R_{111}/3$. The intersections of the various orders of the layer lines and the hkl rings, for which $l'' = h + k + l$ is satisfied, give the positions of the diffractions, and in particular, arcing of the 111, 222, 333 rings at the plane of incidence will take place for this orientation.

In the case of two degree orientation the crystallites are arranged on the substrate in such a manner that three definite directions in the crystal lattice are fixed relative to the beam. The pattern is then obtained from the intersection of the three sets of Laue zones with indices h' , k' and l' . For example, two degree orientation of the (111) planes of face centred cubic crystals of silver grown on mica cleavage faces at about 200°C. results in the two types of pattern at azimuths 30° apart, as shown in Figs. 3 and 4.



TWO DEGREE ORIENTATION - BEAM ALONG $[101]$.

Fig-3

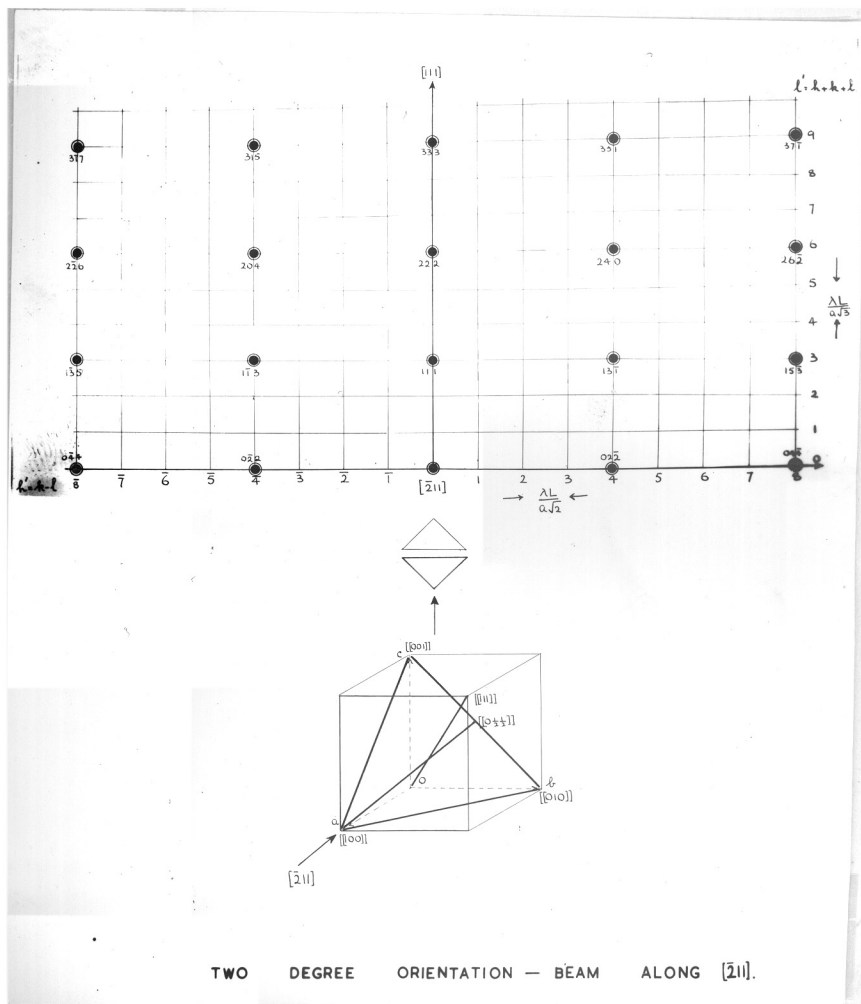


Fig. 4

IV. RESULTS WITH ZINC SINGLE CRYSTALS

(1) The Surface Structure of the Cleavage Face of Zinc Single Crystals.

The zinc crystals prepared by the above method (i) described on page 33, when carefully cleaved, gave smooth and shining cleavage planes (001) on which three main sets of parallel lines can be observed at 60° to each other. Fig. 5 shows the Kikuchi bands (camera length = 25 cms.) obtained from such a cleavage plane when the electron beam is along one set of the parallel lines, while Fig. 6 shows the Kikuchi bands when the beam is at 30° or 90° to one set of the lines. The Kikuchi bands from the cleavage plane indicate the perfection of the zinc crystals prepared and the highly smooth surface, which is also shown by the pattern of elongated spots, Fig. 7 (at camera length 47.5 cm.) shows the spot pattern of the cleavage plane when the beam is along one set of parallel lines, while Fig. 8 shows the same when the beam is at 30° to these lines.

It is interesting to point out here the hitherto unnoticed fact that while the Kikuchi bands correspond to metallic zinc, which is close packed hexagonal with $a = 2.6595$ and $c/a = 1.856$ (Hume Rothery, 1945); the strong elongated spots in the same pattern are due to a Zinc oxide lattice (cf. Fig. 5 and 6), which is also close packed hexagonal but with $a = 3.2426$ and $c/a = 1.6020$ (Bunn 1935).



Fig. 5

A 7143



Fig. 6

A. 7126

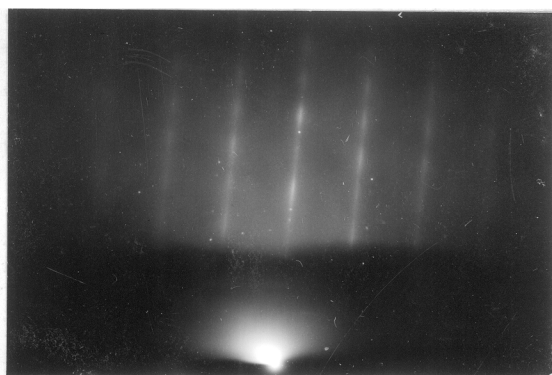


Fig. 7

A 7251



Fig. 8

A 7150

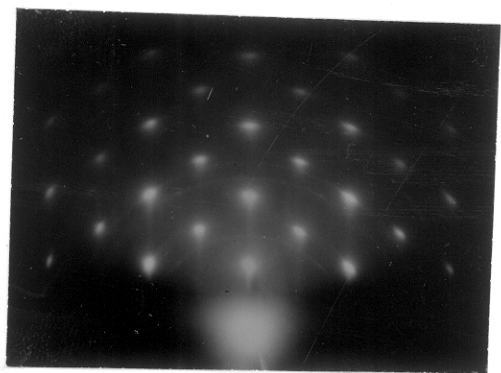


fig. 8A. NaCl on pyrites cube face.
Beam along $\langle 110 \rangle$ of pyrites.

These zinc oxide spots appear strongly even if the specimen is put in the camera within five minutes after cleaving. From the size and shape of these spots the ZnO crystals were estimated to be at least 500 Å in diameter in directions parallel to the surface, but the elongation of the ZnO spots, coupled with the fact that the Zn Kikuchi line pattern is so clear, suggests that the thickness of most of the ZnO crystals is no more than at most a few atoms, though the surfaces of some (001) oriented ZnO crystals are evidently in part slightly rough with projections of about 20-30 Å. in height. Since the zinc Kikuchi line pattern is strong, and normally no zinc spots appear, the zinc surface must also be highly smooth and the ZnO crystals must be only 15-20 Å. thick over at least much of the surface; they may be thicker, but cover proportionately less of the surface, as might possibly occur due to local preferential oxidation for example, where the surfaces are less smooth. The spot positions showed that the hexagonal ZnO crystals had their lattices parallel to that of the zinc substrate crystal, Fig. 17a. Rarely, however, very small sharp circular spots were observed as in Fig. 6, which were due to zinc, the electron beam passing through rough surface regions present in appreciable proportion. The patterns from the shining and apparently smooth (001) surface of the (10 $\bar{1}$ 2)-twinned zinc crystals, always contained an extensive pattern of sharp zinc spots (Fig. 9) showing that these surfaces were much rougher



Fig. 9

A7452

than the cleavage plane. Measurements of Fig. 6 gave $a = 3.215 \text{ Kx}$ for ZnO relative to $a = 2.6595 \text{ Kx}$ for zinc (Hume-Rothery 1945); while from Fig. 4, value $a = 3.236 \text{ Kx}$ was estimated relative to zinc spot spacing. These values are slightly less than Bunn's (1935) X-ray value, $a = 3.2426 \text{ Kx}$.

Darbyshire (1934) who also obtained a spot pattern from the zinc cleavage planes, attributed these spots to the zinc lattice, but measurement of his published patterns show clearly that they must be due to zinc oxide, since they agree with the zinc oxide axial ratio.

Vernon, Akeroyd and Stroud (1939) observed that abrasion of polycrystalline zinc with emery powder gave a surface in which a certain amount of oxide, believed to be amorphous, was embedded, the reinforcement of which on heating gave a continuous film. They have been able to isolate this oxide film by volatilization of the underlying zinc; under favourable conditions the film is highly resistant and may permit the melting without rupture.

(2) Oxidation of the Basal Plane of Zinc Single Crystals.

(i) Oxidation at 200°C .

On heating zinc cleavage faces in air at 200°C . for five hours the Kikuchi bands became fainter and the single crystal spot pattern of zinc oxide was little changed. Fig. 10 shows these results when the beam is along one set of

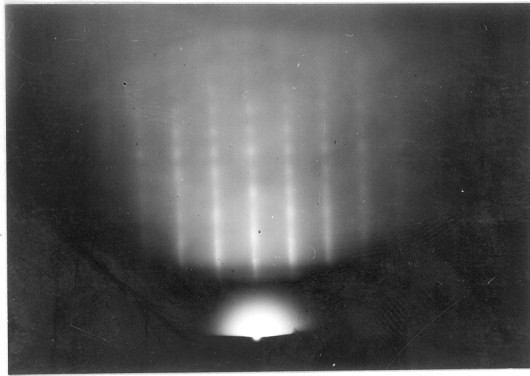


Fig. 10 A6960

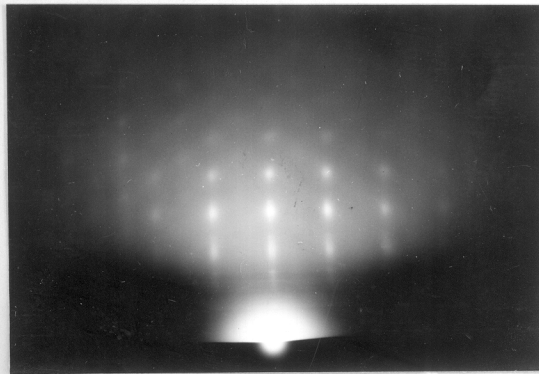


Fig. 11 A6961

parallel lines while Fig. 11 shows the same when the beam is at 30° to these parallel lines.

On heating the same crystal for eight hours, the spot pattern became clearer indicating the growth of the crystals, but the oxide coating was still thin since the Kikuchi lines are still visible.

On further heating of the same crystal in air for twelve hours the zinc oxide spot pattern had become much clearer. The spots were less elongated vertically and sharper laterally, thus the zinc oxide crystals had increased in diameter in directions parallel to the surface. Very faint Kikuchi bands however still indicate the thinness of the oxide film over at least a considerable portion of the surface.

(ii) Oxidation at 400°C .

The cleavage surfaces of zinc crystals when heated at 400° for five minutes, still showed the Kikuchi lines and single crystal patterns of zinc oxide spots indicating the ZnO coating to be not more than about 20A thick over much of the surface. Even after being heated at the same temperature for two hours, the faint Kikuchi lines were still visible. The ZnO crystals, however, had grown larger, especially sideways, but not much in thickness. Only after three hours heating at 400°C . did the ZnO ring pattern appear. The ZnO spot pattern, however, was still present. Fig. 12

indicates these results. After four hours heating at the same temperature similar results as shown were obtained (fig. 12), with slight arcing of the rings. After eleven hours heating at 400°C . the ring pattern became incompletely formed, i.e., spotty, indicating that these crystals of ZnO were of the order of 1000 Å or more in diameters but the spot pattern due to the oriented crystals of zinc oxide was also present, as shown in Fig. 13.

(3) Oxidation after treatment with Benzene.

One cleavage face of a zinc crystal which gave clear Kikuchi bands and ZnO spot patterns was washed with "crystallisable benzene". Washing with benzene, however, did not change the nature of the Kikuchi bands or original spot pattern of ZnO . This cleavage face now on being heated at 400°C . for half an hour gave an arced ~~ring~~ pattern indicating spiky ZnO crystals (along $[001]$), partly randomly distributed and partly in preferential (101) and (001) orientation, as well as the strong spot pattern due to the initial (001) oriented ZnO . These results are shown in Fig. 14. On prolonged heating at 400°C . for eight hours the arcs on the ZnO rings and the ZnO spot pattern remained the same, while the rings became sharper indicating the growth of random ZnO crystals (needles). The pattern did not change even after fifteen hours heating at the same temperature.

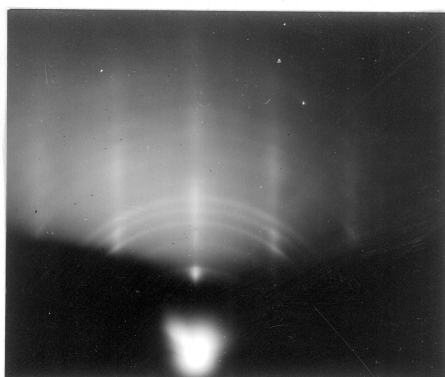


Fig. 12 A7081

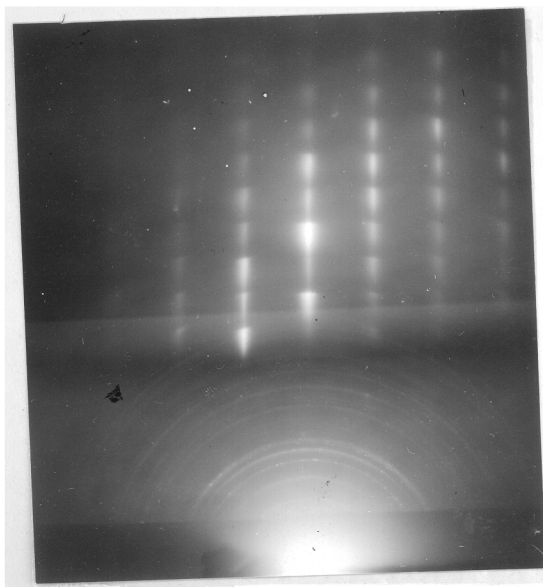


Fig. 13 A 7314

The two degree nature of the ZnO (101) orientation relative to the zinc substrate is immediately clear from the change in the pattern in different azimuths. The azimuthal orientations are best deduced from Fig. 15, where the beam was perpendicular to one set of the lines on the zinc cleavage face, so that the (001) oriented ZnO also present yielded elongated spots in a large rectangular pattern. On the vertical rows through these spots lie also some of the more prominent arcs from the (101) oriented ZnO, and these correspond in position to an azimuthal orientation such that a basal axis ($[010]$ type) in the (101) plane lay parallel to a basal axis of the zinc crystal, Fig. 17(a), just as in the case of the parallel (001) orientation. The other arcs also present in this pattern show that other ZnO crystals occurred at azimuths about 17° from those of the first group, and that these orientations were such that either -

(i) the next most densely populated lattice rows (of $[101]$ type) in the (101) plane lay parallel to one of the basal axes in the zinc (001) plane, Fig. 17(b), or (ii) a 010 type of ZnO lattice row was along the $[\bar{1}20]$ Zn row and a $[21\bar{2}]$ ZnO row was along a Zn $[540]$ row, as also shown in Fig. 17(b). The alternative (ii) seems the more likely since it results in smaller distances between the regions of lattice fitting and since in this case two relatively densely populated (perpendicular) lattice rows show a fair fitting with two in the substrate. This case (ii) would thus be 19°

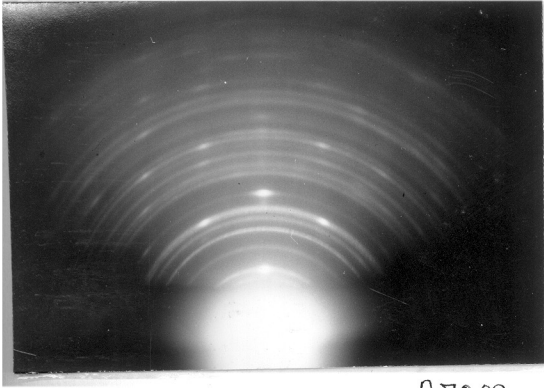


Fig. 14 A7209

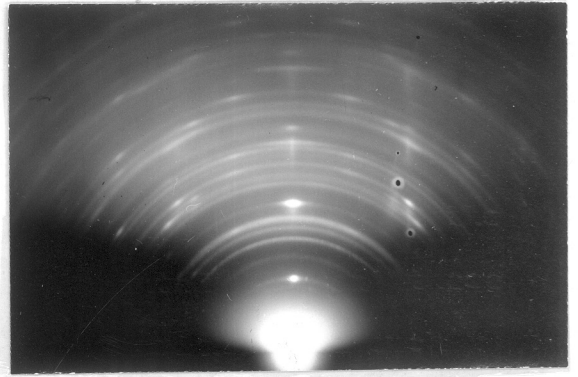


Fig. 15 A7193

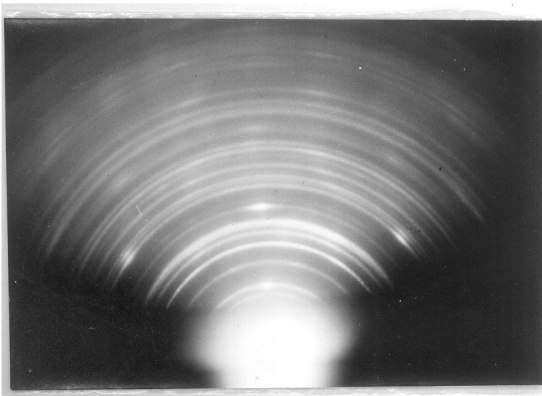
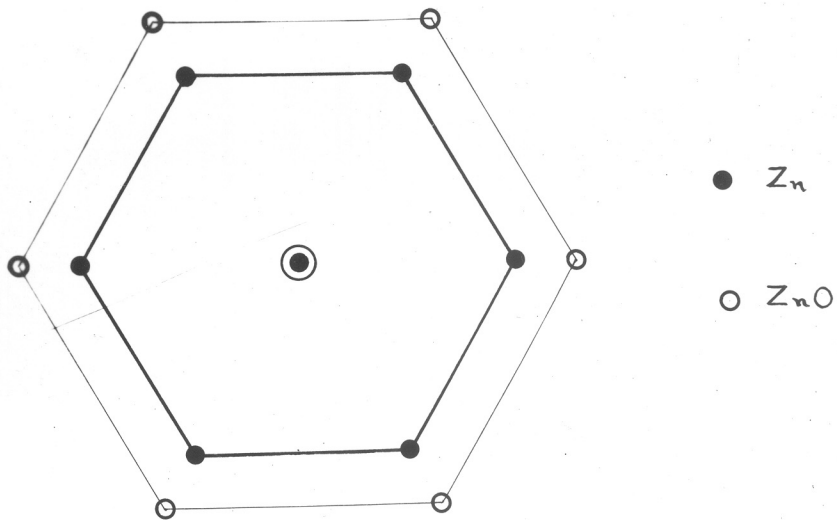


Fig. 16 A7205



PARALLEL GROWTH OF
 $ZnO(001)$ ON $Zn(001)$

Fig. 17a

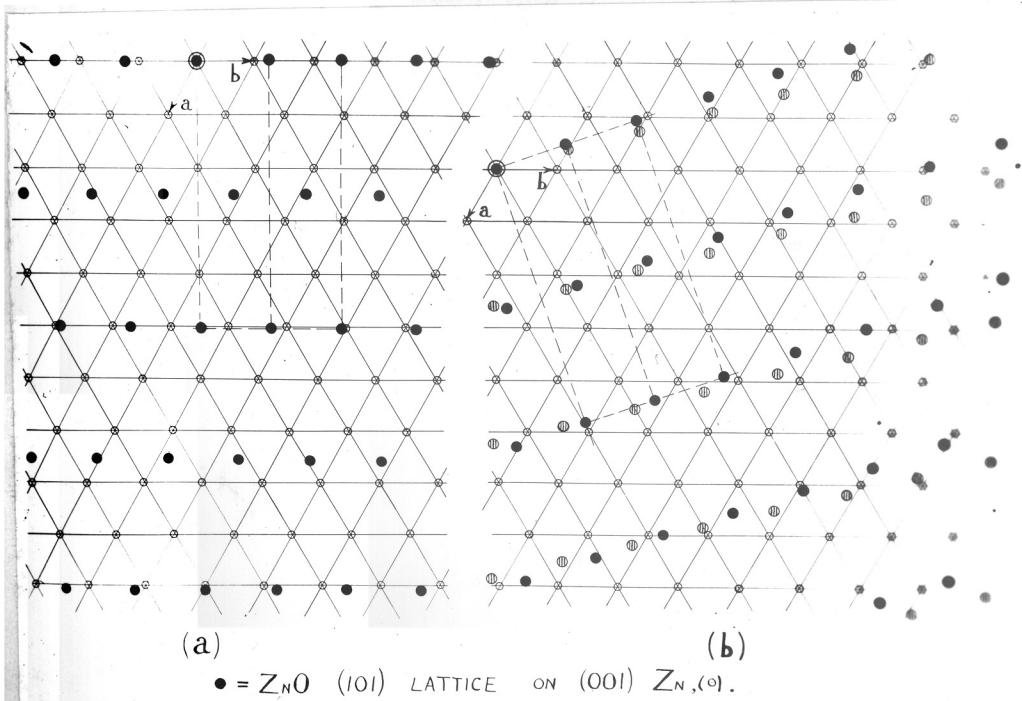


Fig. 17b

different in azimuth from the former (101) orientation, while (i) would be about $15^{\circ}21'$ from it, if $c/a = 1.6020$ as Bunn found. Fig. 17 shows the lattice-point relationships of the ZnO and zinc in the typical (101) orientations. It will be seen that here relatively large distances occur before fitting of lattice points recurs.

Figs. 16 and 14 obtained with the beam respectively practically parallel to, and at 14° to, one set of lines on the zinc cleavage face provide further confirmation of the above azimuthal orientations.

(4) Oxidation after treatment with Hydrogen Sulphide Gas.

A cleavage face, on being exposed to a high concentration of H_2S gas in air for 15 minutes did not give any pattern. On heating the same face which had been exposed to H_2S gas at $400^{\circ}C$. for only 15 minutes, however, ring patterns due to random oxide crystals were obtained, which did not change even after one hour's heating at the same temperature (Fig. 18).

Another cleavage face which was exposed to a very low concentration of H_2S gas for half an hour, gave a sharp spot and ring pattern due to Zn besides the original vertically elongated spot pattern due to (001) orientated ZnO. This cleavage face now being heated at $400^{\circ}C$. for 15 minutes showed no change in the diffraction pattern. The same crystal being heated for a further 2 hours gave arced ring pattern with (101) orientation and single crystal spot pattern due to ZnO (Fig. 19). The elongation of the spots shows that the cleavage face is still very smooth. The cleavage face which has been exposed to a low concentration of H_2S gas, on being heated at $400^{\circ}C$. for eight hours gave

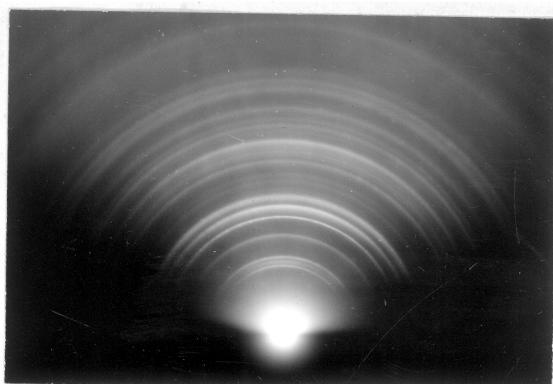


Fig. 18

A 7235

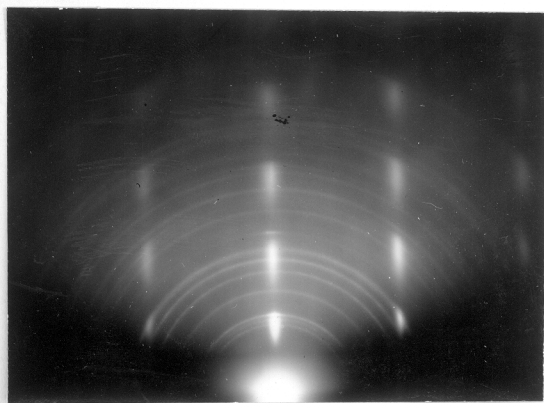


Fig. 19

A 7373

a sharp spot pattern of ZnO showing (001) orientation parallel to the zinc and also an arced ring pattern with (101) and (001) orientation (Fig. 20). However, in this specimen, as the shadow edge was lowered, the spot pattern became fainter and the ring pattern became stronger. When the beam was moved over the specimen, rings and spot patterns also changed in relative intensity indicating the non-homogeneous character of the surface. This result is clearly shown in the micro-photograph (Fig. 21) taken from the same specimen as that of Fig. 20.

Yamaguti (1935) studied the effects of oxidation of cleaved surfaces of zinc blende (110) and found that the oxidised product ZnO was so oriented that the (103) plane of ZnO was resting on the cleaved face of ZnS and the [010] axis of the former to be parallel to the (110) axis of the latter. Aminoff and Broome (1936) found that when a crystal of sphalerite (ZnS) is heated in air an oxide layer is formed which shows orientation relative to the ZnS structure.

(5) Surface Structure and Oxidation of (001)
Faces of (10 $\bar{1}$ 2)-twins formed by Mechanical
Fracture.

A cleavage slab about 2 mm. thick was given a slight hit with a sharp knife edge placed perpendicular to the cleavage face along the direction of one set of parallel lines on this face. The surface thus obtained was fairly smooth.

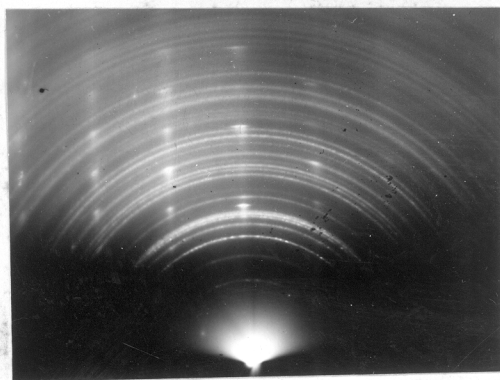


Fig. 20

A7375

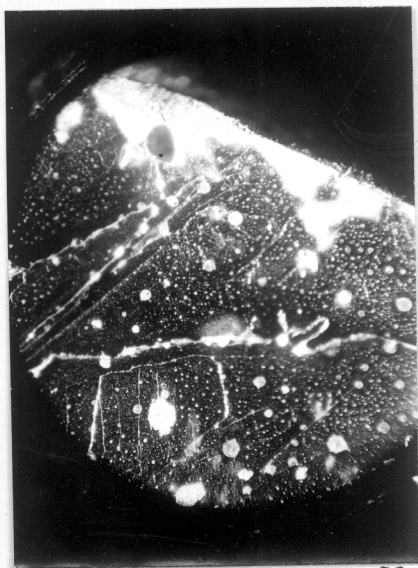


Fig 21

x50

The Kikuchi bands and zinc oxide spot pattern in the two azimuths, one along one set of parallel lines (Fig. 9) and the other at 30° to them are quite similar to those obtained from the same azimuth of the basal plane (cf. Figs. 5 and 6).

However, on heating this surface at 400°C. for 15 minutes an arced ring pattern appeared, which however showed weak (001) orientation as in the patterns obtained from cleavage planes oxidised for three hours (cf. Fig. 12). This result is shown in Fig. 22. On further heating the same surface at the same temperature the ring pattern became sharper indicating growth of the ZnO crystals. However, after one hour's heating at the same temperature only a ZnO ring pattern without any indication of orientation appeared but the rings were much sharper, indicating further growth of the random ZnO crystals.



Fig. 22

A7483

V. RESULTS WITH ANTIMONY SINGLE CRYSTALS

(1) The Surface structure of the Cleavage Face of Antimony Single Crystals.

The antimony crystals prepared by the method (i) described in section III have very smooth and shining cleavage faces (111) on which three sets of parallel lines at 60° to each other can be seen. Fig. 23 shows the Kikuchi bands obtained from such a cleavage face when examined by an electron beam along one set of the parallel lines, while Fig. 24 was obtained with the beam at 30° to one set of these lines. The Kikuchi bands correspond to those to be expected in these azimuths of the cleavage plane and indicate the high perfection of these antimony crystals.

The cleavage faces (111) of antimony, however, did not show any spot pattern as had been found in the case of cleavage faces (001) of zinc single crystals; thus they were very highly smooth and if any oxide was present at all it must have been less than 10A thick.

(2) Oxidation of Cleavage Faces of Antimony Single Crystals.

The cleavage face of antimony, on being heated at $250^\circ\text{C}.$ for half an hour in air did not give any coherent pattern. However, the same specimen, on being reheated at $400^\circ\text{C}.$ for

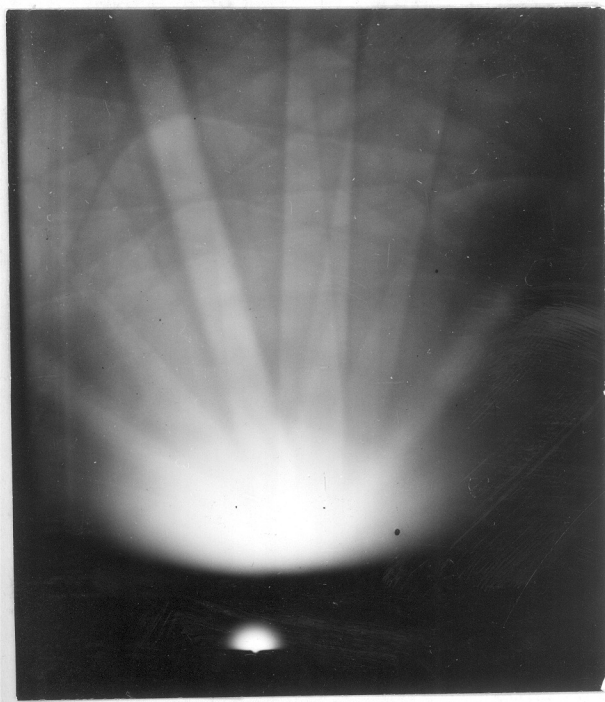


Fig. 23 A7631

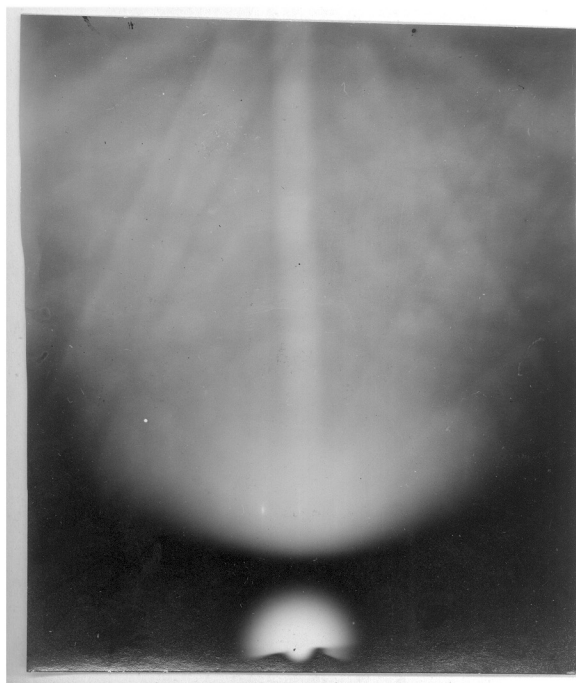


Fig. 24 A7630

ten minutes gave a spot pattern showing (111) orientation. Another freshly cleaved surface on being heated at 300°C. for half an hour gave a ring pattern but the same specimen on being reheated at 400°C. for ten minutes gave rings and a spot pattern showing two degree (111) orientation.

A specimen was then directly heated at 400°C. for eight minutes. This specimen gave a very clear ring and spot pattern. Fig. 25 shows the pattern when the beam is along one set of the parallel lines while Fig. 26 was with the beam at 30° to these lines. Both Figs. 25 and 26 also show the same two degree (111) orientation of the oxide pattern on the antimony cleavage face. The analysis and comparison of the pattern of Fig. 26 with X-ray data for face-centred cubic Sb_2O_3 has been given in Table I. The axial lattice spacings of Sb_2O_3 were calculated by comparing with graphite rings from a trace of graphite dusted onto the same specimen, and was found to be $a = 11.20 \text{ \AA}$, in reasonable agreement with the X-ray data which give $a = 11.14 \text{ \AA}$. It will be noticed that some of the rings which are missing in the X-ray patterns are present in the electron diffraction pattern. The patterns from the surface after oxidation show further that the hexagonal lattice plane (111) of the face-centred cubic Sb_2O_3 unit cell had its lattice rows parallel to the corresponding lattice rows of the (111) face of the rhombohedral cell of antimony (Fig. 27) for which $a = 4.49762 \text{ \AA}$ and $\alpha = 57^\circ 6' 19''$ (Hume-Rothery, 1945). The details of the different specimens investigated are recorded in Table II.

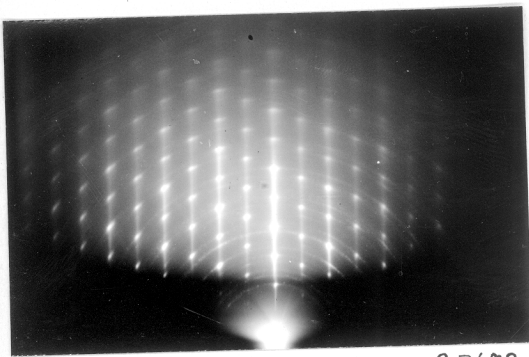


Fig. 25

A7653

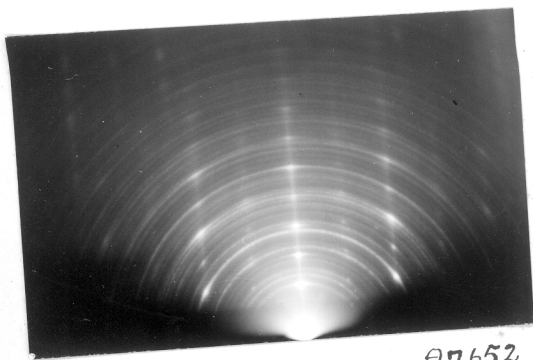


Fig. 26

A7652

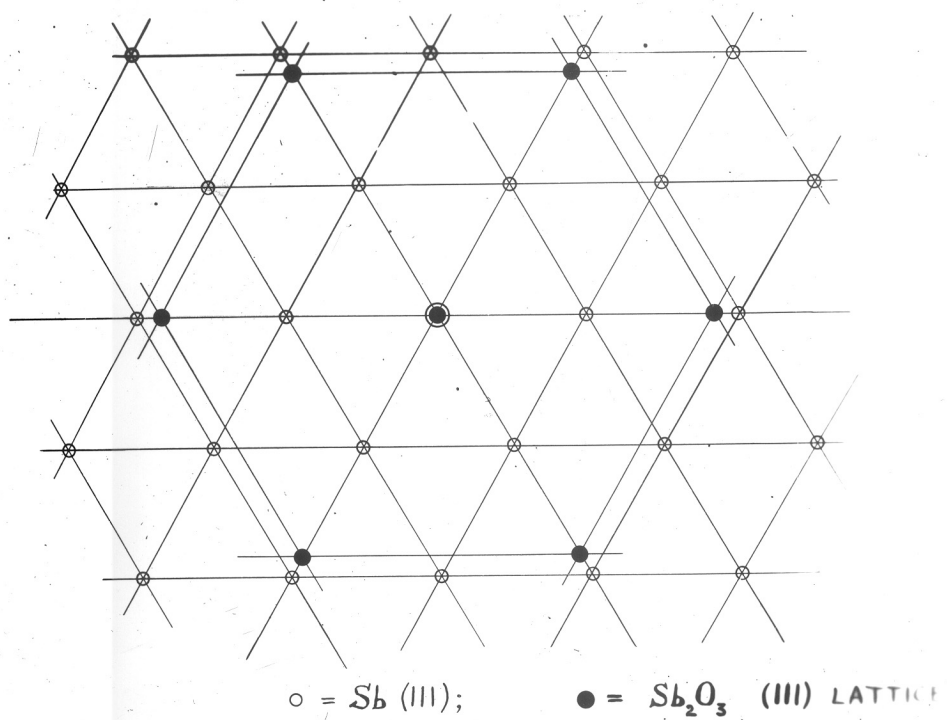


Fig. 27

TABLE I.

Analysis of the Pattern of Fig. 26. Antimony cleavage face (111), heated in air at 400°C. for eight minutes.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05194 \text{ A.}$$

Radius in cm.	Intensity	d in A *	hkl	X-ray data for Sb_2O_3 .	
				d in A.	I/I ₁
0.376	vf	6.258	111	6.4	0.10
0.423	vf	5.603	200		
0.613	vf	3.937	200		
0.752	vs	3.232	222	3.22	1.00
0.869	ms	2.810	400	2.78	0.30
0.946	mf	2.587	331	2.56	0.08
1.068	mf	2.299	422		
1.141	m	2.155	333		
1.229	m	2.005		1.96	0.50
1.242	f	1.988			
1.297	vf	1.901			
1.385	s	1.782			
1.458	m	1.694	444	1.68	0.50
1.527	m	1.602		1.61	0.10
1.574	f	1.572		1.56	0.10
1.638	mf	1.512			
1.698	f	1.459		1.45	0.02
1.762	mf	1.407		1.394	0.06
1.812	mf	1.369		1.355	0.04
1.873	mf	1.324			
1.920	m	1.293	555	1.283	0.15
1.979	mf	1.254		1.247	0.10
2.016	f	1.232		1.217	0.10
2.076		1.197			
2.110	vf	1.178		1.184	0.01
2.168	f	1.147		1.138	0.04
2.210	mf	1.125			
2.306	f	1.078		1.073	0.08
2.375	ms	1.047	660		
2.460	mf	1.013			
2.538	m	0.981			
2.617	mf	0.952			
2.660	m	0.936			
2.695	f	0.925			

*Referred to $d_{111} = 11.20/\sqrt{3}$ as derived from graphite comparison.

†Hanawaldt, Rinn and Frevel, 1938.

TABLE II.

Oxidation of Different Cleavage Faces of Antimony.

Specimen No.	Heat treatment		Nature of Pattern	Orientation
	Temp.	Time		
1	600°C.	30 mins.	Became matt grey.	
2	250°C. then 400°C.	15 mins. further 10 mins.	No pattern Spot pattern	(111)
3	300°C.	30 mins.	Spot pattern	(111)
4	250°C.	30 mins.	No pattern	
5	300°C.	30 mins.	Ring pattern	
6	300°C. then 400°C.	30 mins. further 10 mins.	Ring pattern Ring and spot patterns	(111)
7	400°C.	8 mins.	Ring and spot patterns	(111)

Kirchner (1932) studied evaporated films of antimony on collodion. The films so prepared gave diffuse rings, indicating the existence of extremely small crystals. Bound and Richards (1939) however obtained sharp-ringed patterns from evaporated antimony films on collodion. The patterns obtained before the films were exposed to air agreed with the X-ray structure for antimony which is rhombohedral with $a = 6.23\text{\AA}$ and $\alpha = 87^\circ 24'$ and has a deformed face-centred cubic lattice. The films showed no preferential orientation and did not change even

after being exposed to air for a week. No detectable oxidation was observed with this antimony film up to a temperature of 250°C . Above this temperature the patterns obtained were found to be due to a cubic structure with $a = 11.1 \text{ \AA}$ which is in agreement with the X-ray data for Sb_2O_3 ($a = 11.0 \text{ \AA}$).

Miyake (1938) who studied the formation of antimony oxide on a cleavage of stibnite (Sb_2S_3) upon heating in air, found that the orientation of Sb_2O_3 with respect to the stibnite cleavage is such that the (110) plane of Sb_2O_3 lies parallel to the cleavage (010) and the a-axis 001 of the Sb_2O_3 is in a direction parallel to the cube edge 001 of the Sb_2S_3 .

According to Wyckoff (1931) the oxides of antimony present a striking case of several compounds of very different composition with almost identical X-ray diffraction pattern. The X-ray patterns from four oxides have been obtained, Sb_2O_3 , Sb_2O_4 , Sb_6O_{13} and Sb_2O_5 . All but Sb_6O_{13} are cubic and give practically the same X-ray powder lines, with similar positions and intensities. The oxide Sb_6O_{13} gives in addition some faint lines which are not to be ascribed to a cubic crystal. In As_2O_3 the nearest approach of As and O atoms is $2.01 \text{ \AA}$, in Sb_2O_3 the Sb-O distance is $2.22 \text{ \AA}$. The shortest O-O separation is about $2.81 \text{ \AA}$ in each crystal. It has been suggested that the atoms in Sb_2O_4 have the same positions as in Sb_2O_3 with the addition of sixteen oxygens.

According to Tutton (1926) the diamorphism of antimony oxide, Sb_2O_3 , is readily demonstrated. If a little of the oxide be treated in a test tube and a microscope glass slip be held over the mouth, crystals of the substance are deposited by sublimation on it. These crystals are of two very distinct forms, long sharp needles of the rhombic form, and octahedra of the cubic form, which are often perched on the needles. Temperature, then, is obviously a prime factor determinative of the form in the cases of polymorphous substances and as a general principle it may be considered that each form has its life-range of temperature. Consequently, at the ordinary temperature one form is stable and the other unstable.

The results of the present investigation show that the oxidation of the cleavage face (111) of antimony by heating in air at 400°C . yields only a cubic form of antimony oxide.

VI. RESULTS WITH BISMUTH SINGLE CRYSTALS.

(1) The Structure of the (111) and (100) Faces of Bismuth Single Crystals.

(i) Cleavage Face (111).

Bismuth is rhombohedral and the lattice constants are $a = 4.7364\text{\AA}$ and $\alpha = 57^\circ 14' 13''$ at 25°C . (Hume-Rothery, 1945). For the interpretation of the electron diffraction patterns, however, it is simplest to use the face-centred pseudo-cubic cell for which $a' = 6.558\text{\AA}$ and $\alpha' = 87^\circ 32'$.

The bismuth single crystals, prepared by the method (i) described in section III have very shining and perfect cleavage faces on which three sets of parallel lines at about 60° to each other can be seen. Fig. 28 shows the Kikuchi bands when the electron beam is along one set of the parallel lines, while Fig. 29 represents the same when the beam is at 30° to these lines on the cleavage face. The Kikuchi bands which correspond to the cleavage plane (111) and also the absence of diffraction spots indicate the perfection and also the nearly perfect smoothness of the bismuth crystals prepared. The cleavage faces of bismuth do not normally show any trace of a coherent spot pattern due to the bismuth or an oxide as do the cleavage faces of zinc single crystals; hence any oxide layer present must be scarcely more than monomolecular in thickness. In these respects bismuth behaves like antimony.



Fig. 28

A7658

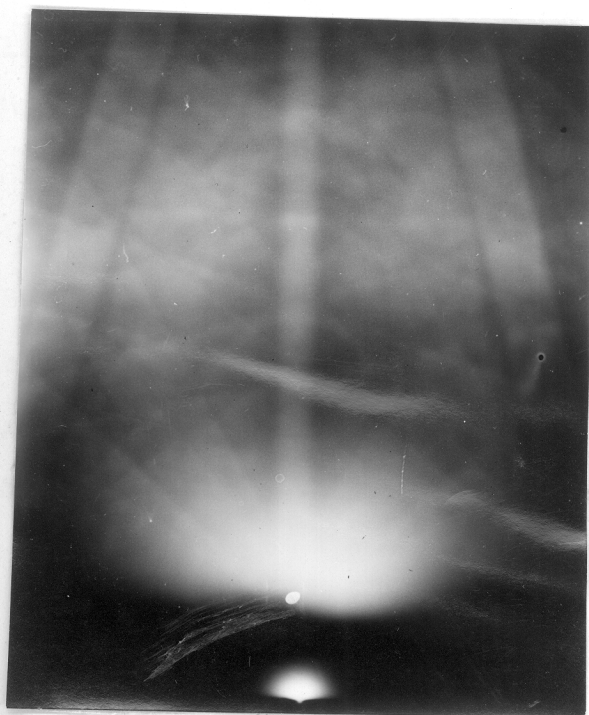


Fig. 29

A7663

(ii) Cast Surface (100) relative to the pseudo cube axes.

Molten bismuth cast on hot glass or on cleavage faces of mica as in the method (ii) described in Section III gives a very smooth and shining surface in contact with the substrate. On removing the substrate and examining the surface in contact with it by electron diffraction, the surfaces gave clear Kikuchi bands, characteristic of the pseudo cubic (100) face of bismuth single crystals. The substrate, however, even in the case of the mica, seems to have no direct effect on the orientation of the face developed and merely acts as a more or less smooth inert supporting surface. Figs. 30 and 31 show the Kikuchi bands obtained from two different crystals both cast on mica. Fig. 30 shows that the (100) plane was at an angle of about 11° to the substrate while Fig. 31 indicates that the (100) face was parallel to the same. Fig. 32 shows Kikuchi bands obtained from a crystal cast on glass. The cubic spot pattern of bismuth in Fig. 32 confirms the analysis of the Fig. 30 and Fig. 31 and shows that the (100) face is at about 11° to the glass substrate.

From these results it seems that if the top of the molten drop of bismuth is allowed to cool more rapidly than the bottom, so that crystallisation is initiated there, it may often do so not at the central nearly horizontal uppermost surface, A in the Fig. a but at a point such as B where the surface is inclined by up to $10-20^\circ$ to the substrate. In



Fig. 30

A 7530

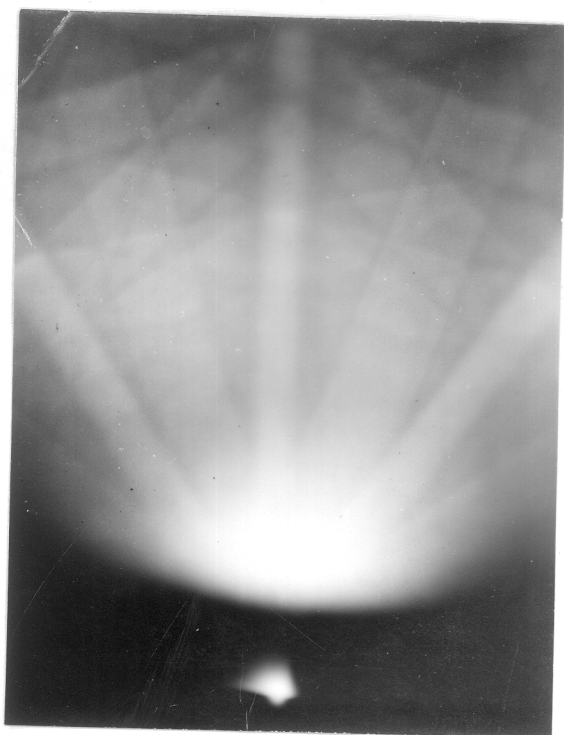


Fig. 31

A 7609

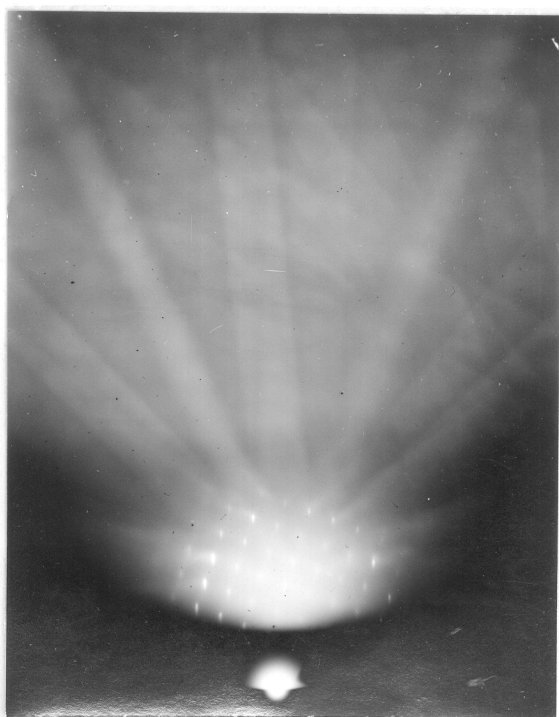


Fig. 32

A 8005

all cases, however, the initially formed crystal nucleus presumably grows with a pseudo-cubic (100) face parallel to the surface where it first forms. On the other hand, when it was arranged so that the lower surface in contact with the glass solidified first before the upper surface, the (100) planes grew accurately parallel to the substrate (Fig. 31).

(2) Thermal Oxidation in Air of the (100) and (111) faces of Bismuth Single Crystals.

The (100) faces of bismuth were found to be much more easily oxidisable than the cleavage planes (111) though apparently about equally smooth. The cast surfaces (100) when heated in air at 250°C. for one hour gave clear oxide ring pattern, as in Fig. 33 when examined by electron diffraction. This oxide shows a face centred cubic structure with $a = 5.40\text{\AA}$ as will be seen from Table III.

The cleavage faces (111) heated in air at the same temperature for equal length of time gave very diffuse rings. These diffuse rings became clear as in Fig. 34 only when the specimen was further heated at 250°C. for 3-4 hours. These patterns obtained from oxidised cleavage faces however indicated the same oxide structure as that on the (100) face.

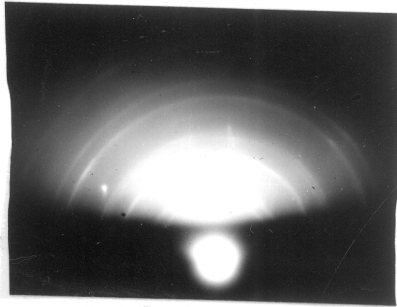


Fig. 33 A7615

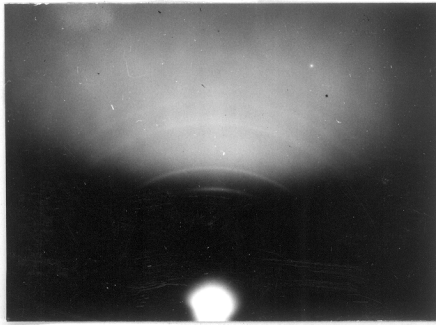


Fig. 34 A7671

TABLE III.

Analysis of the Pattern of Fig. 33. (100) Face
of Bismuth crystal heated in air at 250°C, for
one hour.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05300 \text{ A.}$$

Radius in cm.	Intensity	d in A	Cubic indices hkl	"a" calcu- lated.	X-ray data for Bi_2O_3 *	
					d in A	I/I ₁
0.803	m	3.14	111	5.44	3.42	0.05
0.927	ms	2.72	200	5.45	3.25	1.00
		1			2.69	0.88
					2.54	0.05
					2.39	0.15
					2.03	0.05
1.313	s	1.92	220	5.42	1.95	0.25
					1.87	0.15
					1.82	0.05
					1.75	0.20
1.544	mf	1.63	311	5.40	1.66	0.10
1.617	mf	1.56	222	5.42	1.58	0.10
					1.490	0.10
1.866	vf	1.35	400	5.40	1.395	0.05
					1.305	0.05
2.026	vf	1.24	331	5.42	1.270	0.05
2.100	s	1.20	420	5.42	1.225	0.05
					1.195	0.05
2.290	ms	1.10	422	5.40	1.120	0.05
2.430	vf	1.040	333, 511	5.39		
2.462	vf	1.022				
2.796	m	0.900	600	5.40		

Hanawaldt, Rinn and Frevel, 1938.

Very little is known about the structure of Bi_2O_3 , the only oxide of bismuth which has been studied crystallographically. It is given as a new structure type by Zachariasen (1928). From the work on the mixed crystals by Goldschmidt (1925) it has been concluded that the oxide would have a cubic structure resembling Y_2O_3 and the lattice constants predicted by extrapolation as $a = 11.0 \text{ \AA}$. Randall (1933) found the X-ray pattern of Bi_2O_3 to indicate a face-centred cubic structure ($a = 5.51 \text{ \AA}$) the complete structure has not been determined "on account of certain lines which are missing from the crystalline pattern of Bi_2O_3 ; this is due to the fact that the scattering power of bismuth for X-rays is very great compared with that of oxygen" and he quotes the (111) ring as having a spacing of $3.18 \text{ \AA}$ which makes $a = 5.51 \text{ \AA}$. Schumb and Rittner (1943) found that Bi_2O_3 crystallizes at least in three different forms. The tetragonal β is a modification stable at higher temperature than the monoclinic α -variety and the γ - Bi_2O_3 is a form having a body-centred cubic structure ($a = 10.245 \text{ \AA}$).

Darbyshire and Cooper (1934) investigated the oxide films obtained by removing the surface skin from molten bismuth by means of a wire loop and obtained two types of patterns, one indicating a face-centred cubic structure of axial length $5.43 \text{ \AA}$ and the other a complex pattern which they found to be due to a body centred tetragonal structure with $a = 10.85$ and $c = 11.28 \text{ \AA}$. Jenkins (1935) investigated oxide

films on molten bismuth both by reflection and transmission methods and found that the oxide had a close-packed hexagonal structure with axial ratio 1.57 and $a = 4.02\text{\AA}$ and that the crystals of the oxide layer were all resting on the (001) faces.

Bound and Richards (1939) prepared films of bismuth by evaporation on collodion and on glass and found that the films showed a marked orientation such that the (111) planes with reference to the rhombohedral axes were parallel to the surface of the film, as in those prepared by Kirchner (1932). On exposing the bismuth films to air for sixteen hours, the pattern showed a band just outside the (200) ring, but no further change was observed after an interval of 32 days. On heating the specimen at 150°C . the lengths of the arcs began to increase and after heating at about 200°C . all signs of the preferred orientation were completely eliminated. During this heating, there was no detectable oxidation of the film beyond that found at room temperature. After heating at 300°C . for one hour different results were obtained from transmission and from reflexion specimens. Reflexion specimens showed a face-centred cubic structure with $a = 5.7\text{\AA}$ but transmission patterns gave strong rings of a face-centred cubic structure with $a = 5.50\text{\AA}$ but other faint rings not belonging to a face-centred cubic pattern were also present in addition to the (111) ring which was diffuse.

(3) The Reaction of Dry Iodine Vapour with the (100) and (111) faces of Bismuth Single Crystals.

A speck of pure iodine was placed on a small watchglass which was placed in a desiccator together with another small watch glass on which the crystals were placed with the (100) or (111) face upwards. The desiccator was tightly covered and left overnight.

Fig.35 was obtained subsequently from the (100) face. The analysis of the pattern is recorded in Table IV* and it agrees with the X-ray data (A.S.T.M. 1945) for bismuth triiodide (BiI_3), the crystals being randomly disposed. Wyckoff (1935) states that BiI_3 has a rhombohedral lattice with $a = 8.13 \text{ \AA}$ and $\alpha = 54^\circ 50'$, which corresponds to a rhombohedrally distorted pseudo-face-centred cubic lattice.

Fig.36 was obtained from the cleavage (111) face of bismuth after reaction with iodine as above and the analysis is given in Table IV. The results again agree with the X-ray data for BiI_3 (A.S.T.M., 1945) and in this case the patterns show a two-degree (111) orientation of the BiI_3 crystals relative to the bismuth substrate. Although the azimuthal relationship was not directly determined, the epitaxial relationship of the BiI_3 (111) lattice related to the (111) bismuth lattice, must evidently be as shown in

* The electron diffraction d-values in Table IV are standardised relative to the same value $1.96 \text{ \AA}$ assumed for a certain strong sharp ring which occurred clearly in all the patterns with about the same spacing as estimated from the ΔL values.

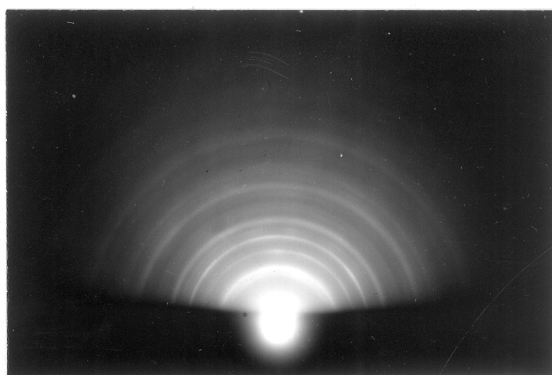


Fig. 35 A 8009

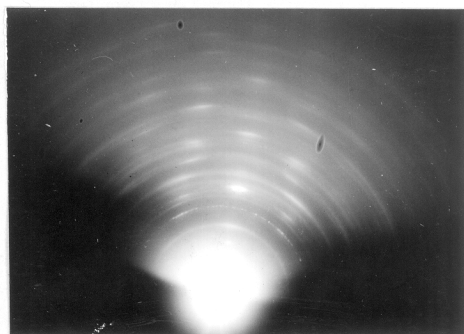


Fig. 36 A 8003

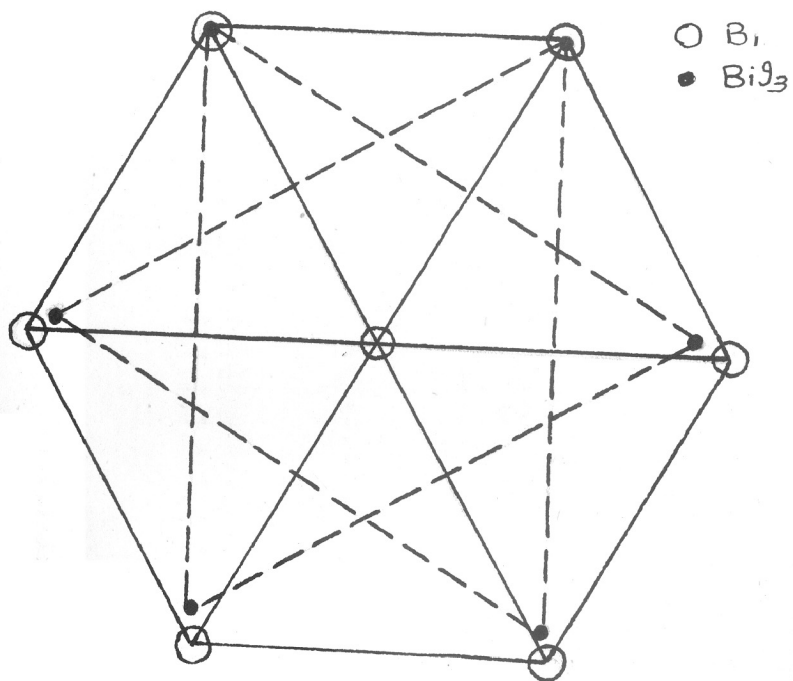


Fig-37

TABLE IV.

Analysis of the Patterns of Figs. 35,
36, and 38.

Fig. 35		Fig. 36		Fig. 38		X-ray data for BiI_3^*	
in A	Inten- sity	d in A	Inten- sity.	d in A	Inten- sity.	d in A	I/I ₁
5.56	mf	-	-	-	-	-	-
-	-	4.64	vf	-	-	-	-
3.34	m	3.24	f	3.35	vf	3.25	0.7
2.98	s	2.92	f	3.02	s	3.00	1.0
2.75	f	2.78	f	-	-	-	-
-	-	-	-	-	-	3.538	0.78
2.49	vf	2.47	ms	2.42	s	2.48	0.5
2.32	ms	2.28	vf	-	-	2.27	0.7
2.19	f	2.21	vf	2.20	f	2.15	1.0
-	-	2.03	vf	2.08	vf	2.07	0.9
1.96	s	1.96	s	1.96	s	1.962	0.9
-	-	-	-	-	-	1.906	0.78
1.87	f	1.88	f	-	-	1.868	1.0
1.82	-	1.83	-	1.82	-	1.809	1.0
-	-	1.76	ms	-	-	-	-
1.68	ms	1.68	ms	1.71	ms	1.724	0.6
1.63	m	-	-	1.65	f	-	-
-	-	1.61	-	1.62	m	-	-
-	-	1.54	m	-	-	1.576	0.6
1.52	mf	1.51	f	1.53	m	-	-
-	-	1.47	f	1.48	m	1.497	0.6
1.45	f	1.45	ms	-	-	-	-
-	-	1.43	mf	1.43	f	1.438	0.68
-	-	1.41	mf	-	-	-	-
-	-	1.39	f	1.38	m	-	-
1.33	f	1.34	vf	1.33	f	1.312	0.6
1.28	ms	1.28	mf	-	-	1.293	0.7
1.26	ms	1.24	m	1.25	f	1.253	0.7
1.19	mf	-	-	1.20	m	1.207	0.6
-	-	1.18	m	1.19	f	-	-
-	-	1.17	f	-	-	-	-
1.15	mf	1.16	m	1.16	-	-	-
-	-	1.14	mf	1.14	mf	-	-
1.13	mf	1.13	mf	1.12	mf	-	-
-	-	1.115	f	-	-	-	-
1.10	mf	1.10	f	-	-	1.104	0.7
-	-	1.08	f	1.08	mf	1.086	0.7
-	-	1.07	f	-	-	-	-
-	-	1.06	f	-	-	-	-
-	-	-	-	-	-	1.046	0.5
1.04	f	1.04	f	1.03	mf	1.032	0.7
1.00	f	-	-	-	-	-	-
-	-	-	-	0.984	mf	1.015	0.7

Fig. 37, the equilateral triangle side (7.49Å) of the BiI_3 (111) lattice being at 30° to that (7.857Å) of the bismuth (111) lattice.

The pattern of Fig. 36 affords satisfactory identification of the reaction product as the pseudo face centred cubic BiI_3 from which the ring intensities in Figs. 35 and 38 show considerable variations which are apparently due to the large crystal size and the variable habit resulting in strong absorption of certain groups of diffractions.

(4) The Reaction of Moist Halogen Vapours on the (100) face of bismuth single crystals.

A speck of iodine was dipped in two drops of distilled water in a watch glass, which was placed in a desiccator together with another watch glass on which the bismuth crystal was placed with the (100) face upwards. The desiccator was tightly covered and left overnight. The electron diffraction pattern from this face is shown in Fig. 38, the analysis of which is recorded in Table IV, which agrees with the X-ray data for bismuth tri-iodide (A.S.T.M.1945), showing slight orientation. This result may be compared with the formation of random bismuth tri-iodide (BiI_3) on the (100) face (Fig. 35) and oriented BiI_3 on the (111) face (Fig. 36) when the respective faces were exposed to dry iodine (Section VI, (3)).

One (100) face of bismuth crystal was placed in a

desiccator with the (100) face upwards. The desiccator was then partially evacuated. A few cubic centimetres of moist chlorine gas, free from hydrochloric acid gas, was let into the desiccator into which air was then admitted to atmospheric pressure. After about half an hour the crystal face was examined and yielded the pattern shown in Fig. 39, the analysis of which is given in Table V. Although the data have similarities with the X-ray values for bismuth oxychloride (Hanawaldt, Rinn and Frevel, 1938), Fig. 39 is closely similar to Fig. 38 in relative ring positions and intensities and since Fig. 38 corresponds well with the BiI_3 structure Fig. 39 may quite likely be due to BiCl_3 isomorphic in structure to BiI_3 .

Two drops of freshly prepared saturated bromine-water were placed on a watch glass, which was placed in a desiccator together with another watch glass on which the bismuth crystal was placed with the (100) face upwards. The desiccator was tightly covered and left overnight. The electron diffraction pattern from such a face is shown in Fig. 40, the analysis of which is given in Table VI which agrees with the X-ray data for bismuth oxybromide (Hanawaldt, Rinn and Frevel, 1938). There is, however, a slight orientation in the pattern.

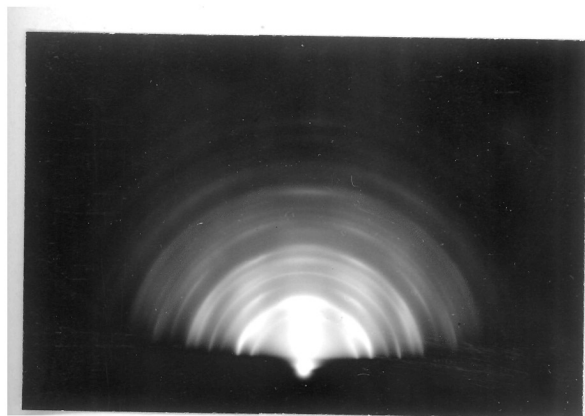


Fig. 38

A 7973

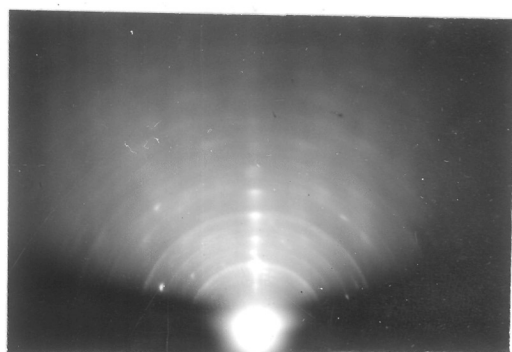


Fig. 39

A 7980

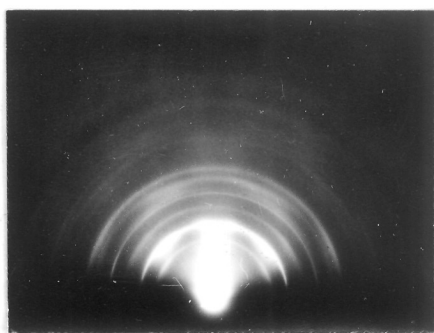


Fig. 40

A 7941

TABLE V.

Analysis of the pattern of Fig. 39.
 (100) face of bismuth crystal exposed
 to moist chlorine gas.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05144 \text{ A.}$$

Radius in cm.	Intensity	d in A	X-ray Data for BiOCl. *	
			d in A	I/I ₁
			7.4	0.70
			3.71	0.08
0.702	v. s arc	3.48	3.45	1.00
0.900	v. s arc	2.71	2.75	0.40
			2.65	0.80
			2.45	0.08
1.095	v f	2.22	2.20	0.20
1.254	s	1.94	1.94	0.24
			1.87	0.04
			1.83	0.24
1.417	s. d arc	1.72	1.69	0.24
			1.66	0.16
1.557	s d	1.57	1.57	0.36
1.605	s arc	1.52	1.52	0.16
1.807	v f	1.35	1.375	0.16
1.912	f	1.27	1.263	0.16
1.987	f	1.23	1.225	0.20
			1.200	0.04
2.085	f	1.17	1.165	0.08
2.209	v f	1.10	1.121	0.08
2.294	s. d arc	1.06	1.065	0.08
2.360	m s d	1.03	1.036	0.12

TABLE VI

An analysis of the pattern of Fig. 40
(100) face of bismuth single crystal
exposed to moist bromine vapour.

$$L = 47.5 \text{ cm. } \lambda = 0.05144 \text{ A}$$

Radius	Intensity	d in A	X-ray Data for BiOBr. *	
			d in A	I/I ₁
-	-	-	8.1	0.12
0.695	f	3.511	3.52	0.2
0.780	f	3.128	-	-
0.840	mf spot in the plane of inci- dence.	2.905	-	-
0.874	ms spot in the plane of inci- dence.	2.792	2.80	1.0
1.022	s spot in the plane of inci- dence.	2.389	-	-
1.077	f spot in the plane of inci- dence.	2.266	2.29	0.08
1.198	s	2.036	-	-
1.268	f	1.912	1.95	0.12
1.367	f	1.785	1.80	0.08
-	-	-	1.71	0.04
1.496	s	1.631	1.61	0.28
(1.535	f)	1.590	-	-
1.800	sd	1.355	1.320	0.04
-	-	-	1.238	0.08
-	-	-	1.049	0.04

*Hanawaldt, Rinn and Frevel, 1938. According to Bannister and Hey (1934, 1935) the bismuth oxyhalides are tetragonal with two molecules in the unit cell and lattice constants:-

BiOCl $a = 3.89\text{A}$, $c = 7.37\text{A}$, $c/a = 1.895$

BiOBr $a = 3.92\text{A}$, $c = 8.11\text{A}$, $c/a = 2.068$

BiOI $a = 4.01\text{A}$, $c = 9.14\text{A}$, $c/a = 2.279$

(5) The reaction of bismuth crystal (100) faces with Iodine Vapour from various Solutions.

A speck of pure iodine was dissolved in two drops of solvents such as benzene, absolute alcohol and acetone on a small watch glass, which was placed in a desiccator together with another small watch glass on which the crystal was placed with the (100) face upwards. The desiccator was tightly covered and was left overnight. The electron diffraction pattern subsequently obtained from the (100) face exposed to iodine vapour from benzene solution is shown in Fig. 41. The analysis is given in Table VII and shows that the results are in agreement with X-ray data for hexagonal bismuth tri-iodide (A.S.T.M., 1945). The arcings of the rings indicate a slight orientation of the crystals.

The pattern obtained from the (100) face of bismuth exposed to iodine vapour from its solution in absolute alcohol is shown in Fig. 42, and the analysis given in Table VII. The results again agree with the X-ray data for hexagonal bismuth tri-iodide (A.S.T.M., 1945). The rings are sharper, and spotty in this case, indicating the presence of large but unorientated crystals.

The pattern obtained from the (100) face exposed to iodine vapour from its solution in acetone is shown in Fig. 43, the analysis of which is given in Table VII. The pattern, which again agrees with the X-ray data for bismuth

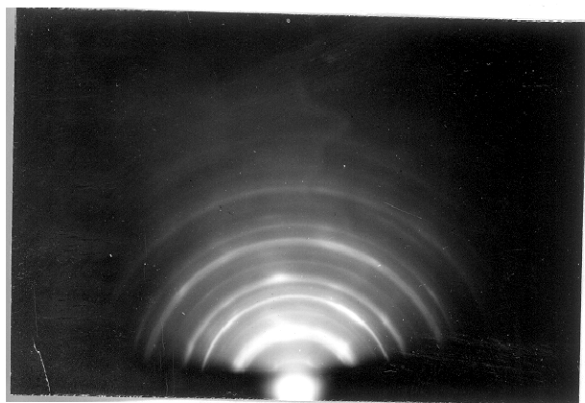


Fig. 41 A7976

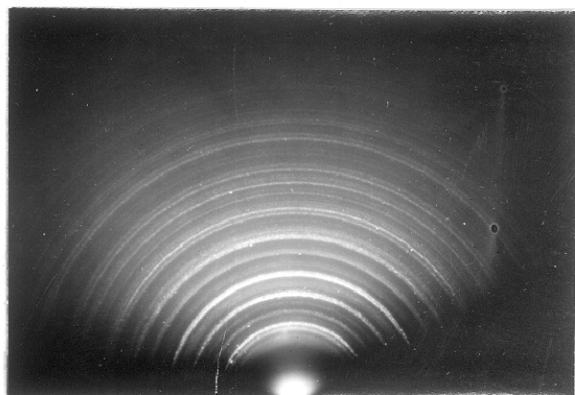


Fig. 42 A7991

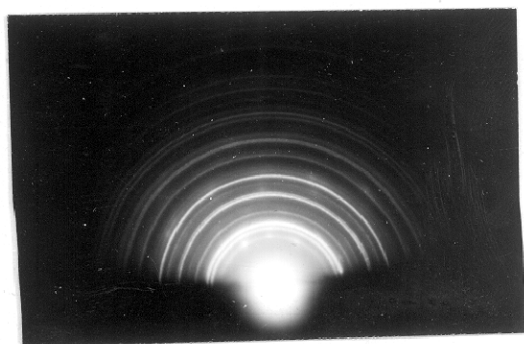


Fig. 43 A7998

tri-iodide (A.S.T.M., 1945) is very sharp, showing that the crystals were of the order of 500 Å in diameter, and the rings are continuous and quite distinct from those of Fig. 41. There are, however, a few diffraction spots, probably due to metallic bismuth.

TABLE VII.

An Analysis of the patterns of Figs. 41, 42 and 43

Fig. 41		Fig. 42		Fig. 43		X-ray data for BiI ₃ *	
d in Å	Intensity.	d in Å	Intensity.	d in Å	Intensity.	d in Å	I/I ₁
5.83	ms	-	-	-	-	-	-
3.47	s	3.48	vf	3.34	ms	3.25	0.7
3.08	vs	3.10	f	2.94	s	3.00	1.0
2.91	f	2.77	s	2.71	vs	-	-
-	-	2.60	vs	-	-	2.53	0.7
2.41	vf	-	-	-	-	2.48	0.5
2.26	vf	2.22	s	2.34	s	2.27	0.7
2.20	vf	-	-	-	-	2.15	1.0
-	-	2.03	ms	-	-	2.07	0.9
-	-	-	-	1.95	vs	1.962	0.9
-	-	-	-	-	-	1.906	0.7
1.85	f	1.87	vs	1.88	ms	1.868	1.0
-	-	1.83	vs	-	-	1.809	1.0
1.71	ms	1.71	f	1.74	-	1.724	0.6
-	-	1.67	f	1.63	vf	-	-
-	-	1.57	vs	1.57	f	1.576	0.6
1.49	ms	1.53	s	1.51	f	1.497	0.6
-	-	1.42	f	-	-	1.438	0.6

(contd. over

Fig. 41		Fig. 42		Fig. 43		X-ray data for BiI ₃ *	
d in Å	Inten- sity	d in Å	Inten- sity	d in Å	Inten- sity	d in Å	I/I ₁
1.39	vf	-	-	1.39	-	-	-
1.31	s	1.32	s	1.35	-	1.312	0.6
1.28	s	1.29	f	-	-	1.293	0.7
-	-	-	-	-	-	1.253	0.7
1.20	ms	1.20	s	-	-	1.207	0.6
-	-	1.18	s	-	-	-	-
1.10	f	1.14	ms	-	-	1.104	0.7
-	-	1.08	f	-	-	1.086	0.7
-	-	1.04	s	-	-	1.046	0.5
-	-	-	-	-	-	1.032	0.7
-	-	1.01	s	-	-	1.015	0.7
-	-	0.99	f	-	-	-	-
-	-	0.98	f	-	-	-	-
-	-	-	-	0.96	s	-	-
-	-	0.94	ms	-	-	-	-
-	-	0.92	f	0.91	s	-	-
-	-	0.89	s	-	-	-	-
-	-	0.87	f	-	-	-	-
-	-	(double)		-	-	-	-
-	-	0.84	s	-	-	-	-
-	-	0.82	ms	-	-	-	-
-	-	0.78	f	-	-	-	-
-	-	0.77	vf	-	-	-	-
-	-	0.74	s	-	-	-	-
-	-	0.73	ms	-	-	-	-
-	-	0.71	vf	-	-	-	-
-	-	0.69	f	-	-	-	-
-	-	0.68	f	-	-	-	-
-	-	0.67	vf	-	-	-	-
-	-	0.65	f	0.64	ms	-	-
-	-	-	-	0.59	ms	-	-

(6) Effect of Dipping the (100) face of Bismuth Single Crystal in Iodine Solution in Benzene.

One (100) face of the bismuth single crystal was dipped in iodine in pure benzene solution for two minutes after which the crystal face was washed with distilled water and examined by the electron diffraction method. The pattern obtained is shown in Fig. 44 and the analysis in Table VIII, which again agrees with the X-ray data for bismuth tri-iodide (A.S.T.M., 1945) and shows a slight orientation.

(7) Effect of Carbon Di-Sulphide Vapour on the (100) face of Bismuth Single Crystals.

Two drops of pure carbon di-sulphide were placed on a small watch glass, which was then put in a desiccator together with another small watch glass on which the bismuth crystal was placed with the (100) face upwards. The desiccator was now covered tightly and left overnight.

The electron diffraction pattern obtained from such a face is shown in Fig. 45 and the analysis in Table IX, which has a fair agreement with X-ray data for Bi_2S_3 (A.S.T.M., 1945).

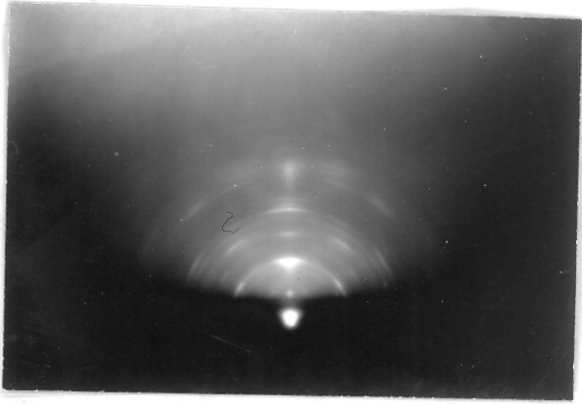


Fig. 44 A7974

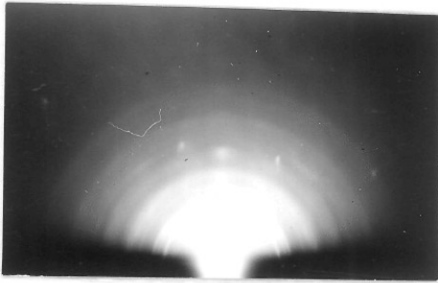


Fig. 45 A8000

TABLE VIII.

An Analysis of the pattern of Fig. 44. (100) face
of Bismuth Single Crystal dipped in iodine solution
in benzene.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05246 \text{ \AA.}$$

Radius in cm.	Intensity	d in A	X-ray data for BiI ₃ *	
			d in A	I/I ₁
0.659	f	3.789	-	-
0.768	s (arc)	3.242	3.25	0.7
			3.00	1.0
			2.53	0.7
			2.48	0.5
1.104	s (arc)	2.256	2.27	0.7
			2.15	1.0
			2.07	0.9
			1.962	0.9
1.300	f	1.915	1.906	0.7
			1.868	1.0
			1.809	1.0
1.414	s (arc)	1.761	1.724	0.6
1.468	ms (arc)	1.673	-	-
1.548	ms (arc)	1.608	1.576	0.6
			1.497	0.6
			1.438	0.6
			1.312	0.6
			1.293	0.7
			1.253	0.7
2.169	f (arc)	1.148	1.207	0.6
			1.104	0.7
			1.086	0.7
			1.046	0.5
			1.032	0.7
			1.015	0.7

* A.S.T.M., 1945

TABLE IX.

An Analysis of the pattern of Fig. 45.

(100) face of Bismuth Single Crystal exposed
to carbon di-sulphide vapour.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05144 \text{ A}$$

Radius in cm.	Intensity	d in A	X-ray data for Bi_2S_3 .*
			d in A.
0.652	f	3.743	3.50
0.761	s	3.206	3.08
0.842	f	2.898	
0.902	ms	2.711	
1.082	f	2.255	
1.154	vf	2.113	
1.195	f	2.042	
1.236	ms	1.974	1.94

A.S.T.M., 1945.

(8) Effect of Etching on the (100) Face of Bismuth Single Crystals.

(i) Dilute hydrochloric acid and bromine water.

One (100) face of the bismuth single crystal was etched with an aqueous solution of hydrochloric acid (1:1) for one minute, after which the crystal face was washed thoroughly with distilled water. The electron diffraction pattern from such a face is shown in Fig. 46 and its analysis in Table X, which shows that the pattern agrees with the X-ray data (Hanawaldt, Rinn and Frevel, 1938) for bismuth oxychloride (BiOCl). The pattern also shows a few spots due to metallic bismuth, which indicates that the oxychloride film is very thin. A similar result was obtained when the (100) face was exposed to moist chlorine gas (Fig. 40).

Another (100) face of a bismuth single crystal was etched with freshly prepared saturated bromine water for one minute, after which the crystal face was washed with distilled water as before. The electron diffraction pattern from this face is shown in Fig. 47 and its analysis in Table XI, which shows agreement with the X-ray data (Hanawaldt, Rinn and Frevel, 1938) for bismuth-oxybromide (BiOBr), the crystals of which are, however, randomly oriented on the substrate. An oxybromide pattern was also obtained when the (100) face was exposed to moist bromine vapour.

TABLE X.

An Analysis of the pattern of Fig. 46
(100) face of Bismuth Crystal Etched
with (1:1) hydrochloric acid.

$$L = 47.5 \text{ cm} \quad \lambda = 0.05246 \text{ A.}$$

Radius in cm.	Intensity	d in A	X-ray data for BiOCl.*	
			d in A	I/I ₁
-	-	-	7.4	0.70
0.713	f	3.42	3.71	0.08
			3.45	1.00
			2.75	0.40
0.885	s	2.76	2.65	0.80
1.035	vf	2.36	2.45	0.08
			2.20	0.24
			1.94	0.24
			1.87	0.04
1.315	ms	1.86	1.83	0.24
			1.69	0.24
			1.66	0.16
1.576	mfd	1.55	1.57	0.36
			1.52	0.16
1.817	f	1.35	1.375	0.16
			1.263	0.16
2.017	mf	1.21	1.225	0.20
			1.200	0.04
			1.165	0.08
			1.121	0.08
			1.095	0.08
2.383	vfd	1.02	1.065	0.08
			1.036	0.12
2.690	vf	0.72		

* Hanawaldt, Rinn and Frevel, 1938)

TABLE XI.

An Analysis of the pattern of Fig. 47
(100) face of Bismuth single crystal
etched with freshly prepared bromine water.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05246$$

Radius in cm.	Intensity	d in A	X-ray data for BiOBr.*	
			d in A	I/I ₁
-	-	-	8.1	0.12
0.709	s	3.508	3.52	0.2
0.805	f (centre)	3.097	2.80	1.0
1.160	ms	2.147	2.29	0.08
1.336	mf	1.862	1.95	0.12
1.365	mf	1.824	1.80	0.08
			1.71	0.04
			1.61	0.28
1.784	fd	1.393	1.386	0.04
			1.320	0.04
			1.238	0.08
1.980	vf	0.989	1.049	0.04

* Hanawaldt, Rinn and Frevel, 1938

(ii) Nitric and Acetic Acids.

One (100) face of a bismuth single crystal was etched ^{an} with aqueous solution of nitric acid (1:2) for three minutes, after which the crystal face was washed with distilled water. The electron diffraction pattern from this face, Fig. 48, shows a roughly square spot pattern, the dimensions of which agree with the lattice of metallic bismuth. The practically square pattern from this face confirms the results obtained from the analysis of Kikuchi bands from such a face and that the cast bismuth crystal had a (100) surface nearly parallel to the substrate.

A similar nearly square pattern was obtained when another (100) face of a bismuth single crystal was etched with concentrated acetic acid for five minutes and finally washed with distilled water. The electron-diffraction pattern obtained from this face is shown in Fig. 49. The dimensions of the nearly square pattern again agree with the lattice constants of metallic bismuth and also confirm that the etched surface was nearly a (100) face of the bismuth single crystal.

(iii) Yellow ammonium sulphide

One (100) face of bismuth crystal was similarly etched with an aqueous solution of yellow ammonium sulphide (1:1) for three minutes and subsequently washed with distilled water. The pattern, Fig. 50, was obtained from such a face and the diffuse rings are perhaps due to the formation of sulphide of bismuth while a few spots can be seen due to the bismuth crystal.

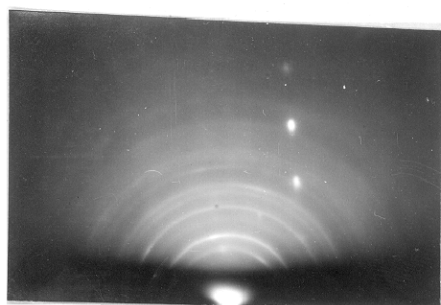


Fig. 46 A7431

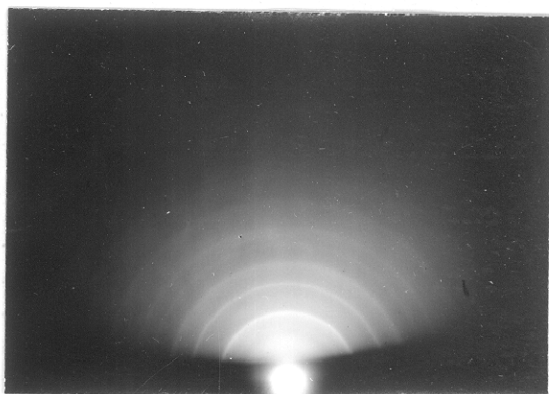


Fig. 47 A8006

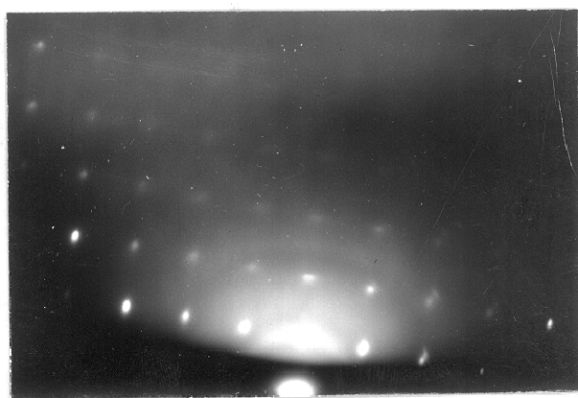


Fig. 48 A7911

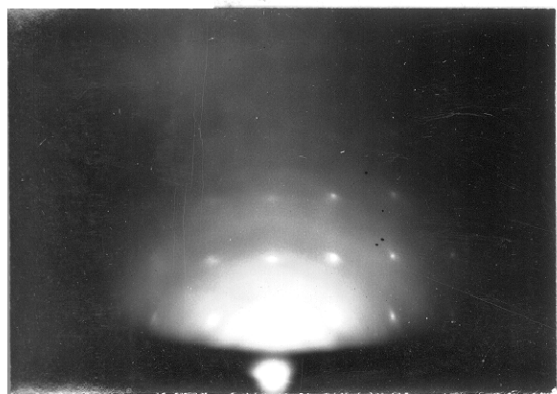


Fig. 49 A7924



Fig. 50 A7959

VII. RESULTS WITH TIN SINGLE CRYSTALS

(1). The Structure of the Natural Face of Tin Single Crystals.

The tin single crystals prepared by casting molten tin on glass by the method (ii) described in Section III show very shining and smooth surfaces in contact with the glass. After removing the glass and on examination of the face in contact with it by electron diffraction, these surfaces show very well defined Kikuchi bands indicating the high perfection of the crystals. Fig. 51 represents the Kikuchi bands when the beam is along one of the main axes, and an identical pattern was obtained at an azimuth 43° from that of Fig. 51. An analysis of these Kikuchi band patterns shows that the (100) face of the crystal is in all cases parallel to the glass surface or within about 11° from parallelism; thus it appears that as in the case of bismuth, if solidification begins at a more rapidly cooled upper free surface of the drop the (100) face of this initial small crystal grows parallel to the surface where it is formed. Bryant (1936) in this laboratory had previously observed this orientation to be developed in the case of tin cast on scratched glass and had also shown that the azimuthal orientation of the crystal can be determined by the direction of the scratches on the glass surface.

(2) The Effect of Etching of the (100) Face of the Tin Single Crystal.

One cast surface of the tin single crystal was etched with 10% hydrochloric acid for three minutes, after which it was washed with distilled water. The electron diffraction pattern obtained from such an etched surface is given in Fig. 52 which shows a square spot pattern of single crystals, which again confirms that the cast surface is a (100) face of the tin crystal. The dimensions of the square pattern agree with the lattice constants of tetragonal tin, which are $a = 5.8194\text{\AA}$ and $c = 3.1753\text{\AA}$ (Hume-Rothery, 1945). It will be noticed that the square pattern is inclined to the shadow edge at an angle of about 11° which is in agreement with the analysis of Kikuchi bands from the cast faces.

(3) Oxidation of the (100) Face of Tin Single Crystals.

When (100) faces of tin crystals were heated in air at 200°C . for an hour or more, a surface film was formed. The diffraction patterns obtained from such surfaces are indicated in Figs. 53a and 53b. The patterns correspond (Table XII) to a cubic structure with axial length a near to that of SnI_4 . The patterns appear to contain no diffractions due to the normal structure of either SnO or



Fig. 51 A7732

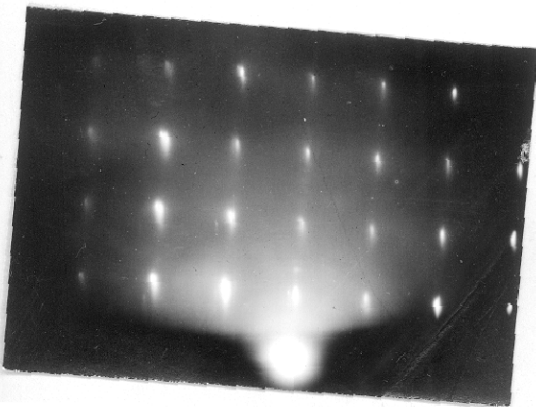


Fig. 52 A6951

TABLE XII.

An Analysis of the patterns of Figs. 53a and 53b.
(100) faces of tin crystals heated in
air at 200°C.

Fig. 53a			Fig. 53b			X-ray data for SnI ₄ .*		
d in A	Inten- sity	hkl	d in A	Inten- sity	hkl	d in A	I/I ₁	hkl
						6.9	0.10	111
						5.5	0.27	210
						5.0	0.10	211
			3.938	vf	220			
			3.608	vf	221	3.53	1.00	222
						3.28	0.03	321
3.068	ms	222	3.082	f	222	3.05	0.23	400
2.827	vf	312	2.907	m	321	2.80	0.03	331
2.610	m	400	2.628	mf	400	2.66	0.03	421
2.334	f	420	2.477	f	331	2.27	0.03	432
2.141	mf	422				2.16	0.50	440
1.972	f	520						
1.854	s	440	1.886	s	440	1.84	0.33	632
1.764	vf	531	1.793	f	442	1.76	0.03	444
1.664	vf	620	1.619	m	622	1.66	0.03	721
1.588	m	533	1.547	vf	444	1.56	0.03	
1.502	vf	444				1.53	0.05	
1.422	f	720	1.443	vf	642	1.402	0.10	
1.318	f		1.337	vf	800	1.368	0.03	
1.188	vf		1.222	mf	660	1.248	0.07	
						1.178	0.05	
			1.089	mf	622			
1.073	vf		1.074	vf				
1.014	vf		0.986	vf				
			0.956	vf				
			0.904	mf				

* Hanawalt, Rinn and Frevel, 1938

or SnO_2 , both of which are tetragonal, and this surface compound was evidently due to heating the tin crystals in laboratory air which contained a trace of iodine. Further confirmation of this interpretation was afforded by Fig. 55 (Section VII, (4)) which was from SnI_4 formed on a tin (100) face exposed to iodine vapour at room temperature. The intensities of the rings in Figs. 53a, 53b and 55 show appreciable variations, especially in the three stronger rings corresponding to spacings near $3A$; and this feature, as in the case of BiI_3 (Section VI) is attributable to the large crystal size and high absorbing power in conjunction with development of definite crystal habit.

TABLE XIII

Oxidation of different specimens of
cube face (100) of tin single crystal

Specimen No.	Heat Treatment		Nature of Pattern
	Temperature	Time	
1.	200°C.	1 hr.	Ring pattern.
2.	200°C.	1 hr.	Ring pattern.
3.	200°C.	6 hrs.	Ring pattern.
4.	200°C.	15 hrs.	Ring pattern.
5.	200°C.	18 hrs.	Ring pattern.
6.	200°C.	16 hrs.	Ring pattern.
7.	200°C.	2 hrs.	Ring pattern.
8.	225°C.	15 mins.	Ring pattern with faint spot in the plane of incidence.
9.	100°C.	5 hrs.	Arched rings pattern.
"	200°C.	1 hr.	Arched rings pattern.

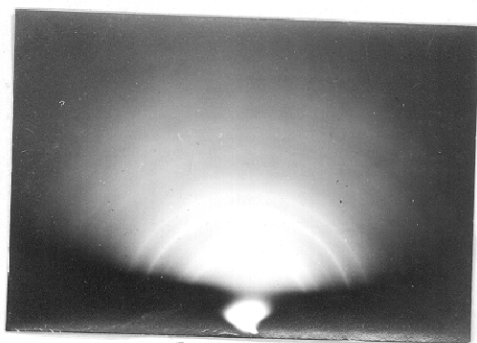


Fig. 53a A7731

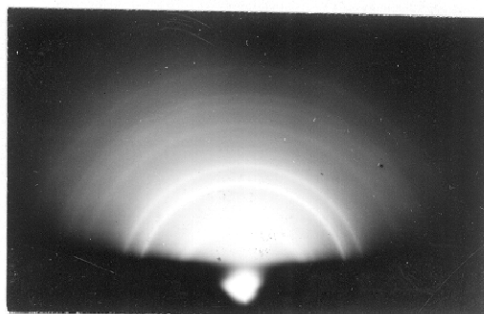


Fig. 53b A7734

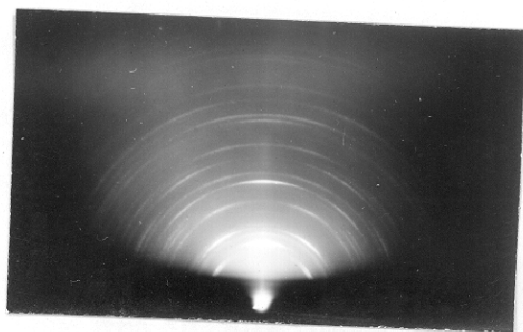


Fig. 54 A7943

A tin crystal (100) face heated at 100°C. in air for four hours, however, gave Fig. 54, which is quite different from that of Fig. 53, the 200°C. oxidised surfaces. Table XIV gives the measurements and analysis of Fig. 54 which shows some agreement with SnO and SnO₂ lattice spacing. The arced rings of this pattern however do not correspond to the normal tetragonal SnO₂ or SnO structure, and there are a few much fainter and rather more diffuse rings, showing some randomly disposed Sn to be present. This result, therefore, was not completely identified.

It is remarkable that two different oxides are formed on tin single crystal surfaces (100) when heated at two different temperatures, namely 100°C. and 200°C. A further interesting observation was that the pattern obtained from a specimen heated at 100°C. did not change to that characteristic of the specimens heated at 200°C. when the specimen was subsequently heated at 200°C. for two hours.

On some metals the nature of the oxide depends on the temperature. Thus, de Bronckère (1945) finds that the film on aluminium which has been melted consists of crystalline γ -Al₂O₃, although rapid heating to 700°C. for short times gives a mixture of the amorphous and γ -oxides. Aluminium heated at temperatures between 400° and 500°C. for a comparatively long time causes the formation of an amorphous alumina film. According to de Bronckère the formation of alumina is determined by the relative speeds

TABLE XIV

An Analysis of the pattern of Fig. 54.
Cube face (100) of tin single crystal
heated at 100°C. for five hours.

$$L = 47.5 \text{ cm.} \quad \lambda = 0.05144 \text{ A.}$$

Radius in cm.	Intensity.	d in A	X-ray for SnO_2^*		X-ray for SnO^*	
			d in A	I/I ₁	d in A	I/I ₁
0.729	arc s	3.95	3.34	1.00		
0.838	arc mf	2.91			2.97	1.00
0.900	f	2.71	2.64	0.63		
0.941	arc f	2.59			2.66	0.25
1.029	vf	2.37	2.36	0.18		
1.096	arc f	2.23				
1.226	f	1.99				
1.273	vf	1.91			1.89	0.15
1.323	vf	1.85				
1.389	vf	1.76	1.75	0.63	1.79	0.30
1.457	arc vs	1.68	1.67	0.1		
1.515	vf	1.61			1.59	0.40
1.564	mf	1.56	1.58	0.05		
1.619	vf	1.51	1.49	0.10		
1.681	vf	1.45	1.435	0.10	1.480	0.15
1.744	vf	1.40	1.41	0.15		
1.810	vf	1.34			1.332	0.05
1.899	m	1.28			1.22	0.05
2.187	m	1.12	1.11	0.03		
2.249	m	1.08	1.085	0.08		
2.435	mf	1.02			1.025	0.05
2.604	mf	0.94	0.948	0.08		

* Hanawalt, Rinn and Frenzel, 1938

of oxidation and crystallisation. Similar results were obtained with aluminium by Darbyshire and Cooper (1934) and Preston and Bircumshaw (1936). In general, the film was found to be amorphous below 600°C . and to consist mainly of well-crystallised $\gamma\text{-Al}_2\text{O}_3$ above 600°C . This face-centred cubic compound was strongly oriented, with a cube face parallel to the metal surface. On heating the oxide to 1400°C . it changed from the γ to the α modification.

Oxide films on tin prepared by oxidising a sheet of tin-foil in a flame have been examined by Bragg and Darbyshire (1932) who found that the film yielded an electron diffraction pattern characteristic of a body-centred tetragonal unit with side $a = 4.72\text{\AA}$ and height $c = 3.17\text{\AA}$ identical with the unit cell of SnO_2 . This result was confirmed by Preston & Bircumshaw (1935a) by examination of material prepared by fusing a small sheet of tin-foil mounted on a loop of copper wire, and of a specimen obtained by drawing a film from the surface of molten tin on to a wire loop. The oxide films of tin yielded electron diffraction patterns characteristic of the usual SnO_2 structure. Traces of SnO were possibly present and the SnO_2 film was probably oriented with the "c" axis perpendicular to the surface of the drop. Steinheil (1934) has also detected on tin-foil heated over a flame the ordinary tetragonal structure of SnO_2 in some cases and that of SnO in others. Jenkins (1935) prepared an oxide

surface on molten tin in vacuum, just above its melting point. The reflection pattern thus obtained showed that the film consisted of the tetragonal form of SnO ($a = 3.80\text{\AA}$; $c = 4.81\text{\AA}$) all the crystals resting on their 001 faces. Jenkins also prepared tin oxide films on nickel gauze, the tin being maintained at a temperature slightly above the melting point. The resultant transmission pattern showed that the film made in this way consisted almost entirely of the monoxide (SnO), the crystals being partially oriented with their $[001]$ faces in the plane of the film. In addition to films consisting of the monoxide, some composed of the dioxide (SnO_2) were also made in a similar way with the tin at a rather higher temperature. This oxide layer probably started as the monoxide and changed almost entirely to the dioxide owing to the higher temperature. The orientation was presumably destroyed on the transition from monoxide to dioxide.

Bound and Richards (1939) prepared transmission films of tin by evaporation. The patterns obtained from these unexposed films agree with a tetragonal structure having axial ratio of 0.54 in agreement with the X-ray data. These films exhibited no preferred orientation. Patterns of a film of tin taken at intervals up to a month showed no detectable oxidation, a fact which points to the conclusion that the film formed on tin in air is very thin. After $2\frac{1}{2}$ hours' heating at 100°C . no change was observed in the

pattern for tin but after heating to 190°C . a different pattern was obtained: this was found to be due to a tetragonal structure with $a = 3.80\text{\AA}$; $c = 4.80\text{\AA}$, the axial ratio being 1.27 in agreement with the X-ray data for SnO . These authors noticed SnO to be present on the surface of the melt of solder, the oxide exhibiting marked orientation with the (001) planes parallel to the surface.

(4) The reaction of I_2 vapour on (100) faces of tin single crystals.

One tin crystal was exposed to iodine vapour in air at room temperature in a desiccator for about 14 hours. On examining the crystal face by electron diffraction a ring pattern as shown in Fig. 55 was obtained. An analysis of the pattern, given in Table **XV** shows that it agrees with the X-ray data for cubic tin tetra-iodide. The estimated axial length, however, as calculated from the λL value which was not accurately known, was slightly less than the X-ray value $a = 12.23\text{\AA}$ (Wyckoff, 1931, Hanawalt, Rinn and Frevel, 1938). Fig. 55 shows ring intensities somewhat different from those quoted for the X-ray data in Table **XV** but this is likely to be due to the nature of the crystal habit and the strong absorbing power of SnI_4 , as in the case of BiI_3 (Section VI).

The similarity of the patterns, Figs **53a** and Figs **53b** with the SnI_4 pattern, Fig. 55, has already been noted



Fig. 55

A 8029

above in Section VII (3), indicating that Fig. 58 was evidently due to adventitious formation of SnI_4 on the surface, resulting from heating the crystal in air in the presence of traces of iodine vapour.

TABLE XV.

AN ANALYSIS OF THE PATTERN OF Fig. 55.
(100) face of tin crystal exposed to iodine vapour.

 $L = 47.5 \text{ cm.}$
 $\lambda = 0.05096 \text{ \AA.}$

Radius in cms.	Inten- sity.	d in A	hkl	a	X-ray Data for SnI_4		
					d in A*	I/I_1^*	Indices hkl
0.384	f	6.3	111	11.9	6.9	0.1	111
					5.5	0.27	210
					5.0	0.10	211
0.705	mf	3.42	311	11.35	3.53	1.00	222
0.772	mf	3.14	320	11.3	3.28	0.03	321
0.861	ms	2.82	400	11.28	3.05	0.23	400
					2.80	0.03	331
0.895	f	2.71	401, (11.19) 322.		2.66	0.03	421
0.993	vfd	2.44	(332)	11.45	2.27	0.03	432) 520)
1.203	s	2.02	440	11.43	2.16	0.50	440
1.265	mf	1.91	531	11.32	1.84	0.33	632
1.419	md	1.71			1.76	0.03	444
1.477	md	1.64			1.66	0.03	721
1.552	f	1.56			1.56	0.03	
1.669	fd	1.45			1.53	0.05	
1.711	fd	1.415			1.402	0.10	
1.871	m	1.293			1.368	0.03	
1.922	m	1.259			1.248	0.07	
1.963	m	1.232					
2.087	mf	1.157			1.178	0.05	
2.197	f	1.102					
2.507	vf	0.991					

*Hanawaldt, Rinn and Frevel, 1938

VIII. GENERAL DISCUSSION

(1). Views on the Mechanism of Formation of Oxide Films on Metal Surfaces.

In recent years much interest has been shown in the study of kinetics and structures involved in the formation of thin oxide films on metals.

In 1922 Tammann (1922) proposed an equation in which the thickness of the oxide film formed on metals at low temperatures is an exponential function of the time

$$t = a e^{-c\theta}$$

where t is the time, θ the thickness of the film, e the base of natural logarithm and a and c constants. The oxidation rate of solid iron, copper, nickel, zinc, cadmium, tin, lead, chromium and manganese as well as liquid tin and lead as determined by the temper colours of the films formed on these metals seemed to support Tammann's views. The temper colour method used to test the applicability of the equation is, however, of doubtful validity (Evans, 1946) and in the absence of any positive proof as to the equation's applicability it was not generally accepted. Recently, however, two researches on the oxidation of metals by a more acceptable method have indicated the validity of the Tammann

equation. Thus, Vernon, Akeroyd and Stroud (1939) measured the low temperature oxidation velocity of zinc gravimetrically and found it to obey the Tammann equation. Lustman and Mehl (1941) investigated the oxidation of copper by a polarimetric method and again found the Tammann equation explained the shape of the oxidation curves.

According to Mott (1939) the type of oxidation observed with aluminium, which follows the usual parabolic law for protective layers up to a limiting (small) thickness of oxide and then ceases completely, may be accounted for by supposing that in such cases ions may pass from metal to oxide but no electrons can be excited sufficiently to enter the conduction band of the oxide. A sufficiently thin film may then still grow, at a rate determined by the diffusion of the ions, owing to quantum mechanical 'tunnelling' of electrons. The limiting thickness predicted is of the observed order of magnitude. Mott (1940) has also shown on the basis of the previous theory the rate of growth of such protective oxide films on metals to be governed by a parabolic law when the film is either very thin or very thick and by a logarithmic law for thickness approximately 30-40Å. The film thicknesses calculated for the cases where the work needed to bring an electron from metal to the oxide is more than that needed to bring a metal ion to an interstitial position in the oxide, agree in order of magnitude with experimental data for mercury, aluminium and iron and stainless steel in dry air. Recently

Mott (1947) has put forward another hypothesis to explain the formation of protective films on aluminium according to which the work function ϕ is small enough to allow the thermionic emission of electrons from the metal into the conduction levels of the oxide. If then oxygen is adsorbed on to the surface of the oxide and oxide ions are formed, a strong electric field will be set up in the oxide. The solubility of metal ions in the oxide is, at the temperatures considered, too small for any passage of metal by diffusion. It can, however, be shown that under these very strong fields migration of ions can take place.

According to Frenkel (1944) the formation of thin oxide films on a metal surface in air starts in the case of not too low temperatures with the dissociation of adsorbed oxygen molecules into atoms (chemisorption) which thereafter gradually penetrate the metal. This penetration proceeds apparently, at least in the initial stages of the process, by the intrusion of oxygen atoms into the interstices of the crystalline lattice of the metal and by diffusion over these interstices. The lattice suffers a more or less considerable deformation, which is connected with the appearance of inner stresses. If the surface layer with a large concentration of oxygen (lying close to the stoichiometrical value for the oxide) is sufficiently thick, this layer must suffer a kind of phase transition, the unstable (or metastable) lattice of the metal

with the O atoms in the interstices being transformed into a stable oxide lattice, compressed or extended depending on the ratio between the atomic volume of the metal and the molecular volume of the oxide. The mechanism of the oxidation process must therefore suffer an essential alteration, which is reduced to a sharp slowing down of this process, which apparently explains the protective action of thin oxide films.

According to Evans (1946), three laws have been experimentally established expressing the increase of oxide film thickness 'y' with time 't' in different cases:

$$y = K_1 t + K_2 \text{ (The Rectilinear Equation)}$$

$$y = K_3 \log(K_4 t + K_5) \text{ (The Logarithmic Equation)}$$

$$y^2 = K_6 t + K_7 \text{ (The Parabolic Equation)}$$

It is possible to divide metals into two classes according to the relation between the volume occupied by the oxide and that of the metal eliminated in producing it. If 'M' is the molecular weight of the oxide and 'D' its density the volume occupied by one gram-molecular weight is M/D . If 'm' is the weight of metal contained in 'M' of oxide and 'd' the density of the metal, the volume of metal destroyed in producing that volume of oxide is m/d . Thus, if M/D is less than m/d that is to say if Md/mD is less than 1, the oxide-film is likely at the outset to be in a state of abnormal distention, and may easily develop large cracks. On the other hand, when Md/mD is greater than 1 the film is likely to be in

compression, and discontinuities are less likely, provided that its strength is sufficient to withstand the compressional stresses.

A simple calculation shows that M_d/mD is less than unity in the ultra-light metals such as sodium (0.57), potassium (0.41), magnesium (0.79), and calcium (0.64) but exceeds unity for heavy metals such as iron (2.16), nickel (1.60), zinc (1.58) and copper (1.71) and even for two comparatively light metals beryllium (1.70) and aluminium (1.24).

The oxidation of zinc in air and in oxygen has been examined by several workers. Pilling and Bedworth (1923) from gravimetric data at 400°C. concluded that oxidation follows the parabolic law as illustrated typically by copper at all temperatures and iron above 200°C. From observations of colour changes at 390°-412°C. Tammann and Köster (1922) deduced an exponential relationship between film thickness and time. Their procedure which has been criticised on optical grounds is, however, of doubtful value in the case of zinc, in which isolated colour changes are restricted to the high temperatures. Bangham and Stafford (1925) (method of experiment and other details not stated) suggested that the rate of oxidation is proportional to $t^{-(1-a)}$ where 't' represents time and 'a' is small compared with unity. These several observations, although based on fragmentary evidence which precludes general application, agree in attributing protective properties to the zinc oxide film and in assigning a rate of oxidation which falls off with time. A similar

conclusion was reached by Dunn (1931) with respect to the zinc oxide film which forms on brasses containing less than 80% of copper.

The direct oxidation of zinc in air has been studied at temperatures ranging from 25° - 400°C (melting point 419°C) by Vernon, Akeroyd and Stroud (1939) who find that up to a critical temperature of 225°C. the rate of oxidation remains extremely low, but increases greatly when this temperature is exceeded. Abrasion with emery gives a surface in which a certain amount of oxide, believed to be amorphous, is embedded, the reinforcement of which on heating gives a continuous film. This surface oxide film was isolated by volatilization of the underlying zinc. The relationship between oxidation and time was given by the equation

$$W = K \log (at + 1)$$

where W is the amount of oxidation in time t, i.e., except for short periods of exposure, there is a linear relationship between oxidation and logarithm of time. This relationship holds typically above, but only approximately below, 225°C, the discrepancy being the more marked the lower the temperature and the shorter the exposure. The constants 'K' and 'a' were worked out and it was thus possible to predict the amount of oxidation for any given temperature and time. The relationship between oxidation and temperature above 225°C. was represented by the equation:

$$d \log W/dt = - Q/RT^2$$

a straight line (of identical slope and differing only slightly quantitatively for etched and abraded specimens) being obtained when logarithms of weight-increments after an arbitrary time are plotted against reciprocals of absolute temperature.

(2) Nature of Oxidation of Cleavage Faces of Zinc Single Crystals.

The presence of a very thin film of zinc oxide, having a single crystal structure on the freshly cleaved face of zinc crystals (p.46) shows the result of the spontaneous oxidation of the zinc surface. A similar observation was made by Vernon, Akeroyd and Stroud (1939) who found an oxide layer which they described, however, as amorphous on polycrystalline zinc surfaces. Further, Daniels and Cobly (1937) grew single crystals of zinc in hydrogen, carbon dioxide, nitrogen and in vacuo and cleaved these in vacuum and measured the contact potential difference against platinum; they plotted the potential difference against time and found that after a rapid initial rise a small decrease at 10^{-5} mm. pressure occurred over about one hour; they attributed the rise to formation of surface layer of gas and the subsequent decrease to gradual diffusion of this layer into the crystal.

The zinc oxide films observed in the present experiments showed an epitaxial growth on cleavage faces of zinc. This oxide layer must be exceedingly thin, since the Kikuchi

bands due to zinc are still clearly visible. The oxide film, however, did not change appreciably even after being heated at 200°C . for twelve hours. Vernon, Akeroyd and Stroud (1939) also found that, up to a critical temperature of 225°C . the rate of oxidation of polycrystalline zinc remained extremely low, but increased greatly when this temperature was exceeded. This result agrees with the theory put forward by Mott (1939) to account for the formation of protective oxide coatings on metal surfaces.

The constancy on the zinc cleavage plane of the film thickness of ZnO which, even at 200°C ., retains its single crystal structure, also shows the inability of zinc atoms to diffuse through the oxide skin. It may be that zinc atoms need abnormally high kinetic energies to penetrate through this thin oxide film. Huntington (1942) found that the self-diffusion rate in zinc is markedly anisotropic, and taking into account the observed departure from close-packing and a rapidly increasing close range repulsive potential it could be shown that the mechanism of vacancy diffusion predicted, at least qualitatively, the observed anisotropic behaviour of the temperature-independent factor in the expression for the diffusion constant. Measurements in the temperature range $340\text{--}410^{\circ}$ by means of a sectioning method with long lived " ^{65}Zn " as indicator, are reported by Miller and Banks (1942) for 18 single crystals of various orientations and for polycrystalline zinc, which indicate that diffusion in zinc is strongly anisotropic and the

energy of activation is about 0.85 ev along the 'c' axis and about 1.24 ev in the basal plane. Again, using long-lived radio-active " ^{65}Zn " as an indicator, Banks (1941) measured self-diffusion along the c-axis of zinc single crystals at six different temperatures and found that the activation energy is 19,000 cal. per mol. and that the diffusion co-efficient at $410-4^\circ$ is 9.89×10^{-4} sq.cm. per day.

Fig. 12 shows that a random oxide layer (ring pattern) appeared and the Kikuchi line pattern disappeared only when the crystal was heated at 400°C. in air for three hours and even after fifteen hours' heating at the same temperature (melting point of zinc is 419.5°C. ; (Kaye and Laby, 1944)) the ring and spot pattern of ZnO remained practically unaltered, except that the rings became slightly spotty showing growth of the random ZnO crystals (Fig.13). These results show that the protective nature of the ZnO film disappears at 400°C. , though even at this stage the oxide film remains smooth and fine-grained.

According to Mott (1940), at higher temperatures the heat motion increases and more kinetic energy may be transferred to electrons in the metal. These may then penetrate into the oxide layer to a distance greater than $50\text{\AA}$ by a kind of thermionic emission which is superimposed on the quantum-mechanical effect. Moreover, on heating the film may, and generally does, recrystallise; that is, the continuous envelope breaks up into separate fragments. In consequence

an entirely new growth mechanism may set in. The interstitial diffusion of ions and electrons is replaced or accompanied by intercrystalline diffusion of neutral molecules and atoms which react together on the surface of existing crystal nuclei. Thus films may attain considerable thickness. This view of Mott's is borne out by the above result.

The mobility of surface atoms was first shown by Volmer (1921), and later a number of other workers confirmed this view (Volmer, 1932). Muller (1937, 1938, 1939) has shown that the angular distribution of field emission from the metal points can be related to the crystal structure of the metal, and also suggested that the modifications in the pattern from tungsten, which took place when the point-temperature was raised, could be attributed to a movement of the surface atoms causing local changes in the work-function. Similar experiments were carried out using tungsten, molybdenum and nickel, by Benjamin and Jenkins (1940) who have shown that this surface mobility occurs above 1170°K for tungsten, 770°K . for molybdenum and 370°K . for nickel; the changes in emission distribution, which are very much more marked for molybdenum and nickel than for tungsten, can be completely explained in terms of a change in the geometrical shape of the point which is brought about by the action of the high external field upon the mobile surface atoms; they suggested that heating the point at a higher temperature results in a surface mobility and the surface atoms rearrange themselves in a manner which is

determined by the periodic forces due to the underlying net works of atoms which cause the surface tension to be a function of crystallographic direction, and the surface atoms form a new surface of minimum free surface energy which is very much smoother but shows departures from the perfect smoothness due to surface forces in a liquid: they place the work function of different regions in order of increasing work function as (100), (111), (110) which is in agreement with the results obtained by Martin (1939) who has examined the low magnification image produced by thermionic emission from a single crystal and has given the same order for the work function.

Further, the properties of clean metals change in marked degree when a film appears on the surface. Metals which have been carefully cleaned in vacuo exhibit unusually high friction, which falls as soon as a trace of oxygen has access to the surface (Bowden and Hughes, 1939; Hughes and Whittingham, 1942). Again, the presence of an oxide film diminishes the power of metals to emit electrons when exposed to ultra-violet light. The photo-electric activity of iron is reduced when the metal becomes passive (Alten, 1914). The threshold wave-length, at which the photo-electric effects set in is shifted when oxygen has access to a metallic surface, although not always in the same direction (Rentscher and Henry, 1936, 1945; Hunter, 1936). More than one interpretation has been offered for this fact, but it seems to be due to an oxide film since gold, which is not readily oxidised,

shows no change of threshold wave length on the admission of oxygen, while silver, which forms an oxide unstable above 180°C . regains its original sensitivity on heating. Brüche (1934) who has used electron emission to obtain photographs of the grain-structure of metals by the aid of a "magnetic lens" has found that the presence of either an oxide or grease film greatly decreases the emission of electrons from zinc.

Fowler (1931) developed a theory of the effect of temperature on sensitivity and explained the experimental data by the effect of temperature on the number of electrons available for extraction according to Sommerfeld's theory of metals, and also described a method of finding thresholds from the curves. Dillon (1931) measured photo-electric properties after outgassing polycrystalline and cleaved emitting surfaces by irradiation with ultra-violet and thermally evaporating some on the zinc, and observed that the stable condition produced a difference in long-wavelength limits of the two types of surfaces of approximately 260Å. Kluge and Skeyskal (1940) pointed out that the cleavage of a single crystal of a metal in a high vacuum provided a method of determining the effect of crystal orientation on the electronic properties of various boundary surfaces and also the effect of secondary structure: they describe a method for determining the photo-emission of a (0001) face of a zinc single crystal and find that the λ limit of the photo-effect is $\lambda_0 = 290 \pm 0.7 \text{ m}\mu$ and the value of the emission work function is 4.26 ev.

It will be evident from the above that the surface properties of metal surfaces change with rise of temperature with respect to their electronic properties such as work function, activation energy, etc. and particularly the mobility of surface atoms as mentioned before.

The process by which oxygen molecules react with clean metallic surfaces to form the initial oxide film has been studied by Roberts (1935). On exposure of a clean metallic surface to oxygen, a discontinuous two-dimensional atomic film of oxygen forms and by diffusion through this film the initial three-dimensional oxide results. On hydrogen covered tungsten wire this adsorption of oxygen was found to be a comparatively slow process. Confirmation of the conclusions was found by Lustman and Mehl (1941) in low temperature oxidation of single crystals of copper. When air was admitted to the specimens after reduction but without a preliminary evacuation of the hydrogen, a period of 30 to 40 seconds was observed during which the specimen surface showed no apparent change, i.e., no refracting film 1 to 2A thick was formed; after this initial period oxidation began at a maximum rate. Presumably during this initial period the adsorbed hydrogen film was being replaced by an adsorbed oxygen film. When the hydrogen was first evacuated the oxidation process began immediately at maximum rate; most or all of the adsorbed hydrogen film was apparently driven off.

A considerable variety of behaviour is manifested in the reaction of different metals towards oxygen, for some, such as platinum and gold, are only slightly oxidised superficially by oxygen even at a few hundred degrees centigrade, whilst others such as the alkali metals burn vigorously in oxygen at relatively low temperatures. Apart from the physical state of the metal, the nature of the oxidation must be determined by the chemical affinity of the metal for oxygen and the volatility of the metal and other related physical properties of the oxide. The alkali and alkaline-earth metals combine a strong chemical affinity for oxygen with a relatively high volatility, while mercury, although highly volatile for a metal, does not possess the requisite affinity for oxygen. Aluminium is an example of a metal which has a high chemical affinity, but the physical properties of the oxide product formed at the surface prevent further rapid oxidation of the massive metal. The physical properties of the oxide may vary with the conditions of production, but in general if a compact skin of oxide is formed it may protect the underlying metal from further oxidation by preventing the diffusion of more oxygen. One of the properties involved is specific volume, a fact rendered clear by the work of Pilling and Bedworth (1923) who were able to correlate the protective effect of an oxide film with the relative densities of the metal and the oxide. If the formation of the oxide is accompanied by a decrease of volume, the oxide film must shrink and crack, so providing channels

for the further access of oxygen. Such a film will not be protective. When, however, the formation of the oxide involves an expansion, the underlying metal will at all times be covered by the film of oxide, which can exert a protective effect. At the same time, if the increase of volume is large, the expansion involved may easily cause cracking of the film and the coating will be poorly protective (also Evans, 1946).

In addition to the specific volume, another property which determines the protective effect of an oxide film is probably a specific adherence of the oxide to the metal. It is to be expected that the adherence will depend in part on the relation of the space lattice of the oxide to that of the metal, being greatest, perhaps, where these are similar.

(3) Nature of Oxidation of Cleavage Faces of Zinc Single Crystal which have been exposed to Sulphur.

A cleavage face of zinc which had been washed with "crystallisable benzene" gave on subsequent heating in air at 400°C . for fifteen minutes an arced ring pattern of zinc oxide showing (101) and (001) orientation. Another cleavage face which was exposed to dilute hydrogen sulphide gas in air gave on subsequent heating in air at 400° for a short time an oxide pattern with (101) and (001) orientation closely similar to that obtained from the cleavage face washed with benzene. A cleavage face, however, which had

been exposed to a higher concentration of hydrogen sulphide gas, when heated in air at 400°C. , gave a random ZnO ring pattern. It would seem that the benzene used for degreasing contained a trace of sulphur compounds such as thiophene. This sulphur must have attacked the cleavage face exactly in the manner that hydrogen sulphide gas does and formed a very thin layer of zinc sulphide which, on heating in air, gave (101) orientated crystals in addition to crystals of (001) orientation as normally furnished by direct oxidation

This result is in agreement with those obtained by Yamaguti (1935) from oxidation of cleavage faces of zinc blende (ZnS) and by Aminoff and Brömè (1936,1938) from cleavages of sphalerite (ZnS) or zincblende. Both the authors observed an orientation relationship of the ZnO formed on the cleavage surface. Further it may be mentioned here that Vernon (1924) also observed that polycrystalline copper surfaces exposed to sulphur were more easily oxidisable than pure copper.

(4) Nature of Oxidation of (001) faces of (10 $\bar{1}$ 2) twins of Zinc Cleavage.

The nature of the oxidation of (001) faces of (10 $\bar{1}$ 2) twins of Zinc differs markedly from that of the natural cleavage faces. On heating this plane at 400°C. in air for a relatively short time an arced ring pattern was obtained, showing only (001) orientation, which on further

heating at the same temperature changed to a sharp ring pattern without any arcing and indicating a spike-like growth of the random ZnO crystals. This result with a twin face, which is much rougher than the cleavage face, shows the effect of roughness on the oxidation of metal surfaces and hence on the diffusion of oxygen through such faces.

(5) Nature of Oxidation of Antimony and Bismuth Single Crystal Surfaces.

The antimony cleavage face (111) which is perfectly smooth gives clear Kikuchi bands but does not show any oxide pattern. However, on being heated at 400°C. (melting point of antimony 630.5°C. (Kaye and Laby, 1944)), in air for eight minutes, the cleavage face gave an arced ring pattern of Sb_2O_3 showing a preferred (111) orientation (Figs. 25, 26 and 27), but the surface became very rough indicating no protective property of the oxide film. This result shows that the epitaxial growth of the oxide films of antimony is similar in type to that of zinc but at 400°C. as in the case of zinc, the oxide is not protective.

Again, the bismuth cleavage face (111) which is very smooth, gives clear Kikuchi bands but does not show any oxide pattern. In this respect the cleavage face of bismuth shows similarity to antimony, although it differed from antimony in that, when heated at 250°C. (melting point of bismuth 269°C., (Kaye and Laby, 1944)), for one hour,

the bismuth cleavage face gave diffuse haloes due to amorphous oxide, which obscured the single crystal substrate, and only faint traces of rings due to crystalline bismuth oxide. The bismuth oxide crystals grew larger after three hours heating at the same temperature (Fig. 34), but did not show any orientation such as was observed in the case of antimony. The surface, however, did not show any visible oxide film.

The nature of oxidation of cube faces again is quite different from those of the cleavage faces of metals. Bismuth pseudo-cube faces when heated at 250°C. in air for one hour gave a relatively sharp ring pattern (Fig. 33) showing that the Bi_2O_3 crystals were quite large. Heating at 100°C. for longer periods gave the same results.

(6) The rate of Oxidation of (111) and (100) Faces of Bismuth Single Crystals.

Although the cleavage (111) and the pseudo-cube (100) faces of bismuth crystals have almost the same smoothness, as they gave clear Kikuchi lines (Figs. 28, 29, 30, 31 and 32), yet they show different rates of oxidation. Since various crystal planes have different atomic population densities, which necessarily affect, inter alia, the work function, and hence no doubt the progress of chemical reaction, it is not surprising that the rates of oxidation

at the (111) and (100) should be found to differ appreciably.

Bénard and Talbot (1947) found that the rates of oxidation at 900°C . of copper crystal faces increased in the order (123), (100), (111), (110) = (210) = (221), the times of oxidation being several hours; the differences according to these authors are due to variation in the rate of diffusion of oxygen through the Cu_2O layer, the orientation of which is related to that of the underlying metal, though variations of the intrinsic rate of oxidation may play a part in the first few minutes; similar but less definite results were obtained for iron. Gwathmey and Benton (1939) found that amalgamation of a copper single crystal with mercury is most rapid at the poles of the (111) planes; oxygen bubbled through 50% alcohol in water produced etch pattern first at the (100) poles and later at the (111) and (110) poles; distortion in H_2CO_3 was restricted to the atoms in surfaces parallel to the (111) planes; electrolytic etching in H_3PO_4 was more rapid at the (111) poles than at the (100) poles. Gwathmey and Benton (1940) also heated a single crystal of copper at different temperatures and pressures and found that the reactivity of the crystal varied with the crystal plane along which the surface was prepared. Gwathmey and Benton (1942) further found that the reaction between oxygen and a copper single crystal depended on the crystal plane which was exposed on the spherical surface; the rate of oxidation was greatest on the (100) and (210) planes and least on the (111) plane.

(7) Nature of Oxidation of (100) Faces of Tin Single Crystals.

The (100) faces of tin single crystals, which gave clear Kikuchi bands, when heated in air at 100°C . for five hours gave an arced ring pattern (Fig. 54) perhaps due to SnO , SnO_2 and Sn, which could not be completely identified. The similar faces, however, when heated in air at 200°C . (melting point of tin 231.86°C . (Kaye and Laby, 1944)) for one hour, gave a ring pattern (Figs. 53a and 53b) possibly due to an oxide or oxide mixture which again could not completely be identified. This pattern showed some similarity in intensity and ring position to a tin tetra-iodide pattern (Fig. 55).

It will thus appear that, apart from the nature of crystal faces such as its atomic population density, the nature of thermal oxidation depends also on the prevailing temperature. Similar results were obtained by de Bronckère (1945) in this laboratory in the case of aluminium.

Tammann (1922) and his co-workers (1923) have suggested that crystallisation velocity depends on the numbers of nuclei and on the speed at which they grow by fixing molecules from the surrounding amorphous material. In the case of aluminium it is suggested that at 400°C . the rate of growth is small, so that the tendency is for the formation of numerous minute crystals which when heated to 500°C . act as nuclei on which the newly formed oxide is deposited.

But if the metal is heated directly to 500°C . very few nuclei exist and the crystallisation proceeds from a few centres only and is on the whole slower.

(8) Other Chemical Reactions with Bismuth and Tin Single Crystal Surfaces.

Iodine vapour reacts with the smooth (111) cleavage faces of bismuth single crystals to give bismuth tri-iodide crystals in two degree orientation, the (111) plane of the BiI_3 being parallel to the bismuth (111) cleavage face; while the (100) faces of bismuth crystals reacted with iodine vapour under similar conditions to form random bismuth tri-iodide. These results indicate that the (111) cleavage face had a much stronger orientating effect on the BiI_3 formed than the pseudo cube (100) faces of bismuth, though the latter were apparently extremely smooth like the cleavage faces.

Iodine vapour from different solvents such as benzene, alcohol and acetone reacted with the (100) faces of bismuth to give random bismuth tri-iodide. Further, while moist chlorine gas and bromine vapour reacted with the (100) face of bismuth to give random bismuth oxychloride and oxybromide respectively, moist iodine vapour gave random bismuth tri-iodide. The formation of random BiOCl and BiOBr has also been observed in etching the (100) faces of bismuth with aqueous solutions of hydrochloric acid and saturated

bromine water respectively. Carbon di-sulphide vapour reacted with the (100) faces of bismuth to form the corresponding sulphide and a similar reaction had also been observed in etching the (100) face of bismuth with yellow ammonium sulphide, which formed diffuse ring pattern of the sulphide on the surface. These results again show the inability of the (100) faces of bismuth to form oriented reaction product as in the case of iodine vapour on the (111) cleavage faces.

The (100) faces of tin crystals, under similar conditions as in the case of (111) and (100) faces of bismuth, reacted with iodine vapour to form tin tetra-iodide.

(9) Nature of the Epitaxial Orientations Observed.

The four principal epitaxial orientation relationships observed in the present investigation are as follows:-

The freshly cleaved (001) faces of zinc crystals are always covered with a thin film of zinc oxide in two degree (001) orientation.

The cleavage (001) faces of zinc crystals which have been exposed to slight attack by sulphur and subsequently further oxidised by heating in air, at 400°C. , gave patterns of zinc oxide in two degree orientation, i.e., (001) and (101). (P.51)

The cleavage (111) faces of antimony crystals when

heated in air at 400°C . for a short time gave an oxide pattern of Sb_2O_3 in two-degree (111) orientation. (P.56)

The cleavage (111) faces of bismuth crystals when exposed to iodine vapour gave a pattern due to bismuth tri-iodide in two degree (111) orientation. (P.67)

Volmer (1932) has shown that in some cases at least crystals grow by atoms arriving at a face, moving over it till they come to an edge and then prolonging the face. This view is supported by many electron diffraction results. Thus, if, as is usually the case, the atoms are coming up in a stream roughly normal to the surface of the substrate, crystal faces parallel to this surface will receive more atoms per unit area than the others and so grow faster.

The next question is, what determines the relation between the axes of the original and of the growing crystals when the orientation is complete? According to Brück (1936) and Rudiger (1937) the orientation is such as to make the sum of the distances between nearest atoms of the crystal and substrate a minimum, reckoned over the first cell. According to Thomson (1943) however, the determining factor may be the existence of special lines of atoms in the substrate, e.g., the edge of a crack or of a crystal or the re-entrant angle at the bottom of a step on the surface of the substrate which is not likely to be ideally flat. Such a line of atoms would usually be a zone axis of the substrates. If the atoms of the growing crystal form up along this line,

the new crystal will also have this direction as a zone axis. When the crystal grows out sideways it will almost inevitably form a face in contact with the face of the substrate and we get the type of orientation observed. No doubt the choice of the zone axis of the new crystal to coincide with the original atom line will be governed by the relative spacing of the atoms, and this will tend to give something resembling Brück and Rudiger's law.

According to Finch and Whitmore (1938) orientation of the overgrowths is really induced by the atomic arrangement in the substrate crystal surface and not merely controlled by cracks or flaws the direction of which depend on, for example, the cleavage directions. Thus Finch and Whitmore found that the orientation of sodium nitrate overgrowths on calcite was wholly determined by the atomic arrangement of the substrate crystal surface. Thus not only is the atomic arrangement of the calcite continued on the cleavage surface by oriented overgrowths of rhomb habit, but on the other natural faces the orientation of the overgrown rhombohedra is such as to show clearly that the calcite atomic arrangement is likewise continued as closely as possible.

This view of Finch and Whitmore (1938) is borne out by the epitaxial orientations observed in the present investigation.

IX. S U M M A R Y .

1. Single crystals of more fusible metals, namely zinc, antimony, bismuth and tin, have been prepared by two different methods -

(i) The single crystals of zinc, antimony and bismuth have been prepared by slow cooling of the molten metal from one end in a suitable container.

(ii) Flat and highly smooth shining surfaces of single crystals of bismuth and tin have been prepared by casting the molten metal on clean and smooth glass surfaces, followed by slow cooling.

2. The crystallographic orientation, degree of roughness and crystal perfection of the single crystal surfaces prepared by the above methods have been determined by electron diffraction.

3. The chemical reactions by (a) thermal oxidation in air (b) with halogens and H_2S to form halides and sulphides at room temperature and (c) etching with different chemical reagents, have been studied by electron diffraction on different faces of the single crystals, namely,

(i) (001) cleavage plane and (001) face of the (10 $\bar{1}$ 2) twin of zinc.

(ii) (111) cleavage plane of antimony.

(iii). (111) cleavage plane and the pseudo-cube (100) face of bismuth.

(iv). (100) face of tin.

4. The reaction products in each case have been identified from electron diffraction patterns, and their orientations with respect to the substrate have been determined.
5. The results have been discussed in the light of modern views for the formation of protective films and chemical reactions on solid surfaces.
6. Zinc cleavage surfaces which were relatively perfect since they yielded clear Kikuchi bands also showed a spot pattern due to a thin layer of highly (001) oriented zinc oxide. In this case the important result has been established that even when examined in vacuo within five minutes after cleavage, these surfaces were invariably covered with an extremely thin optically invisible layer of highly oriented zinc oxide crystals having an exceedingly smooth surface parallel to the substrate.
7. When heated in air at 200°C. for twelve hours the oxide spot pattern on the zinc cleavage becomes sharper and also less elongated but otherwise remains unchanged in orientation and thin over much of the surface. This result indicates the protective action of the oriented zinc oxide film.

8. The oxide layer on zinc cleavage planes remains unchanged in form even after two hours' heating in air at 400°C . and only after long further heating at this temperature does the growth of disoriented zinc oxide crystals become appreciable. Micrographs showed that preferentially rapid oxidation had occurred at isolated centres on the surface.
9. Washing the zinc cleavage plane with benzene did not result in a noticeable change of the zinc Kikuchi bands and zinc oxide spot patterns, but on being heated in air subsequently at 400°C . for fifteen minutes the cleavage plane gave arced ring patterns showing two-degree (001) and (101) orientation. This orientation did not change even after fifteen hours' heating in air at the same temperature but the rings became sharper and spotty indicating growth of zinc oxide crystals.
10. On exposing the cleavage plane to higher concentration of hydrogen sulphide gas, the Kikuchi bands disappeared and on subsequently being heated in air at 400°C . for fifteen minutes this specimen gave a ring pattern showing random orientation.
11. On exposing the cleavage plane of zinc to a very low concentration of hydrogen sulphide in air and on subsequent heating in air at 400°C . for 50 hours, zinc oxide ring pattern with (101) orientation appeared as well as the

initial spot pattern due to (001) zinc oxide. After long heating at this temperature the spot pattern of zinc oxide and the arced ring pattern with (001) and (101) orientation still remained nearly unchanged.

12. The (001) plane of the $(10\bar{1}2)$ twin perpendicular to the cleavage plane gives Kikuchi bands and zinc oxide spot pattern exactly similar to that from the cleavage plane but this plane also gave very sharp and round spots due to zinc and had thus relatively rough parts of the surface
13. On heating in air at 400°C . the (001) face of $(10\bar{1}2)$ twin gave in fifteen minutes an arced ring pattern due to (001) orientation but after one hour's heating at the same temperature only ring pattern without any orientation remained. This result was attributed to the roughness of much of the (001) face of $(10\bar{1}2)$ twin with respect to (001) cleavage plane of zinc crystal.
14. Antimony cleavage planes which were atomically smooth gave clear Kikuchi bands, but did not show any spot pattern due to an oxide layer as in the case of zinc cleavage planes.
15. On being heated in air at 400°C . for a very short time, the cleavage plane of antimony gave a ring pattern showing two-degree (111) orientation of the Sb_2O_3 . The ring

pattern of Sb_2O_3 corresponded to a cubic structure with $a = 11.20\text{\AA}$, which agrees with previous X-ray data.

16. The cast surfaces of bismuth single crystals gave clear Kikuchi bands corresponding to the pseudo-cubic (100) face parallel to or within 20° to the surface.
17. The cleavage (111) faces gave clear Kikuchi bands corresponding to (111) face but did not show any spot pattern due to an oxide layer as in the case of zinc.
18. When heated in air at 250°C . for one hour the (100) face gave a random oxide pattern corresponding to Bi_2O_3 having a face-centred cubic structure with $a = 5.40\text{\AA}$. The cleavage plane (111) heated at the same temperature for the same length of time gave only diffuse haloes which became clear rings only after four hours' heating at the same temperature.
19. When exposed to dry iodine vapour the (100) face gave a random ring pattern due to BiI_3 while the cleavage plane (111) being similarly treated gave a pattern showing a two-degree (111) orientation of BiI_3 .
20. When exposed to moist iodine vapour the (100) face of bismuth gave a ring pattern due to BiI_3 and the similar faces exposed to moist chlorine or bromine vapour gave patterns due to chloride and bromide respectively.

21. The (100) faces of bismuth crystals when exposed to iodine vapour from its solution in benzene, alcohol or acetone gave random ring patterns due to BiI_3 .
22. The (100) faces when dipped in a solution of iodine in benzene also gave a ring pattern due to BiI_3 showing some orientation.
23. When exposed to carbon disulphide vapour the (100) face of bismuth crystal gave a diffuse ring pattern which may be due to bismuth sulphide.
24. When etched with (1:1) hydrochloric acid or saturated bromine water the (100) faces of bismuth crystals gave ring patterns due to oxychloride or oxybromide respectively, while similar faces etched with (1:2) nitric acid or concentrated acetic acid gave a spot pattern due to metallic bismuth. Similarly etched with (1:1) yellow ammonium sulphide the (100) face gave a diffuse ring pattern perhaps due to bismuth sulphide and a few spots due to metallic bismuth.
25. The cast surfaces of tin single crystals gave clear Kikuchi bands corresponding to (100) face parallel to or within 11° to the surface, but did not show any spot pattern due to an oxide layer as in the case of zinc cleavage faces.

26. On being etched with (1:1) hydrochloric acid, the cast surface of tin single crystals gave a spot pattern showing roughening of the Sn (100) face.
27. The (100) faces of tin crystals when heated in air at 200°C. for one hour gave a ring pattern of an oxide corresponding to a cubic structure which was believed to be due to SnI_4 formed by chance presence of traces of iodine vapour.
28. The (100) faces of tin crystals when heated in air at 100°C. for five hours gave an arced ring pattern due to SnO and SnO_2 and Sn.
29. The (100) faces when exposed to iodine vapour for a short time gave a ring pattern due to tin tetra-iodide.

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