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AN ELECTRON DIFFRACTION STUDY OF
THE RELATION BETWEEN THE STRUCTURE
AND PROPERTIES OF DEPOSITS AND THE
CONDITIONS OF DEPOSITION.

By

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**AN ELECTRON DIFFRACTION STUDY OF THE RELATION BETWEEN
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INTRODUCTION.

In recent years the properties of deposits both metallic and non-metallic have been much investigated and the results applied to a variety of practical problems. The physical and chemical properties of deposits are not only determined by the kind of atoms or molecules of which they are composed, but may also be influenced by the conditions under which they are formed, such as the rate of deposition, the nature of the substrate surface, the temperature, and the nature of the atmosphere in which the deposition is carried out. These conditions to a large extent determine the structural characteristics such as the size, orientation and boundary faces of the crystal particles of which the layer or surface is composed, and it is through these structural variations that they affect the surface properties.

The fine scale structure of deposits has been investigated in many ways - optical, electrical, magnetic, adsorption, chemical, etc - but these mostly yield only indirect and qualitative information about the crystalline form and structure. The first generally applicable means of determining the form of the atomic arrangement in solid materials was provided by the X-ray diffraction method, but owing to the weak interaction of X rays with matter the structure of thin films even up to the order of a thousand

angstroms thickness cannot be investigated by X rays. The state of affairs is quite different, however, in the case of the diffraction of the electron beam; the high intensity of their interaction with matter is the reason why a film of even only a few atoms in thickness can yield a clear and significant diffraction pattern. In the study of the nature of deposits it is of special importance to determine the structure of such thin initial layers so that their relation to that of the substrate can be understood, and of the surface regions of thicker layers in order to appreciate the effects of other deposition conditions. For these reasons electron diffraction was used in the experiments described below. Outlines of the experimental technique and interpretation of the diffraction patterns have been given for example by Finch, Quarrell and Wilman (1935), Finch and Wilman (1937) and Thomson and Cochrane (1939), and are briefly referred to below in Section II.(3).

Since the discovery of the phenomenon of electron diffraction in 1927, it has indeed provided much valuable and direct information about the structure of many kinds of deposits and surfaces, and has been applied extensively in this laboratory to the study of catalysis, wear and lubrication chemical reactions and corrosion, electrodeposition and electrode processes, photoelectric phenomena, molecular structure,

behaviour of plastics and to the study of the mechanism of crystal growth in general. Hitherto, however, although qualitative indications have been obtained of the effects of some of the main factors which influence the structure of deposits, there have been little or no quantitative results available showing the extent of the influence of these factors in detail, over a range of conditions. The experiments described below aim at supplying some quantitative detail about the effects of the main influencing factors in the special case of deposition of metals by condensation from the vapour in vacuum or low pressure gas, since in this type of deposition several factors can be controlled and studied independently.

In these experiments, I have found, inter alia, that the structure of the surface layers of substrate materials such as fused quartz and mica cleavage faces can be profoundly changed as a result of the thermal radiation which is incident on the surface, given out by the source of hot metal vapour. It has been found that the mica surface layers are converted into several new crystalline materials stable in different though partly overlapping temperature ranges between 20°C. and 850°C. The effect of such a structural change of mica cleavage faces in determining the orientation taken up by crystals of silver growing on them has been demonstrated, and

the crystal growth and development of orientation in initially random deposits on both mica and fused quartz has been studied in relation to time and temperature of heating of the initial deposits. For this purpose the estimation of particle size from electron diffraction reflection patterns has been discussed in detail and it has been concluded that under the conditions stated, valid estimates of crystal size can be derived to a moderate accuracy. The effects of gas pressure (in Argon and Air) have been investigated. Evidence of unusually prominent formation of the hexagonal crystal form of silver has been found in certain cases which suggest that it tends to be favoured by presence of hydrogen or hydrocarbon vapours. This leads to a promising correlation between the effects of hydrogen in this type of deposition, in sputtering of metals in hydrogen, in electrodeposition, and in chemical deposition from solution. Other results of special interest are the demonstration of the higher mobility of silver atoms than gold at 300°C., though gold otherwise behaves in general in a way closely similar to that of silver, in for example its aggregation and orientation on mica.

I.1. CHOICE OF MATERIALS FOR THE EXPERIMENTAL INVESTIGATION.

For the present purpose detailed investigations were made on silver deposits condensed from vapour given out by molten drops heated by a small supporting tungsten filament, so as to obtain deposition conditions in the simplest form possible. Silver was chosen because its general properties, especially optical properties and crystal growth have already been studied in several types of deposition, so that useful comparison can be made; and some experiments were made on gold deposits for comparison with the silver results. Deposits of both these metals, and also of aluminium, are now much used industrially, for example as conducting layers on piezo-electric crystals or on dielectric sheets as condensers, or as substrates or mosaics or initial deposits in photocells, as high resistances, as optical screens, filters, reflectors, etc.

As substrates muscovite mica and fused quartz and pyrex glass were chosen, the mica because its cleavage surfaces are almost atomically flat and it represents a transparent single crystal substrate of known structure, which in general exerts an orientating influence on deposits formed on it, while the amorphous fused silica and glass surfaces have little or no such influence. These substrates also have important industrial application.

I. 2. TECHNIQUES OF PREPARATION OF METAL DEPOSITS FROM THE VAPOUR.

The preparation of deposits from the vapour has a superiority not possessed by the sputtering method in that films free from occluded and adsorbed gas can be obtained. Free from this "gas effect" evaporated films would have simpler properties than sputtered ones. The method is not limited to metals. Furthermore, deposits of metals like Cr and Al which sputter badly have been obtained (see, for example, Strong's Modern Physical Laboratory Practice). With this method, the rate of arrival of atoms at the film can be conveniently varied through wide limits and the atoms have rectilinear motion ("molecular rays") if the vacuum is good, giving very definite direction of incidence. The evaporation of metals in a vacuum was first carried out successfully by Pringsheim and Pohl (1912). They distilled the metal from a magnesia crucible. In 1928, Ritschl (1931) introduced the technique of evaporating silver from a bare tungsten coil. It has the advantage that the outgassing and evaporation of foreign substances from such a filament are much less than from a crucible. The method has been used by Weinhardt and Wehe (1947) for obtaining metal electrodes on quartz crystals.

The technique consists in introducing the metal in the form of wire or strip into an open helical coil of tungsten wire and heating it strongly by an electric current. For

metals not available in the form of wire, close wound conical wire baskets can be used or electrodeposits can be formed on the filament (Strong, 1945). When the vapour pressure of the heated substance becomes about 10^{-2} mm. of mercury or greater the rate of evaporation is relatively rapid and it emits molecular rays. Most of the metals melt before they evaporate, but metals like Zn, Cd and Mg, However, vapourise without melting.

Olsen, Smith and Crittenden (1945) have developed the technique for evaporations in quantity. They found that evaporation from a crucible formed by painting a tungsten conical basket with suspensions of alundum or BeO and baking at a high temperature was most satisfactory for many elements.

Countryman (1937) found that for some metals other filaments than tungsten were to be preferred. He used Ni, Pt, Mo, and Ta. According to Caldwell (1941) three factors should determine the choice of a suitable filament material. They are the adhesion of the metal to the filament, the vapour pressure of the filament material at the evaporation temperature, and the alloy formation of metal and filament. He has listed Ta, Mo, Columbium and Fe as the most suitable for the evaporation of silver. Olsen, Smith and Crittenden prefer tungsten.

I. 3. PREVIOUS KNOWLEDGE OF THE STRUCTURE AND PROPERTIES OF CONDENSED METAL DEPOSITS.

The physical properties of metal deposits may be classified under the three main headings of surface, optical and electrical properties. The adsorption, adherence, and catalytic activity of deposits fall into the first group; the absorption and reflection of light, change of phase by reflection and the magneto optical effects of Faraday and Kerr into the second; and the resistance, photoelectric and thermoelectric effects, the magneto electric effects of change in resistance in a magnetic field and the Hall effect and electrochemical effects into the third group. Of these properties the absorption and reflection of electromagnetic radiation by a film and the resistance of the film seems to have been studied by many investigators.

Optical Properties of Deposits.

Thick metal deposits of about 100-1000 Å., have, in transmitted light, colours characteristic of the metal. For example, silver appears blue, gold and copper green, caesium blue violet, and platinum, iron, nickel and bismuth gray. This characteristic colour is independent of the thickness of the deposit when it is greater than a critical value (Aron, 1946). In thin deposits, usually less than 100 Å., the colour depends on the thickness. It appears (Weinhart and Wehe,

1947) that the colour of deposits of given mean thickness depends on factors such as especially the residual gas pressure.

In the case of silver, which is especially considered here, Fritz (1915) found that the thinnest sputtered films $\approx 24\text{\AA}$. had a red colour and that the colour changed to violet and blue as the thickness increased. Goos (1936) and Rouard (1937) have determined the thickness of silver films corresponding to different colours. Their results are shown in Table I.

Table I.

S I L V E R.

GOOS	ROUARD
Evaporated Films.	Films Sputtered in Anthracene.
Pure blue 70A.	Indigo-blue 60A.
Bluish-pink 50	Purple 52
	Reddish-orange 43
	Yellowish 32
Grey pink 25	Orange gold 21
Yellowish 15	Clear orange 10
Pale Yellow 8	.

For gold, the colours occur at smaller thicknesses. The results of Goos (1937) and Rouard (1937) for gold are set out in Table II.

Table II.

G O L D.

GOOS	ROUARD
Evaporated Films	Films Sputtered in Anthracene.
Light bluish 50A.	Golden Yellow 40A.
Gray Green 25	Yellowish-green 40
	Green 32
	Blue 27
	Indigo 20
	Violet-red 15
Pure Grey 10	

Red, violet, blue and green films of evaporated gold have also been observed by Haringhuizen, Was and Kruithof (1937). Their values of thickness of the variously coloured films are much greater than those of Rouard. According to them the red, blue, and green films are 32A., 100A and 354A. respectively. Haringhuizen, Was and Kruithof also found that the red films were unstable and became blue on standing and that a colour change to red took place on heating a blue film at 150-250°C.

A colour phenomenon associated with a spontaneous disintegration of deposits of alkali metals was observed by

Wood (1919). He found that homogeneous films of sodium and potassium which reflect light with the brilliancy of silver could be deposited on a glass surface cooled with liquid air. On increasing the temperature a disintegration of the film into agglomerates, which was accompanied by the appearance of brilliant colours, was found to occur.

Fukuroi (1937) found that deposits of mercury, cadmium and zinc condensed on cold glass had brilliantly coloured reflections and that films which showed this reflection were not always transparent. He also found that a low rate of deposition, which would favour the formation of coarse grains, also favoured the appearance of the coloured reflections.

On the assumption that the optical constants (n and k) of a metal are fixed, the transmission and reflection from a thin film should show a regular variation with the thickness of the film (Kuidinger and Koller, 1938). Goos (1936, 1937) found for silver and gold that curves of transmission and reflection plotted against film thickness for films less than about 500A., however, exhibit for a particular wave-length region, a maximum and neighbouring minimum. For silver the transmission for λ 5780 A. light increased with increasing thickness in the range 140-180 A. A slight jump in the reflection curve was also observed at these thicknesses.

The same effect was observed for gold films in the range 100-200 Å. and λ 7000 Å. Haringhuizen, Was and Kruithof (1937) found that gold had an anomalous transmission for λ 6980 Å. light at thickness about 140-250 Å. and a rapid increase in the reflection at about 100 Å., which decreased at 150 Å. and increased again at 200 Å. According to them the anomalous behaviour in the optical constants takes place in the region of thickness in which the films show a colour structure. Ultramicroscopic examination of these films showed a particle structure. Since a film which consists of separated particles cannot possess a greater reflection than a thicker homogeneous one, the colours cannot be explained on the assumption of a granular structure only. On the assumption of a homogeneous layer and particles, and applying Lovell's theory (Lovell, 1936) of the decrease of the mean free path of electrons in a metal film below a critical thickness, Haringhuizen, Was and Kruithof were able to explain the anomalous transmission and reflection of gold films down to 70 Å. Below this thickness another effect, probably due to an amorphous structure of film, takes place.

Fukuroi explains his results on mercury, cadmium and zinc by postulating that the deposit consists of minute spheres of varying sizes distributed at random.

The optical constants of a thin film do not remain fixed, but change with time, the effect on the transmission,

especially in the infra-red, being much greater than on the reflection, and the effects increasing with decreasing film thickness. These changes take place in air and in vacuum, the rate of change in vacuum, however, being less than in air. Jagersberger and Schmid (1934) observed the transmission of a silver film in vacuum over a period of 70 days and found a gradual decrease whose rate increased on bringing the film into the air. After about another ten days an increase in the transmission was observed which reached a maximum value greater than the initial after the film had been about two months in air. Finally they observed a decrease again. The changes during exposure to air, however, may well have been due to chemical attack of the surface by impurities in the air.

The Electrical Resistance of Films.

It has been found that the specific resistance of the metal in a thin film, like the optical constants, is not unchangeable and is a function of the thickness of the film (Hamburger, 1931). Many investigators have found that the resistivity of the thinnest films is almost infinite and that the resistivity decreases rapidly with increase in thickness up to a critical value, after which it changes only very slowly. Colomb~~x~~ani (1942) found that the resistivity of films of Ni sputtered in hydrogen decreased exponentially

up to a thickness of 1780 Å. above which it became constant and equal to a value about 80 times that of the bulk metal. Reinders and Hamburger (1931) found that the resistivity of evaporated films of silver less than 100 Å. thick, was from 10^7 - 10^3 times that of the bulk metal.

The resistance of films deposited at low temperatures has been determined by many investigators. Suhrmann and Schnackenberg (1941) found that silver and gold films formed by evaporation in a high vacuum had an abnormally high electrical resistance. This, according to them, is due to the amorphous nature of the metal in these films. In 1934, Kramer (1934) had invoked the same idea of metals tending to have an amorphous state with a deficit in the number of valency electrons below a characteristic "transition" temperature in order to explain the very high resistances of some films. Above this temperature, the metal in the film crystallises out with the formation of an ionic lattice and the liberation of the electrons. Zahn and Kramer (1932) observed a sudden decrease in the resistance of films of Pt, Ni, Fe, Zn, Sn, Cd, and Sb at definite temperatures of the order of 510°, 336°, 440°, 133°, 180°, 150° and 446°K. respectively. This sudden decrease in electrical resistance has not been observed for silver (Suhrmann and Barth, 1934 and 1936) or Au, Cu, Cd and thallium (Suhrmann and Barth, 1936).

For antimony a transition temperature seems to have been observed by others (Mitchell, 1938) and it is probable that the Kramer theory of a transition temperature is true for antimony. It is interesting to note that electrodeposits of antimony explode with rising temperature (Mitchell, 1938).

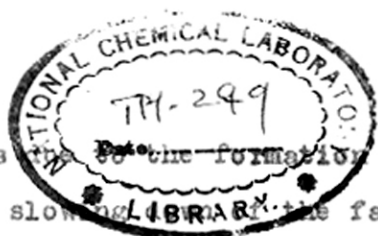
Lovell (1936) found that very thin low resistance films of the alkali metals could be obtained if deposition is made on a clean substrate in a high vacuum. He found that rubidium films of thickness $43\text{\AA}$. deposited on Pyrex glass at 64°Abs . had a specific resistance only 10 times that of the bulk metal. Thicker films, still under $100\text{\AA}$. had a resistivity about 5 or 6 times that of the metal. The conductivity could first be detected with a mean film thickness of only about $0.3\text{\AA}$. (Appleyard and Lovell, 1937). Lovell explained the increase in resistivity over that of the massive metal by the view that the film consists of coherent slices of metal and that the increase in resistivity is a result of the shortening of the mean free path of the electrons by collision with the boundaries. This view of the shortening of the mean free path was originally put forward by J.J. Thomson (1901).

The films undergo an irreversible change in resistance with time after production of the film. This spontaneous change, which is an increase in resistance for thin films

and a decrease for thicker ones is known as "ageing". Lovell (1936) observed only an increase in resistance with the alkali metal films of all thicknesses. (Some of his films were stable). He found that the "decay of conductivity" decreased with increase in film thickness and decrease in deposition temperature. Vand(1936) found that the ageing process for sputtered films of silver and gold was a hyperbolic decrease of resistance with time, a minimum value being approached asymptotically, slightly greater for a film in air than in vacuum.

Artificial ageing of a film takes place on heating or with the passage of a heavy current (Bartlett, 1928). Bartlett found that when gold films 300-700A. were maintained at any temperature below 300°C. there was a decrease in the resistance which was rapid at first and then slower. Films maintained at a temperature greater than 300°C. showed an increase in the resistance.

Suhrmann and Schnackenberg (1942) found a hyperbolic decrease in resistance of evaporated silver and gold films of thickness 100-1000 A. maintained at reduced temperatures. Mitchell (1938) found that at -115°C. zinc films condensed on polished quartz glass decreased in resistance rapidly at first but finally having a constant resistance. After a few hours another rapid decrease was observed, which slowed down again and became constant. According to him the initial



rapid fall in resistance is due to the formation of nuclei of crystallisation and the slow fall is a result of the slow growth of these nuclei. The second rapid fall is a result of the formation of new nuclei and the subsequent decrease in the fall is due to the growth of these nuclei. Mitchell found that increase of temperature caused the formation of the nuclei and the growth around them to be increased.

Fukuroi (1936) observed a decrease in the electrical resistance of films of mercury, cadmium and zinc on exposure of the film to ultra-violet light and explained it on a granular structure of these films and a photo-electric emission from the particles.

The Structure of Condensed and Sputtered Metal Films.

From the above observations of the optical properties and electrical resistance changes of thin metal films it thus appears that the films have some sort of granular structure. Using the optical microscope, however, the separate grains cannot be distinguished in deposits of, for example, thin silver and gold on glass substrates at room temperature. Various types of structure have been observed (Aron, 1946), however, on deposits condensed on hot substrates or heated after deposition on cool substrates. Aron found that films of silver produced by cathodic sputtering without sufficient

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precautions to avoid heating showed the existence of "domes" on the surface. Palladium films on glass substrates observed by Bredig and Allolio (1927) showed after catalysis a large number of clear lines of approximately constant spacing. The spontaneous formation of circular spots and their steady growth has been observed in films of platinum sputtered in oxygen by Finch, Murison, Stuart and Thomson (1933). The heating of a film after its formation usually brings about the appearance of holes or thin "windows" of irregular size and shape (Andrade and Martindale, 1936), (Essig, 1939). If the substrate is a single crystal, however, development of orientation and crystal habit in the deposit may result in a regularity in the shape of the windows. Essig (1939) found, for example, that when a silver film 1000-2000 Å. thick which had been evaporated on to a cold cleavage of muscovite mica previously baked in a vacuum at 450°C. was heated at 400°C. for several hours, the windows produced were bounded by straight lines which were parallel to the hexagonal axes of mica in the cleavage plane.

A granular structure of heated films seems to be the most common. The existence of these granules has been shown in a striking manner by Andrade and Martindale (1936). They examined in parallel plane polarised light films of silver about 200 Å. thick which had been heated to 230°C. for about one hour and found a particle structure which showed up as

black crosses. According to them, the cross is due to a particular type of crystal aggregate (Spherulites) which consists of a centre from which a number of fibres of uniaxial crystal radiate outwards. In the case of glass and fused silica glass surfaces, Andrade and Martindale observed a tendency of the crystalline particles to be arranged along a pattern of lines characteristic of a surface and according to them is strong evidence for the existence of submicroscopic surface cracks. After heating for one hour at about 350°C . octahedral crystals of the order of 10^4 A. in diameter were observable in the microscope.

The particle structure of films has been studied recently with the electron microscope. Marton and Schiff (1941), Hass (1942) and Picard and Duffendack (1943) studied the structure of evaporated films on collodion. Marton and Schiff found a particle structure in films of antimony and Hass that the crystallites in an aluminium film were smaller than in a silver one, those in a silver film about 550A. thick being of the order of 5000A. long. Picard and Duffendack found that films of Au, Al, Cu, Mg, Zn and Cd condensed at room temperature consist of metal particles separated by channels, the channel width varying from metal to metal. In very thin films of gold, which showed no colour, the particle size was about 25A., and even thicker films of Al, Cu, and Mg which reflected light well showed the presence of large

aggregates which were separated by channels of width about 100-500 Å. - some ten times smaller than the wavelength of visible light. As the thickness of the film increased, the aggregates increased in size and with very thick deposits complete covering of the substrate was obtained. Picard and Duffendack found that zinc and cadmium films which had a poor reflectivity consisted of large crystals separated by larger blank spaces which were of the order of the wavelength of light. These metals condensed on collodion at liquid air temperatures still gave poor reflecting surfaces but condensed on glass at the same temperatures they yielded fine mirrors. In the case of zinc warming to room temperature caused the mirror to disappear, but cadmium films retained their reflecting surface.

The first direct evidence of the extent of occurrence of crystal structure and arrangements (size, shape, orientation twinning, etc.) in thin metal deposits was provided by electron diffraction and by now much information has been obtained. It seems probable that, with the exception of antimony deposited at liquid air temperatures and As, Sb and Bi electrodeposits prepared under certain conditions at or near room temperature, the material in a thin film is in a crystalline form. Hass (1937) found that Sb deposited at -175° gave two weak rings corresponding to an amorphous structure. Electron diffraction patterns corresponding to

an amorphous structure have been obtained by RamaSwamy (1936) from thin evaporated layers of silver (orange colour) and gold (deep red) on mica. He found that thicker films showed a polycrystalline structure. On the other hand, Krautkramer (1938) found that films of silver and gold of thickness 20-280A. deposited on fused quartz are not amorphous but are composed of crystallites.

From optical studies Haringhhuizen, Was and Kruithof (1937) concluded that gold films below 70A. are amorphous. Was (1939), however, obtained diffuse electron diffraction ring patterns which became more diffuse with decreasing thickness, from evaporated gold films of thickness 200 (green), 50 (blue) and 15 (red) A. According to him, a crystallisation of the film takes place due to the action of the electron beam. Was found that thin films showed a drop in the electrical conductivity due to agglomeration when an electron beam falls on them. Very thin films - below 20A. and thick ones did not show this effect. By ultra-microscopical examination Was and Tol (1940) were able to prove a change in the structure of gold films on exposure to electrons. They found that the point of impact of a red, gold film and a beam of electrons turns grey and that the electrons moving over the surface produce a blue track. Red and blue films on nitro-cellulose transmission specimens which were exposed to an electron beam showed that the material of the film near the

region of impact had collected on a few crystals.

The particle size, kind and extent of the orientation in a metal deposit, as shown by electron diffraction, depend to a marked degree on the temperature and nature of the substrate. If the temperature of the substrate is low and the mobility of the deposit atoms on the substrate or the deposit be small, amorphous films or films with very small crystals are formed (Finch and Wilman).

Gen, Zelmanoff and Schalnikoff (1933) found that Cd, Hg, Ni and Fe deposited on glass at liquid air temperatures give diffuse ring patterns and that much sharper rings are obtained from films at room temperature. Hass (1937) found the same effect with silver deposits. He also found that the increase in crystal size with temperature was more marked in the case of thin films than thick.

RamaSwamy (1934) found that the crystal size in sputtered films of gold, when heated, was greater and increased at a greater rate in thick (620A.) than in thin films (180A.). Andrade and Martindale (1936) also found that the appearance of "spherulets" takes place at a lower temperature with thick films. Simultaneous heating in vacuo of two silver films 220A. and 30A. thick respectively at 260°C. for 3 hours produced "spherulets" in the thick film but not in the 30A. one in which they appeared only on heating at 420°C.

If the substrate is amorphous and plane to the order of atomic dimensions one degree orientation in which, as a rule, the most densely-packed atom plane is in contact with the substrate surface, is produced (Finch and Wilman). RamaSwamy (1934) found for gold on quartz that heating at 430°C . for an unspecified time produced an orientation of the crystallites with the (111) planes parallel to the substrate in the case of a film 180A. thick and the same orientation with a film 620A. thick only on heating at 640°C . Andrade and Martindale (1936) also found the (111) orientation in heated films of silver and gold on glass of initial mean thickness 100-500A.

Burgers and Dippel (1934) found that the orientation of the crystallites in layers deposited on glass is affected by the direction of the vapour stream and that there is a tendency for the orientation axis to point towards the direction of the source. They found that layers of CaF_2 of thickness 1000A. were oriented with the (111) planes parallel to the substrate when the incidence of the beam of vapour was normal and that strongly oblique incidence caused a slight inclination of these planes. According to them the slight tilt of the orientation axis is due to the fact that although (111) planes normal to the vapour stream receive more matter and can grow faster and do yield larger crystallites, planes parallel to the surface possess the advantage that they can grow in both directions sideways and would consequently yield

crystallites with larger surfaces and the maximum rate of growth would therefore occur for planes between these two directions. Burgers and Dippel found that an angle of incidence of the vapour stream of about 65° caused a tilt of the planes by about 10° to the surface.

Burgers and Ploos van Amstel (1936) observed the same effect with barium. The tendency of the orientation axis to point towards the source in the case of aluminium was observed by Beeching (1936). He found that the cube face is tilted at about 15° to a glass substrate when the direction of the incident vapour is 45° to the surface.

If the substrate is a single crystal various two-degree orientation of deposits are usually developed above characteristic temperatures. In the case of silver and gold Lassen (1934), Lassen and Bruck (1935), Kirchner and Lassen (1935), and Bruck (1936) found that condensation from the vapour on heated rock salt cleavages produced deposits which are oriented with the (100) plane parallel to the cube face of the substrate and the cube edge of the metal parallel to that of the rock salt. With silver films of about 1000A. long they obtained a practically single crystal structure giving spots and Kikuchi lines, when the vapour was deposited on to a substrate at 150°C . With thinner films extra spots and streaks were obtained which Menzer showed to be due to a

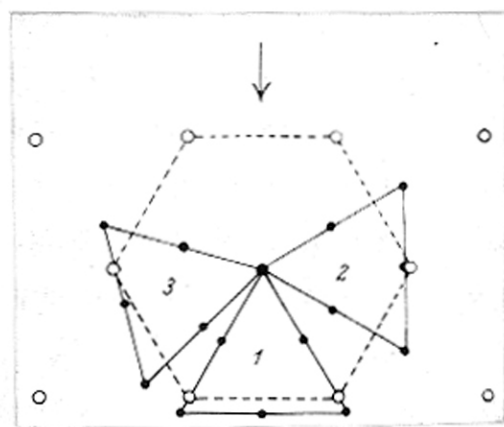


Fig 1.

twinned structure of the films (see e.g. Goche and Wilman, 1939).

The structure of evaporated films of silver and gold of thickness 100-1000A. on mica was studied by Rudiger (1937). He obtained a two-degree orientation of the crystallites with the (111) planes parallel to the substrate, when the evaporation was conducted with the substrate maintained above a certain temperature which is a characteristic of the metal. Rudiger found three types of complete orientation of the (111) planes as shown in Fig.1 as 1, 2 and 3, the direction of the beam being indicated by the arrow. The behaviour of thick and thin silver films was the same, the one degree orientation first appearing at 20°C. and becoming complete at 150°C. A silver film 900A. thick deposited at 150°C. showed moderately large crystals which were accurately orientated parallel to one another in 1 or 2. At 380°C. Rudiger observed all three types of two degree orientation in the same film simultaneously. Thinner films - about 100A. gave the same type of pattern but indicated very small crystal size. The behaviour of gold films was somewhat different. With films 1000A. thick, the beginning of orientation occurred at 300°C. and became complete at 360°C., the pattern from films prepared at this temperature consisting of streaks perpendicular to the shadow edge. With thinner films (200A.), two degree orientation and spot

patterns of the type given by silver were obtained at 460°C. According to Rudiger, the orientation in a thick film is confined to the upper layers and he was able to verify this hypothesis by reflection and transmission photographs from the same specimen, which showed a random orientation of the crystals near the substrate.

The occurrence of two degree orientation in a deposit depends on the existence of some similarity of structure of deposit and substrate (Finch and Wilman). According to Bruck the particular type of two degree orientation obtained is such as to make the sum of the distances between nearest atoms in the deposit and substrate a minimum. Rudiger's films of silver and gold on mica, however, do not confirm this suggestion.

By passing a beam of electrons through a stream of vapour Finch and Quarrell (1933) proved that in the process of evaporation the material released is in the form of a gas without structure. The crystalline nature of the matter in a film must therefore be due to an aggregation of these atoms of vapour after deposition. Indeed, the phenomena of the increase in crystal size and production of orientation with increase in temperature, of the spontaneous disintegration of films on standing and perhaps indirectly the particle aspect of the film itself, testify to marked atomic

arrangements and rearrangements resulting from a high mobility of atoms at the surfaces of the substrate and film, at temperatures which are far removed from the melting point of the metal. Ample direct evidence for such mobility has been obtained by many workers. Estermann (1933) and Cockcroft (1928) have observed the motion of sparsely distributed matter over a substrate and Volmer (1925) the motion of atoms over a crystal of the same material. According to Andrade and Martindale (1936) and Appleyard (1937) and Lovell (1936) such motion of atoms can also take place under surface tension forces. Sir George Beilby (1921) has illustrated the analogy between the break up of liquid films into globules and the aggregation of more or less uniform solid layers into separate particles. Similar photographs of the stages in the break up and aggregation of silver films on glass have also been published by Lubszynski and McGee (1939).

According to Lennard Jones (1932) the periodic structure of a surface has, associated with it, a series of equipotentials and at low temperatures an atom on the surface is held in a pocket of low potential, at the lowest vibrational level. At raised temperatures, the atoms acquire sufficient energy to climb the potential barrier between pockets and free motion on the surface results. Considerably higher energies are, however, required to remove an atom completely from

the surface (evaporation) and this accounts for the mobility of atoms at temperatures far below the melting point. The mobility seems, however, to be dependent on the melting point occurring at a much lower temperature for mercury and cadmium than for silver and gold.

A picture of the growth of a film from the vapour, and the changes in its structure on standing and on heating may be formed thus. Atoms with considerable energy deposited from the hot source on to a comparatively cold substrate retain a part of their energy on impact and consequently move about freely on the surface of the substrate, colliding with each other - the path between impacts being probably short, perhaps only a few tens of Angstroms and in general resembling a two dimensional gas. (In the case of silver atoms Stern (1920) found that the velocity of the atoms evaporated from a source at about 1000°C. was 600 metres/sec. in good agreement with the Kinetic Theory of Gases). Under suitable conditions of impact, such as when a part of the energy is handed to a third body or dissipated in the form of radiation, a nucleus of growth in the form of an aggregate of two atoms takes place. Growth then occurs by addition of other atoms to this nucleus and usually form themselves into crystalline arrangements approximating to the normal structure, even in particles as small as 20A. diameter. The film at this stage consists of islands of isolated crystallites. The

size and separation of the crystallites would depend on the height of the potential barriers on the surface of the substrate for the particular atoms deposited. For substrates of glass and collodion and deposits of zinc and cadmium it is probable that the potential wells are shallow relative to those on the already formed crystals, since these metals deposited at room temperature give large crystals scattered on the substrate (Picard and Duffendack, 1943) and that for cadmium on glass it is deeper than for zinc, since the latter metal deposited at liquid air temperatures aggregated rapidly into large crystals on increase in temperature. The fact that Zn and Cd films condensed on collodion at liquid air temperatures do not yield uniform deposits indicates that the potential wells in collodion are very shallow. Picard and Duffendack obtained uniform deposits of aluminium, copper, and magnesium on both glass and collodion. The potential wells in these cases must therefore be quite deep relative to those on the crystals and the fact that Al crystallites are much finer than those of Ag (Hass, 1942) seems to indicate that the potential barrier with aluminium is one of the highest. Very few actual determinations of the energies required by atoms to traverse these potential barriers have been made.

As deposition proceeds, growth of all crystallites and an increased preferential growth in some, occurs by direct

condensation on the surfaces and also from the transfer of atoms from some crystals to others, until finally the crystallites touch each other and with further deposition a porous film is obtained. On this picture the ageing of a very thin film can be explained as the breaking up of the film under the action of surface tension forces (Appleyard, 1937) or the production of a fine network of cracks as a result of a differential expansion between substrate and deposit or contamination of the deposit by traces of organic material (Finch, 1937). In thick films, it takes the form of a settling down of the porous deposit (Appleyard, 1937).

The acceleration of the ageing process and the orientation and rapid crystal growth of films on heating are a direct result of the greatly increased mobility of atoms at raised temperatures. Goche and Wilman (1939) found that heating a detached silver film of about 500A. for about 4 minutes at a temperature between 500-600°C. caused extensive atomic rearrangement in the film and resulted in the formation of perfect single crystals free from twinning. Andrade and Martindale (1936) working with the microscope found that heating a silver film 200A. thick on quartz for about an hour at 230°C. produced the first signs of recrystallisation in the form of small aggregates, and at 600°C. they observed octahedral crystals.

With gold, the temperature at which atoms develop much

mobility is higher and the crystal size in recrystallised films smaller than with silver. (Andrade and Martindale, 1936). RamaSwamy (1934) and Andrade and Martindale (1936) agree in finding a rapid increase in crystal growth at 400°C. for films on quartz. Rudiger obtained two degree orientation on mica at 460°C. and Bartlett found an increase in the resistance of sputtered films when maintained at a temperature greater than 300°C.

The recrystallisation of gold foils has been found by Preston and Bircumshaw (1936) to start at about 450°C., when the heating is in air. The temperature at which recrystallisation takes place in vacuum seems to be higher. Finch and Fordham (1937) found no recrystallisation up to 550°C. and Preston and Bircumshaw (1936) up to 700°C. According to Trillat and Oketani (1937) the recrystallisation in vacuum and air takes place only at temperatures greater than 650°C.

The difference in behaviour of thick and thin films seems to indicate the existence of a comparatively stable layer of the deposit immediately in contact with the substrate and a greatly increased mobility of the atoms of the deposit on the surface of the film.

I. 4. THE STRUCTURE OF MICA AND QUARTZ SUBSTRATE SURFACES.

The Structure of Muscovite Mica.

The micas were first examined by Tschermak, who suggested for muscovite a monoclinic unit cell with a centred rectangle of sides a and b as base and a monoclinic angle of 95° .

An X ray examination of the micas was first made in 1927 by Mauguin (1927, 1928). He determined the unit cell, the space group and the number of atoms in the unit cell. For the unit cell of muscovite he gave the values $a = 5.17\text{\AA}$, $b = 8.94\text{\AA}$, $c = 20.0\text{\AA}$ and $(a,c) = 96^\circ$. Mauguin considered muscovite as a stacking together of thin plates of thickness $9.95\text{\AA}$ which occurred in pairs and were identical.

The general scheme of structure for all the micas and micaceous minerals was given by Pauling in 1930. He considered the structures in terms of "octahedral" and "tetrahedral" layers and was able to explain the easy cleavage and give the sequence of atomic planes parallel to this plane. The first complete analysis of structure of muscovite was given by Jackson and West (1930, 1933). They established the parameters of the atomic co-ordinates, that is the precise way in which the atomic sheets parallel to the cleavage planes are stacked one on top of the other.

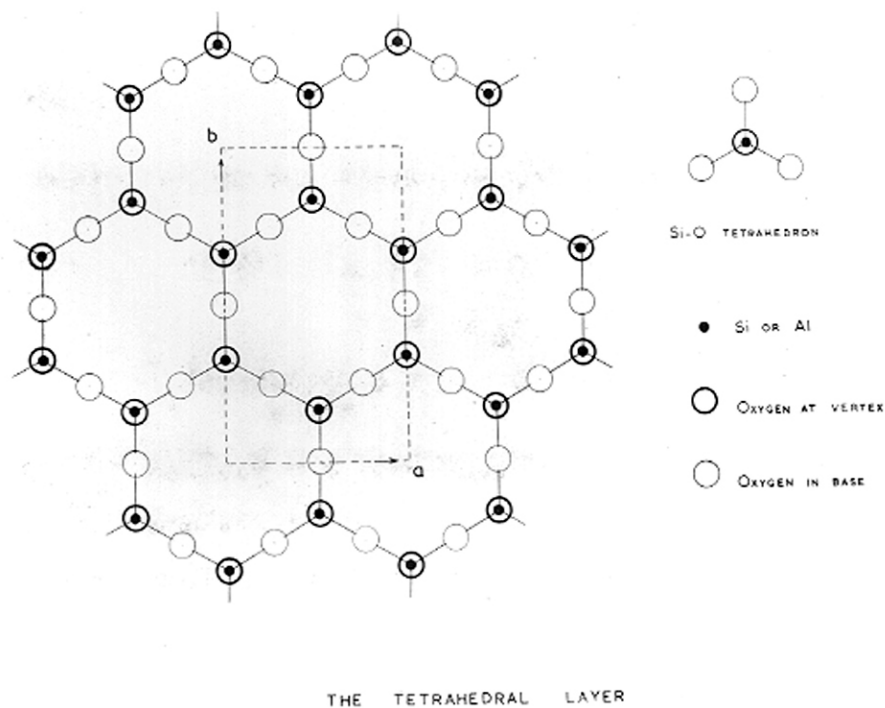


Fig 2.

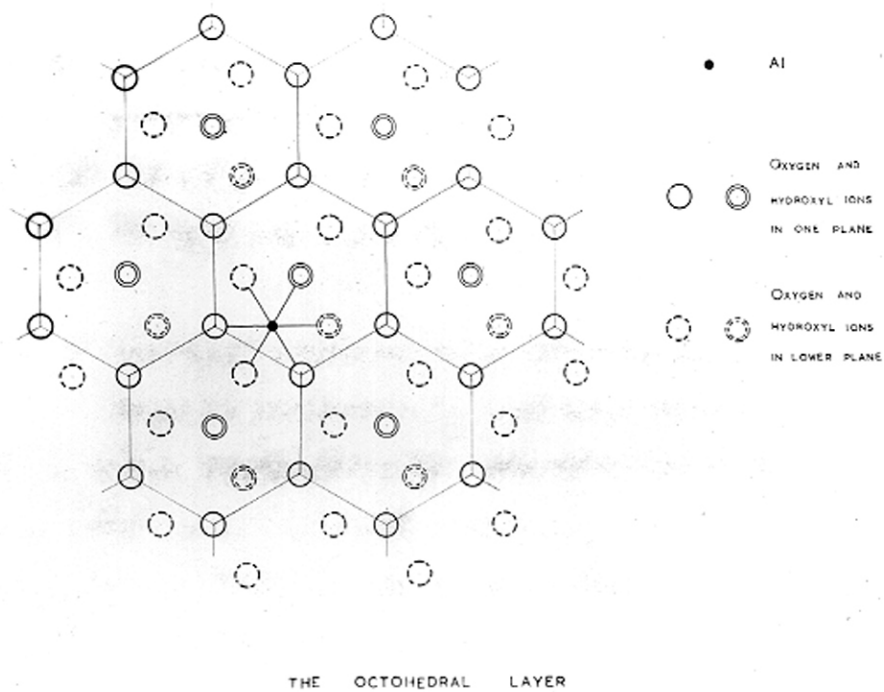


Fig 3.

Jackson and West's results for muscovite are as follows:-

Unit formula:	$K Al_2 (AlSi_3 O_{10}) (OH)_2$
Space group:	$C_2^6 h = C_{2v}$
	Z = 4 Structural units per cell.
Lattice:	Monoclinic $a = 5.18 \text{ \AA}$, $b = 9.02 \text{ \AA}$, $c = 20.04 \text{ \AA}$. $\beta = 95^\circ 30'$

According to Bragg (1930) in all the silicates that have been examined silicon always occurs between four oxygen atoms and the silicon oxygen bond is so strong that the four oxygen atoms are at the corners of a tetrahedron of nearly constant dimensions and regular shape, the silicon oxygen distance being about 1.6 Å. The characteristic feature of the micas and clays, which groups them together and imparts a pseudo-hexagonal symmetry to the structure is the hexagonal network of linked tetrahedra forming layers parallel to the cleavage plane. The structure given by Jackson and West may be considered thus:-

Three corners of each silicon-oxygen tetrahedron are linked to neighbours such that the vertices of each tetrahedron point the same way and a hexagonal arrangement of a silicon oxygen sheet is formed (Fig.2). The sheets constitute the so-called tetrahedral layers in the structure. The silicon in one quarter of the silicon oxygen tetrahedra in a sheet is replaced by four coordinated aluminium atoms.

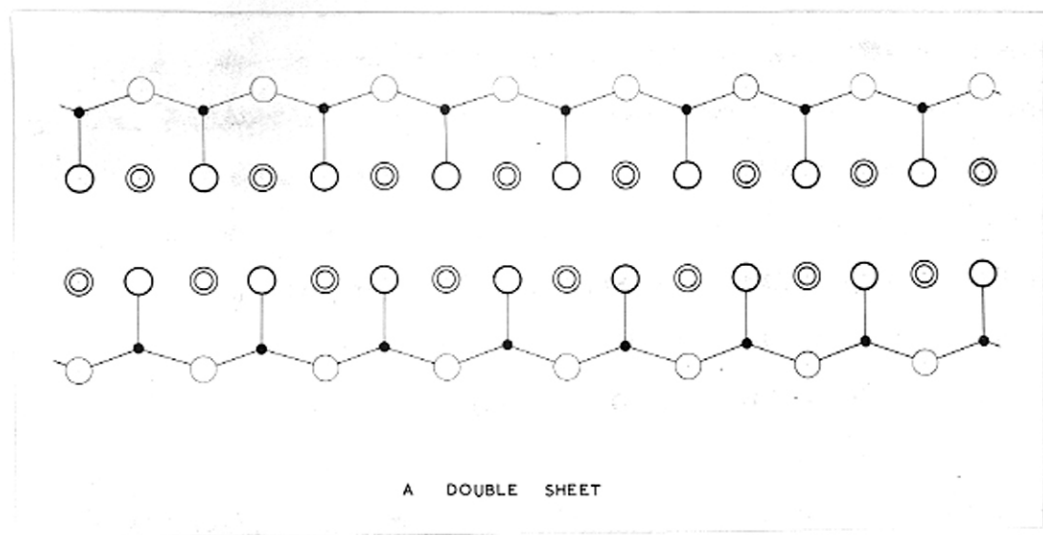


Fig 4.

An "octahedral" layer consists of two sheets of each, containing both oxygen ions and hydroxyl ions in close-packed array and may be considered as formed by placing an OH group at the centre of one of the hexagons in Fig.2 and in the plane of the oxygen atoms at the vertices of the tetrahedra in the layer (Fig.3). The disposition of the second sheet relative to the first can be obtained by considering the first sheet displaced in a direction making 30° with the b axis and through a distance equal to a third of the a axis. Thus, there are two sheets of atoms, each atom of one resting on three atoms of the other. The holes formed by groups of six atoms are occupied by six coordinated atoms of aluminium. Since the oxygen atoms at the vertices of a tetrahedral layer have the same spacial distribution as the oxygen atoms in a sheet of an octahedral layer, two tetrahedral layers can be placed, one on each side of an octahedral layer, with vertices pointing towards each other such that the oxygen atoms in the octahedral layer coincide with those at the vertices of the tetrahedra in the tetrahedral layers. (Fig.4). The mica structure consists of a pile of such double sheets placed parallel to the plane of cleavage. The double sheets are firmly bound and in the large cavities outlined by a succession of double sheets, potassium atoms occur with 12-coordination. When a sheet of mica is cleaved it separates very exactly along planes in which the potassium atoms are situated.

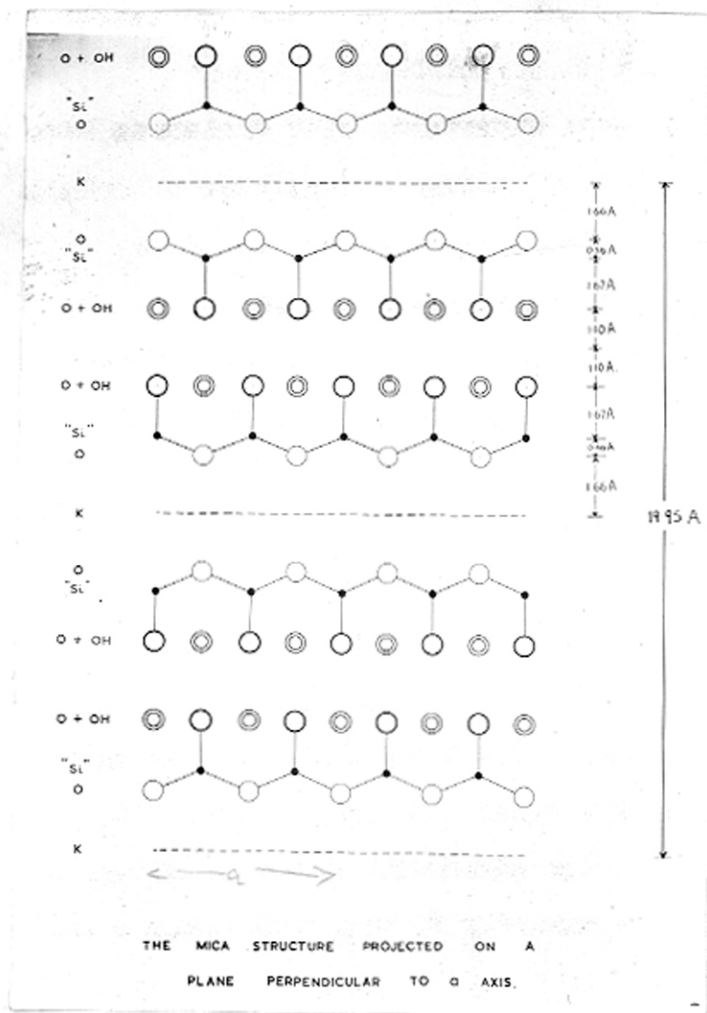


Fig 5.

The pseudo hexagonal symmetry of mica in the cleavage plane which arises from the hexagonal symmetry of the single tetrahedral layer is reduced to monoclinic in the whole structure due to the manner in which two tetrahedral layers are linked through an octahedral layer.

The complete structure, with distances between successive layers of atoms in Angstroms calculated from Jackson and West's paper is shown in Fig.5.

Diffraction of Electrons by Mica.

The first experiments were made by Kikuchi (1928). By tearing off a thin layer from the face of a thicker sheet, he was able to obtain specimens thin enough to allow an electron beam to pass through them. Kikuchi distinguished three types of pattern obtained by transmission flakes. The thinnest specimens gave an extended array of spots (he called it the N pattern) arranged at the corners of equilateral triangles. With thicker flakes, the L pattern, consisting of spots on circular zones and black and white Kikuchi lines were obtained. When the thickness of the flake was so large that the central spot entirely disappeared, only a number of black and white lines and bands were observed. The last type of pattern was called the P pattern. More recent illustrations of these changes of pattern type with crystal thickness have been published by Kirchner (1932), Finch,

Quarrell and Wilman (1935) and Finch and Wilman (1937¹).

When the flake is distorted extra spots are obtained. (Steinheil, 1934; Finch, Quarrell and Wilman, 1935; Darbyshire and Cooper, 1935; Finch and Wilman, 1936¹; Finch and Wilman, 1937³).

Reflection experiments with cleavage faces have been made by Darbyshire (1933). He obtained streaks at right angles to the shadow edge. With distorted specimens the streaks appear in a much wider area of pattern than that in which they usually occur.

Heated Mica.

Although some investigations on the diffraction of X rays by heated mica have been performed, it does not appear that electron diffraction has been applied to a study of structural changes that may take place on heating, although Eisenhut and Kaupp (1931) heated deposits of gold and copper on thin mica transmission specimens to study alloy formation.

In 1929, Linnik (1929) passed a beam of Cu X radiation through a sheet of mica heated to red heat and cooled. He supposed that by heating the crystalline mass of mica was cleft into very thin separate layers which maintained their orientation, but were displaced normal to the surface. He explained the X ray pattern as a "cross-grating" effect produced as a result of the space effect being destroyed

due to incoherence of scattering from the randomly spaced layers.

Hendricks (1929) has also obtained X ray photographs from heated mica similar to the one given by Linnik. According to him the pattern is a three dimensional diffraction effect from a micaceous crystalline mass in which individual crystal fragments diverge from parallelism with the surface. Microscopic examination showed the existence of fragments inclined to the cleavage plane. None of the fragments was rotated about the normal to the surface.

Powell, Griffiths and Wood (1937) studied the X ray structure in connection with the variation of the thermal conductivity of some micas with temperature. They observed no change with muscovite on heating up to 600°C., but certain phlogopites showed a marked decrease in conductivity at 200°C. X ray photographs of heated specimens which showed this change revealed that individual mica crystals became tilted between $\pm 5^\circ$, at this temperature.

Hendricks (1929) found that natural crystals of kaolinite - $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ - give X ray photographs similar to those obtained from heated mica and Gruner (1939) has observed a conversion of muscovite to kaolinite on heating with hydrochloric acid at 300°C.

A recent determination of the structure of kaolinite by

Brindley and Robinson (1946) gives a triclinic unit cell with $a = 5.14\text{\AA}$., $b = 8.93\text{\AA}$., $c = 7.37\text{\AA}$.; $\alpha = 91.8^\circ$, $\beta = 104.5^\circ$, and $\gamma = 90^\circ$.

Many investigators have studied the dehydration and decomposition of kaolinite on heating. According to Lapparent (1937) a little water is given out at 100°C . This terminates at 200°C . and the principal dehydration takes place between 500° - 600°C . Between 900° - 1000°C . there is a strong exothermic effect. A definite decomposition point near 500°C . seems to have been recorded by many investigators. Insley and Swell (1935) found it at 550°C . as a broad endothermic effect which they attributed to dissociation into water and a mixture of amorphous Al_2O_3 and SiO_2 from which the crystallisation of Al_2O_3 occurred at 950°C . According to Nakai and Fukami (1933), the break up of the crystal structure occurs at 350 - 400°C ., a completely amorphous product is obtained at 780°C . and the crystallisation of Al_2O_3 occurs at 900 - 1000°C . An electron optical examination of changes produced in kaolinite by heating has been made by Eitel, Muller and Radczewski (1939). They found that the finest fractions of kaolinite consisted of hexagonal laminae with sharp edges which lost their definition on heating at 500 - 600°C . The faces, however, remained smooth. At 800 - 900° the pseudo-morphs of SiO_2 and Al_2O_3 resulting from the

dehydration and decomposition were in the form of fine particles and crystallised out to large crystals on heating above 1000°C.

The partial dehydration of endellite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) yields a structure (halloysite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) consisting of a superposition of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ layers, similar to that obtained in kaolinite (G.W.Brindley and K.Robinson (1946)). Whereas, however, in an ideal kaolinite there is a perfectly ordered sequence of the layers, in halloysite the layers are stacked regularly in the direction of the c axis but there is a random orientation of the layers in their own planes. X ray diagrams of halloysite show broad basal (001) reflections corresponding to 7.4Å. The reflection becomes sharp and the spacing decreases to about 7.2Å. when the halloysite is heated at temperatures from 100°-350°C. The spacing is, however, always greater than 7.14Å. - the normal value for kaolinite. According to Brindley and Robinson the increased spacing is due to the usually incomplete dehydration of the water layer (3.0Å.). There is, according to them, a possibility that between kaolinite and the ideal halloysite (where there is completely random orientation of the individual layers) there exists a group of minerals with various degrees of randomness in the ordering of the layers.

The Structure of Silica.

Silica is known to exist in different forms - as vitreous silica, quartz, tridymite and cristobalite (See, for example, Bragg "Atomic Structure of Minerals", 1937). The structural unit in all the forms is the silicon oxygen tetrahedral group. It seems to be established that quartz, tridymite and cristobalite are crystalline forms of silica in which the Si-O tetrahedra are linked in definite and different ways. In all the forms, however, each oxygen in a tetrahedron is shared by another silicon and the silicon oxygen ratio becomes SiO_2 . The stable form of crystalline silica is quartz (Bragg). When quartz is heated, tridymite is produced at 870°C . and at temperatures $> 1470^\circ\text{C}$. the stable form is cristobalite. Unless cooled very slowly, however, silica remains in the form of tridymite or cristobalite in a metastable state at lower temperatures. All three forms have a low and a high temperature modification (α and β), the change from the high (β) to the low (α) taking place easily and quickly merely by displacement and a rotation of the tetrahedra, whereas the changes from cristobalite to tridymite or tridymite to quartz require breaking of the linkage and thus these transformations only take place slowly and with difficulty.

In view of the recrystallisation of quartz referred to below it seems to be desirable to consider the structure of the various forms of crystalline silica. These are set down

in tabular form below.

Table III.

Form	Lattice	Unit Cell
α Quartz ¹	Hexagonal	$a = 4.903\text{\AA.}, c = 5.393\text{\AA.},$ $c/a = 1.099$
β Quartz ²	Hexagonal	$a = 4.989\text{\AA.}, c = 5.446\text{\AA.},$ $c/a = 1.09$
α Tridymite ³	Rhombic	$a = 9.88\text{\AA.}, b = 17.1\text{\AA.}, c = 16.3\text{\AA.}$
β Tridymite ³	Hexagonal	$a = 5.03\text{\AA.}, c = 8.22\text{\AA.},$ $c/a = 1.63$
α Cristobalite ⁴	Rhombic	$a = 7.00\text{\AA.}, b = 7.00\text{\AA.}, c = 7.00\text{\AA.}$
β Cristobalite ⁵	Cubic	$a = 7.12\text{\AA.}$

1. Gibbs(1926)¹. 2 Bragg and Gibbs(1925). 3. Gibbs(1926)².
4. Barth(1932). 5. Wyckoff(1925).

The structure of vitreous silica (silica glass) has been determined by Warren (1933, 1934) and Randall, Rooksby and Cooper (1930) using X rays and by Maxwell and Mosely (1935) and Kamogawa (1938, 1940) by electron diffraction. By etching the glass in a thin walled bubble with hydrofluoric acid, Maxwell and Mosely were able to obtain transmission patterns of silica glass. They found strong scattering at small angles and a prominent ring and a diffuse one at $(\frac{1}{\lambda}) \sin \theta_2 = 0.12$ and 0.40 respectively. In addition to these they sometimes obtained sharp spots and partially completed circles, whose identity they were unable to establish, corresponding to Bragg spacings of $4.2\text{\AA.}(S)$,

3.7A.(S) and 2.52A.(W). Kamogawa (1938) found that the studied the effect of heating amorphous films of SiO_2 . film obtained by evaporating silicon in vacuum on to rocksalt. He heated films at 400°C. for 2-3 hours and found the and dissolving the substrate in water consists of diffuse appearance of a ring at $\lambda = 4500\text{\AA}$. rings at $(\frac{1}{\lambda}) \sin \theta_2 = 0.12(\text{S}), 0.29(\text{W}), 0.40(\text{M})$ which according to him is due to amorphous silica resulting from a spontaneous oxidation of the silicon in air. From the freshly polished surface of glass, Kamogawa (1940) obtained halos at $(\frac{1}{\lambda}) \sin \theta_2 = 0.13, 0.20$ and 0.37 . Since these values are different from those obtained in transmission experiments, he concludes that the structure of the polished surface is different from the glass inside.

According to Randall, Hooksby and Cooper (1930), silica glass is made up of extremely small crystallites of cristobalite of average size about $15\text{\AA}$. They obtained by X rays a strong ring due to cristobalite, when the glass was heated at 1200°C . for a few hours. According to Warren the structure is non-crystalline, being built up on a random network of tetrahedral groups, each group having four nearest neighbours at $3.1\text{\AA}$. and twelve next nearest at $5.0\text{\AA}$.

Recrystallisation of Amorphous Silica.

Bresler, Strauff and Zelmanoff (1933) found that a recrystallisation of an amorphous film of quartz obtained by vaporisation in vacuum occurs when it is heated for about 2-3 hours at a temperature of 400°C . Kamogawa (1938) has also

studied the effect of heating amorphous films of SiO_2 . He heated films up to 800°C . for 3 minutes and found the appearance of many weak diffuse rings at about 450°C .

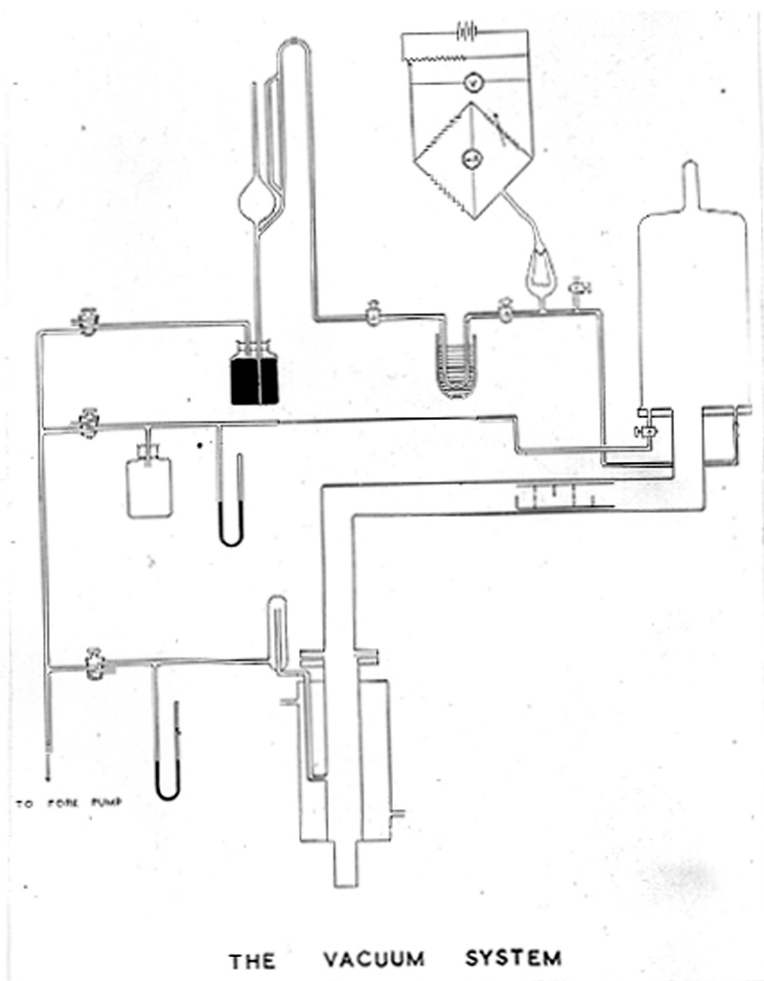


Fig 6.

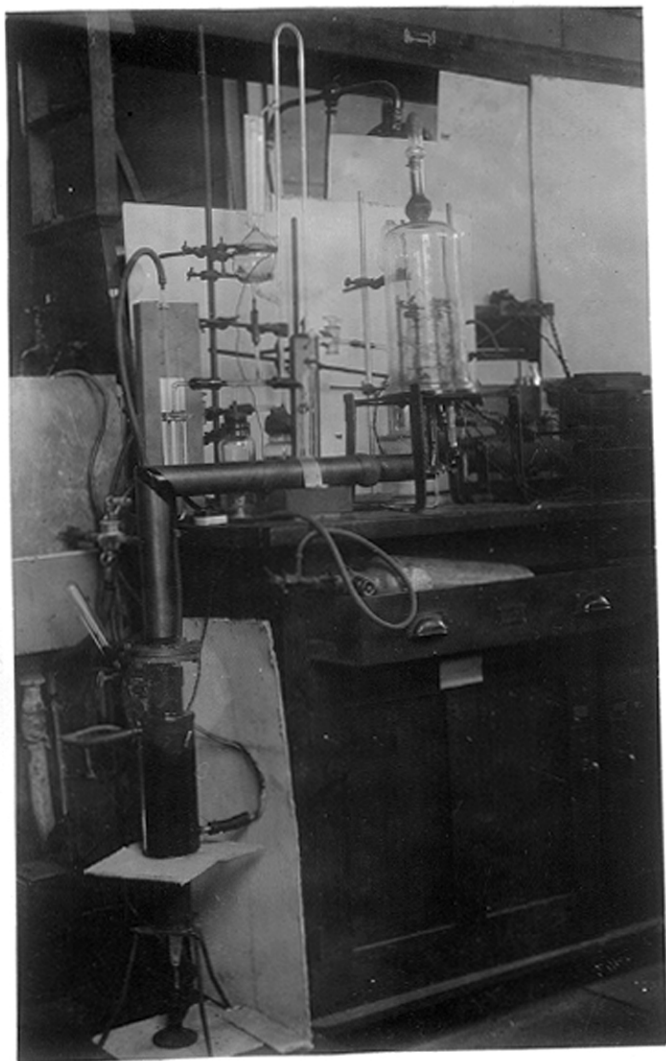


Fig 7.

II. EXPERIMENTAL TECHNIQUE USED IN THE PRESENT INVESTIGATIONS.

II. 1. Preparation of the Deposits.

The vacuum chamber in which the deposits were made and the heating in vacuum conducted (both for the deposits and the work described below in Part IV) consisted essentially of a base plate and a bell jar.

The experiments described have been performed in two different systems. The first used had a silica mercury diffusion pump and was able to get down to a pressure of 5×10^{-3} mm. of mercury. In the later system a steel mercury diffusion pump was employed and together with very wide channels for evacuation of the bell jar enabled a limiting pressure of 10^{-4} mm. to be realised in about 15-20 minutes after the pumps were started. A diagram of the system is shown in Fig.6 and a photograph in Fig.7.

The base plate of brass (Figs.8 and 9) was about $\frac{1}{2}$ " thick and $7\frac{1}{2}$ " in diameter. It had a lapped surface about $\frac{1}{8}$ " high and $1\frac{1}{4}$ " wide on which the vacuum seal to the bell-jar was made with grease. The main pumping inlet at the base plate was 2" in diameter. The speed of pumping could be controlled by a butterfly valve which was operated from outside through a ground glass joint by which it was

rotated by means of a sealing wax plug which did not prevent the withdrawal of the outer part of the ground joint for cleaning and regreasing. For the main mercury vapour trap tinfoil was used, introduced into the pumping line about 12" from the chamber. It consisted of a framework of iron wire in the form of circles laid one on top of the other, at distances of about 5 cms. and joined together. Semi-circular pieces of copper gauze with tinfoil laid on them were fixed by bending and pressure on the circles in such a manner that an indirect pumping path without much reduction in pumping aperture was obtained over a length of about 25 cms.

A second $\frac{1}{8}$ " diameter tube through the base plate connected the chamber to pressure gauges and a tap by which air could be let in to the system to atmospheric pressure. A third inlet allowed a controlled leak of air or gas into the chamber to be made when required. This was obtained by a capillary tube throttle fed from a reservoir of gas at a reduced pressure which could be adjusted. With this arrangement an evaporation could be performed at any desired pressure.

Conducting wires for heating currents and thermocouples for measurement of temperature were led into the chamber through a brass disc about 1- $\frac{3}{8}$ " diam. and $\frac{3}{8}$ " thick which fitted into a hole cut in the plate. Six independent

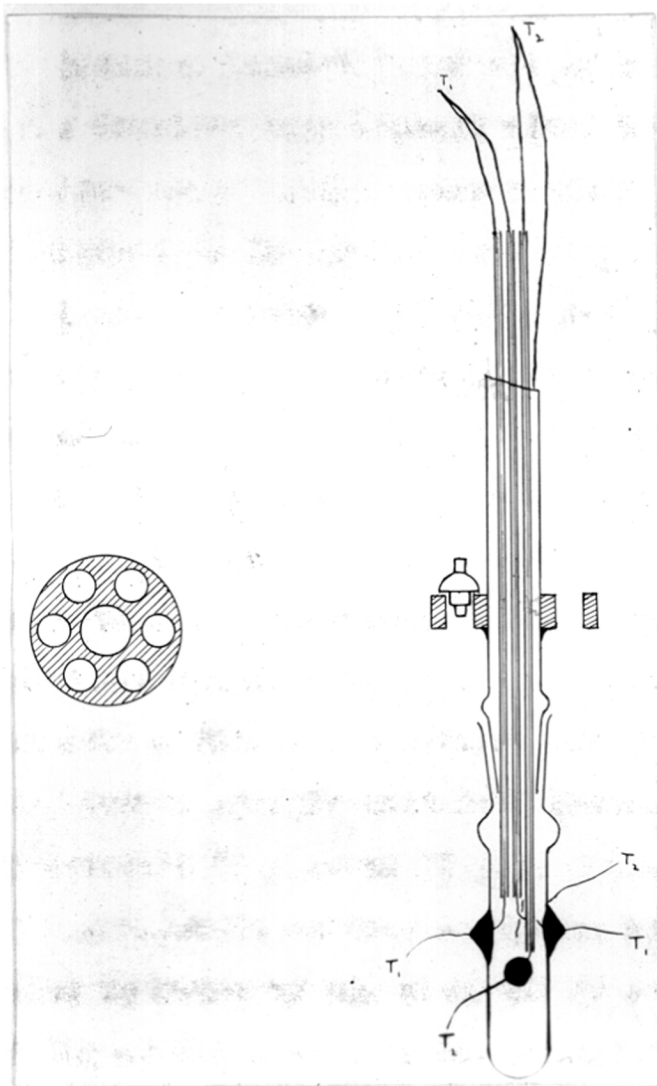


Fig 10.

electrodes for heating were introduced into the system through this disc. Electrical connections which were robust and electrically insulating were obtained by use of glass to metal Kovar seals. The central conductors of the seals passed through six holes drilled symmetrically in the disc (Fig.10) and their flanges were soldered all round so as to make the joints vacuum tight. Wires soldered on either side of a seal gave electrical connection between the chamber and outside. Two thermocouples were let into the chamber through the same disc. The four wires were taken out through four holes in a ground joint and the wires sealed with Picein wax, which was also used to seal the hole carrying the ground joint to the disc. Glass sleeves were used for insulating the thermocouple wires from each other. The disc was sealed to the plate with Apiezon Q compound.

Support for the specimen, filaments, etc. inside the bell jar was obtained from four pillars screwed on to the plate. The pillars were 7" long, $1/4$ " diameter threaded brass rods, rigid enough to prevent vibration. The clamping of filaments etc. to the rods was by pairs of nuts. The rods were filed flat on one side in order to provide free evacuation of the air in the portion of the threads screwed into the plate and occupied by nuts.

Measurement of pressure was made on a McLeod gauge

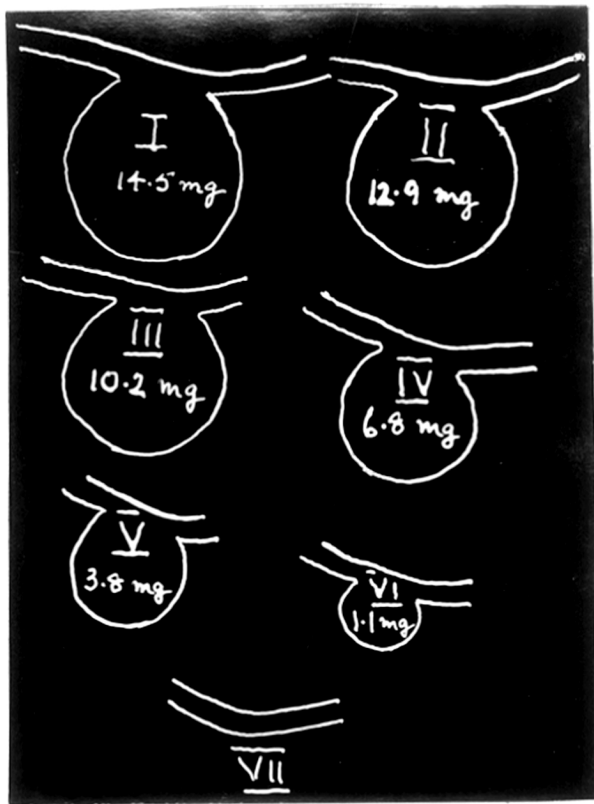


Fig 11.

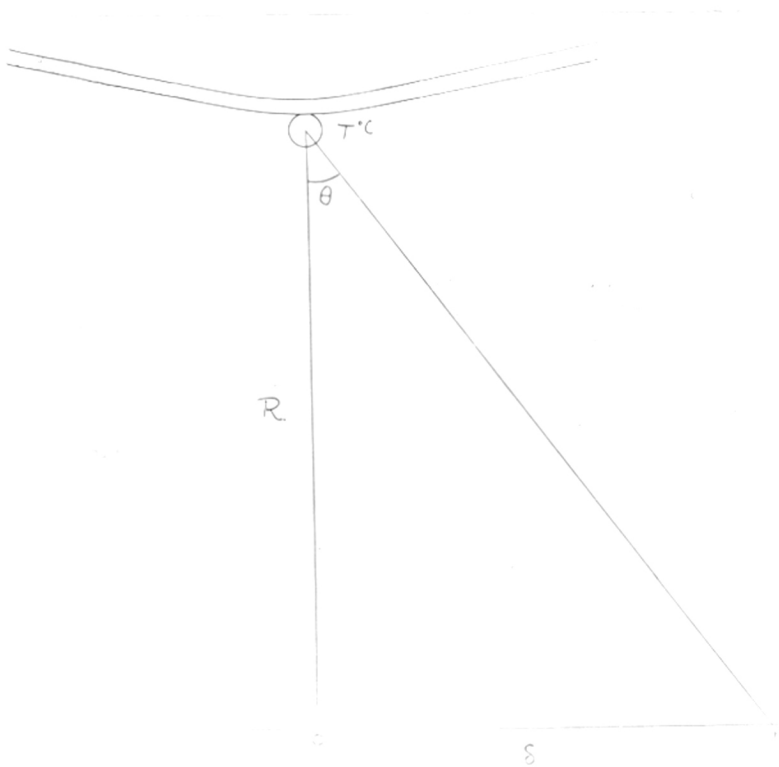


Fig 12.

reading a pressure of 10^{-4} mm. as a difference in mercury levels of $\frac{1}{2}$ cm. It was possible to measure pressures up to 10^{-1} mm. on this gauge. For rapid checks on the pressure before, during and after evaporation, it was found convenient to introduce into the system a Pirani gauge. A Wheatstone bridge arrangement with a similar gauge in an opposite arm was used and the out of balance current was found to be a good measure of the vacuum down to 10^{-4} or below. A liquid air trap was introduced between the McLeod and the Pirani gauge and evaporating chamber, to avoid mercury vapour reaching the evaporation chamber.

The deposits were made by sublimation of a bead hanging from a tungsten wire. Since silver does not wet tungsten well, the bead is approximately spherical as shown in Fig. 11. which was obtained by projecting the bead and filament on to a screen. Preliminary experiments showed that the heat radiation effect due to such a source was considerable. The filament was therefore limited to a short length of narrow gauge wire. It consisted of about 1.5 cms. of .012" diam. wire which was bent to have a small kink at its centre. About 3 mm. of wire at either end of the filament were bent round at right angles to the length of the wire and the filament was gripped in crocodile clips by these two portions. A source of this type was found very convenient for weighing of filament and bead. The shape of the evaporating metal

and the disposition of objects and substrate inside the bell jar was such that a spherically uniform emission of molecular rays could be assumed. Due to uncertainty in the estimation of the film thickness, this would seem to be important.

Under these conditions if M grams of substance is evaporated the thickness d_0 of the deposit at a point P distant δ from the point directly below the bead (Fig.12) would be given in cms. by:-

$$d_\theta = \frac{M \cos^3 \theta}{\rho \cdot 4\pi R^2} = d_0 \cos^3 \theta$$

$$= \frac{M}{4\pi \rho R^2} \frac{1}{\left\{1 + \left(\frac{\delta}{R}\right)^2\right\}^{3/2}}$$

where d_0 = thickness of deposit at the point directly below and ρ = density of silver (gms/cc).

If t is the time of evaporation, the rate of arrival of the metal at the substrate m_0 is given by:-

$$m_0 = \frac{\rho d_\theta}{t}$$

$$= \frac{M}{(4\pi R^2 t)} \cdot \cos^3 \theta$$

Factors which would affect the deposit are m_0 , the pressure of the gas P , the temperature of the evaporating metal T , which would determine the energy transmitted to the substrate and deposit by the arriving atoms and the initial mobility of the atoms on the surface and E_0 the heat radiation on the

substrate from the evaporating metal and filament. The radiation factor E_0 is a function of R , T and the surface area of the filament. The ratio of the heat radiated by a tungsten filament of length 1.5 cms. and diam. .012" to that by a silver bead of diam. .06 cms. (which is the usual size of bead employed) is approx. 8:1. Thus E_0 depends effectively on the contribution from the filament and can be made negligible without affecting the evaporation by the use of a screen.

The crocodile clips gripping the evaporating filament were fixed by stiff wires and binding screws to two pillars. The heating was with D.C. from the mains. One end of the filament was earthed at the metal pillar and the other end insulated from its pillar by a glass rod had an electrical connection made to it from a Kovar seal by means of a crocodile clip. One terminal of a D.C. point (110 v. with respect to earth) was connected through a rheostat to this seal. The rheostat enabled the rate of evaporation to be varied.

The temperature of the evaporating metal was determined by comparison with a tungsten filament, similar to the evaporating filament, which had a Pt-PtRh thermocouple of 40 gauge wire (.0048" diam.) spot welded at its centre. The comparison filament was arranged a centimetre or so above the evaporating filament, its supports to two pillars being made in a similar fashion. Both ends of this filament were insulated from the pillars and the heating was by a step down

transformer. A rheostat was included in the secondary circuit for current adjustment. The thermo e.m.f. was measured on a micro-ammeter with a suitable resistance in series.

The temperature of the evaporating metal could be obtained by comparison (of colour using a red filter or total intensity using a filter of aluminium evaporated on to glass to cut down the intensity) of the evaporating filament with the other whose temperature can be obtained directly with the thermocouple. An attempt was made at evaporating silver from a tungsten filament which had a Pt-PtRh thermocouple spot welded at its centre. It was thus hoped to obtain the temperature of the silver bead directly. The thermocouple junction was found to break off from the filament when the silver melted and formed a bead round it.

Two specimens were placed on a glass plate clamped directly by nuts between two pillars. The distance between this plate and the evaporating filament could be conveniently altered. The angle of incidence of the vapour stream could be varied by altering the position of the specimen on the glass plate.

The fused quartz glass used was supplied in the form of plane polished discs about 2 cms. in diameter and 2 mm. thick. The discs were cleaned in the usual way with nitric acid and

alcohol, washed in distilled water, and dried between clean filter paper. A final dry cleaning of the surface of the glass was effected by passing the tip of a blowpipe flame quickly over the surface.

Clean surfaces of mica were obtained by cleavage. Pieces of mica 5 x 5 cms. were cut with scissors from a larger sheet of thickness $2/1000$ ". A piece was handled with the tweezers or only by the edges. A fresh reflection cleavage was obtained as follows. An edge of a piece was frayed and the sharp point of a pair of tweezers inserted between two nearly equally thick layers obtained by the fraying. The point was then run along, first one edge and then the other, so that the main piece was separated to a depth of 4-5 mm. along the two edges. The two parts along one edge were now held between tweezers and fingers and gently drawn apart, the separation in the main piece being made to start from the other edge where a separation had already been initiated. Cleavages up to about 8 x 8 cms. could be conveniently obtained by this method.

Large cleavages obtained in this manner were found to be much thinner at one end than the other. Transmission flakes were obtained from these large cleavages by tearing the piece with a twisting action, starting from the thick end and proceeding towards the thinner end of the main piece.

Thin flakes, showing interference colours were usually found at the thinner end of the main piece. Very thin, weakly straw coloured flakes can be obtained after a few trials.

A reflection specimen of mica (≈ 1 cm. x 1 cm.) was placed on a flat piece of brass of about the same size as the specimen and both mounted on the specimen holder of the camera. Before mounting the specimen was carefully cut round the edges with scissors. A final cutting of the four edges, where only a narrow band of mica was removed, left the edges free from projections.

The heating of specimens was conducted in electric furnaces of three types. For the heating in air at temperatures up to 575°C . a vertical tubular Pyrex glass furnace 25 cms. long by 6 cms. diameter closed at its upper end and wound with an electric heater coil was used and a horizontal silica glass furnace for temperatures up to 875°C .

The vacuum furnace was mounted inside the main evaporating chamber and consisted of Pyrex tube about 6 cms. long and 2 cms. diameter closed at the lower end. About 20 turns of wire from a coil of a 750 watt electric fire was wrapped round the tube in a single layer. Thick strips of mica placed along the length of the tube provided insulation for one lead, enabled the wire to be wrapped tightly round the tube and also formed supports for the two free ends.

The tube and coil were slipped inside another Pyrex

tube also closed at the lower end and the double cylinder placed inside a Pyrex beaker, 8 cms. high and 7 cms. in diameter. In order to conserve heat radiation and also reduce the time taken by the furnace to reach a steady state, the inside of the beaker was lined with a piece of polished copper foil. The resistance of the furnace coil was about 12 ohms. Alternating current from a step down transformer working off the mains and giving 35 volts was employed for the heating. The arrangement was found to be quite efficient, a current of 2.5 amps. being sufficient to bring the temperature up to 500°C. The temperature was measured with a Pt-PtRh thermocouple which was calibrated at the zinc, lead and tin melting points and the steam point.

The deposition procedure was as follows. A new filament was cleaned from tungsten oxide by heating to bright red or yellow heat in a vacuum. About 5-6 cms. of 35 gauge ^{Ag} wire was made into a fine spiral, by winding it on a piece of stiff wire and the filament was then threaded through it. The spiral was made to lie at the centre of the filament. On heating the spiral melts invariably first at the ends, continues to melt along its length drawing itself together to form a bead at the kink. If the melting is not too rapid at first the silver does not fall off the filament. Once a bead is formed the evaporation can be made as rapid as required. This method was found to be more convenient than

the one usually recommended of introducing hooks of wire on the filament. The hooks had a tendency to fall off and often more than one bead formed. With a good vacuum a rotation of the molten silver is always observed. At high pressures this rotation does not take place.

It was found possible to obtain a bead of about 15 mg. of silver on the filament. The first evaporation serves to clean the filament and silver of grease etc. and also removes any adsorbed or occluded gas. After cleaning, the filament is handled with tweezers only and removed from the clips for weighing. Before letting down the vacuum for this purpose the leak reservoir pressure and, or the butterfly valve are adjusted to give the pressure at which it is hoped to carry out the evaporation experiment. The comparison filament current is now turned on and set at the value which brings this filament to the temperature at which it is desired to evaporate the metal. The evaporating filament current is also turned on and adjusted for equality of temperature of the two filaments. The filaments are switched off, the leak tube tap closed and the vacuum let down. When the filament has been weighed and reintroduced, the specimen substrate is also placed inside and the apparatus pumped down ready for the deposition experiment. When the Pirani gauge indicates the required pressure approximately it is measured on the

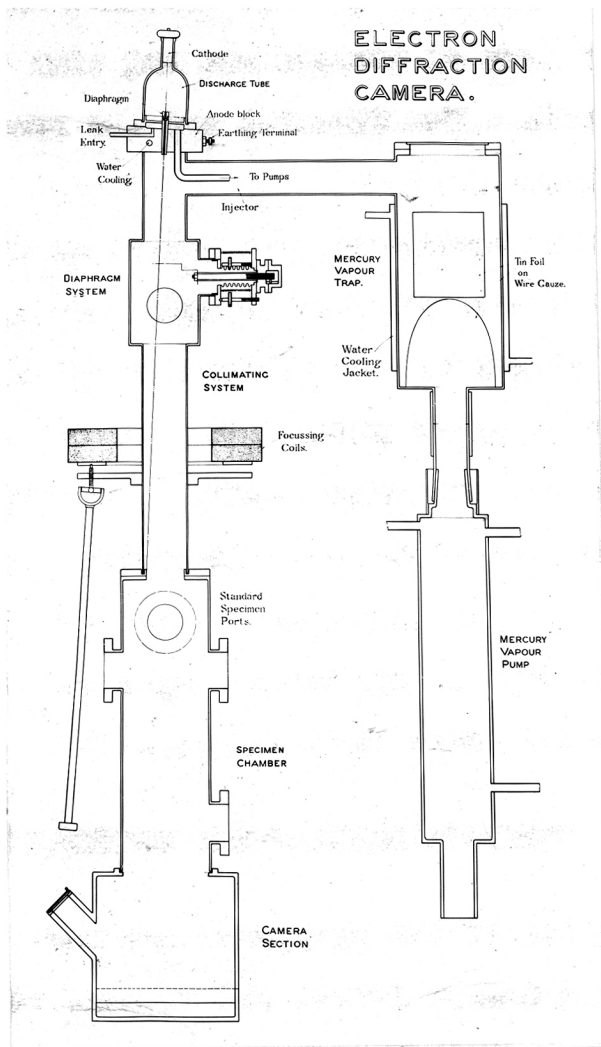


Fig 13.

McLeod gauge, the mercury in the gauge brought down and the system left to itself for a few minutes to settle down to equilibrium pressure. (The Pirani gauge is watched during this time). The filaments are now switched on, a check made for correct conditions of temperature and time is measured until switching off. The filament and the remaining silver is finally weighed.

Glass and mica specimens were heated in air by placing on a tray made of nickel sheet. Larger cleavages of mica (about 5 x 5 cm) were held inside the furnace by a crocodile clip at the end of a stiff wire. Portions of the main cleavage could be cut off after various times of heating. For heating in the vacuum furnace the specimen was placed on a small platform made of thin nickel sheet and lowered inside the furnace. The tip of the thermocouple was arranged to lie a few millimetres above the specimen.

II. 2. ELECTRON DIFFRACTION TECHNIQUE.

The examination of the specimens was made with a Finch type of diffraction camera (Finch and Wilman, 1937³) evacuated by a three-stage Leybold mercury diffusion pump, backed by a rotary oil pump (Fig.13). A convenient working voltage was usually 50-60 kv. These have an associated wavelength of about 0.053-0.049 Å. The beam is focussed by adjusting the focussing coil current and by tilting the coil it is biased

to fall on the specimen. With a reflection specimen the angle of incidence is usually made of the order of $\frac{1}{2}^\circ$ to 1° . The specimen is explored by varying the tilt of the focussing coil.

Non-conducting specimens tend to charge up in the electron beam. This was neutralised by bombarding the specimen with an electron stream from a heated tungsten filament, the electrons being accelerated through 200 volts (Kamogawa, 1940). When the clearest diffraction pattern representative of the whole specimen has been found, the diaphragm above the specimen is brought into position, the photographic plate exposed for about 5 seconds and the voltage measured by a 10 cm. diameter sphere gap. For accurate determination of lattice constants, the specimens were lightly dusted with fine graphite powder so as to obtain patterns which contained graphite diffraction rings, of which the strong and clear 110 ring, corresponding to a spacing of 1.230A. (Trzebiatowski, 1937; Nelson and Riley, 1945; Finch and Fordham, 1936; Finch and Wilman, 1936) was employed for calibration. Ilford Special Rapid plates were used.

II. 3. INTERPRETATION OF THE ELECTRON DIFFRACTION PHOTOGRAPHS.

The effects observed with the diffraction of electrons by crystals are similar to those obtained with X rays and their interpretation also follows along somewhat similar lines.

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

$$a(\cos \alpha - \cos \alpha_0) = h \lambda \quad \text{where } h \text{ is an integer and } \alpha_0 \text{ the angle between the incident waves and the row of atoms.}$$

If there are M_1 atoms of scattering power $\mathbb{F}$ in the row the intensity of the scattered radiation at a screen distant R is given by

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

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

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

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.14) 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 rows at right angles to it 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

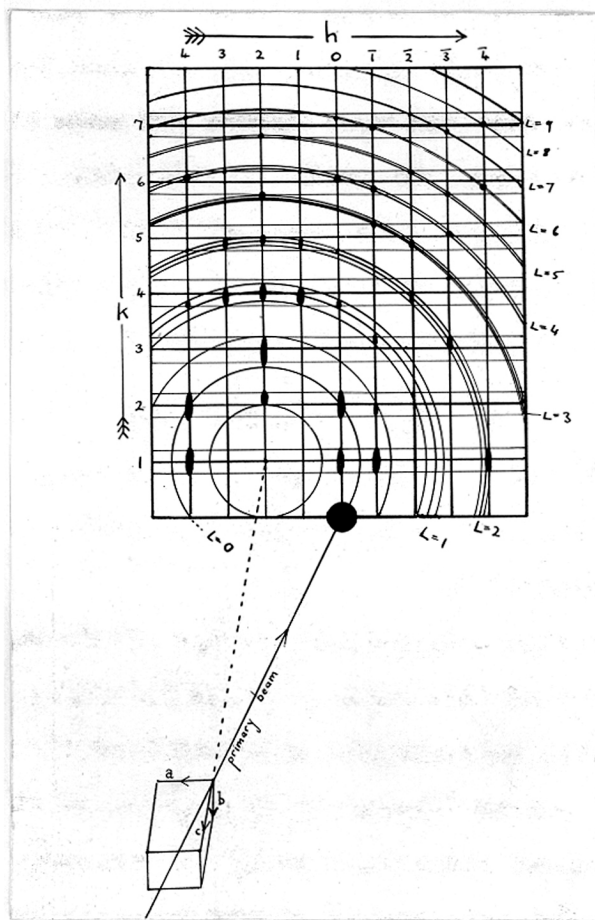


Fig 14.

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 L cms. away is $2\lambda L/Ma'$. 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 greater 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 = width 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 limitation 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 Shirahara (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 reflection specimen the Laue zones on a screen are of the form shown in Fig.14.

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.14. 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 about 5000A. 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 pattern (spots or rings) near the primary beam is only contributed to effectively by the surface region of the crystal to a depth of about 20A. 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 zones 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 make their appearance. With specimens thick enough to just let the electron beam through, 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. They may be considered in principle to be due to selective Bragg reflection of scattered electrons from crystal planes and the lattice-plane spacing d from the line pair separation D is given approximately by

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

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 θ would reflect electron waves in the same manner as X rays according to the equation

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

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 orientated 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 diffractions must lie at the intersection of the hkl rings 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 $R_{111}/3$. 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. We thus see that 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

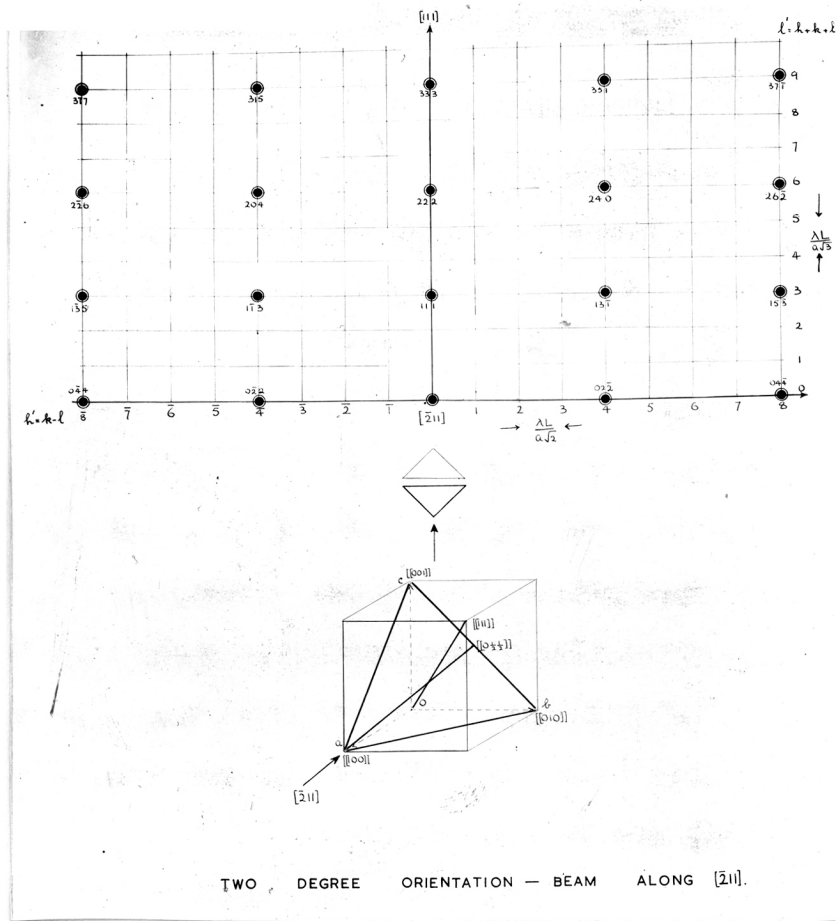


Fig 16.

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 two degree orientation of the 111 planes in the face centred cubic system the two types of pattern obtained are shown in Figs. 15 and 16.

The Estimation of Mean Crystal Size from Reflection Patterns.

In single crystal patterns the shape and size of the spots allows the breadths of three sets of Laue zones to be recognised and this leads to an estimation of the mean crystal extent, for example, $M_1 a$, $M_2 b$ and $M_3 c$ in the corresponding lattice-row directions, by means of the expressions stated above. The elongation of the spots due to low penetration and refraction caused by smooth surfaces on relatively large crystals can be recognised as indicated above, and allowed for in estimating the undisturbed Laue-zone breadths.

In the case of random polycrystalline specimens the mean crystal size must be estimated from the ring breadths by the well-known expression which was derived in its most general form by Laue (1926) and Warren (1938):-

$$\beta = 0.90 \times \lambda L / D \cos \theta$$

where β is the radial breadth of a ring would have, between points of half the maximum intensity, if an infinitely narrow parallel primary beam were used, and D is the effective mean

crystal diameter normal to the corresponding reflecting net plane. For diffraction of high speed electrons $\cos \theta$ is very nearly infinity, thus sufficiently closely

$$\beta = 0.90 \quad \lambda L/D$$

The measured breadth, B , however, is greater than β because of the finite breadth of the primary beam and Warren (1938) and Taylor (1941) concluded that β should be estimated from the relation

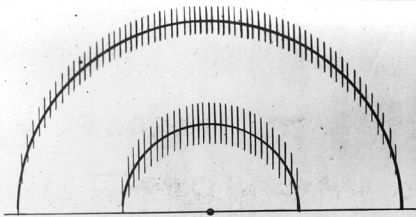
$$\beta = \sqrt{B^2 - b^2}$$

rather than Scherrer's (1920) early assumption that $\beta = B-b$. In X ray diffraction it has recently been recommended by Jones (1938) (and see Taylor, 1941, 1945) that the broadening caused by experimental conditions other than the limited crystal diameter is best allowed for by comparison of the observed breadths B with those obtained for admixed large crystal particles which give practically no further broadening ascribable to the diffraction process. In electron diffraction transmission patterns such a method could be used with, for example, colloidal graphite as the large crystal material (in so far as concerns its $hk0$ diffractions), but when refraction and absorption broadening is recognised to be absent it is sufficiently accurate for most purposes to estimate β from measurements of B and b as above.

In the case of deposits grown atom by atom upon a substrate, however, it is fundamentally more important, for

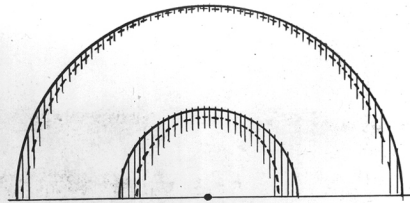
both theoretical and practical purposes, to study the structure of deposits prepared on such smooth substrates as polished fused silica which require use of the reflection method, than by transmission using substrates like collodion films. It is therefore important to consider how valid estimates of crystal size can be obtained from reflection patterns, especially as it appears that no adequate method has yet been described.

As Finch (1937) and Finch and Wilman (1937)² have pointed out, the crystals in deposits on smooth substrates often tend to have smooth surfaces or may have flat-topped obtuse-angled projections with faces more or less parallel to the substrate and thus also to the beam, so that the rings may be much broadened due to low penetration and refraction of the electrons even when the crystals are large. Kirchner (1937) and Papsdorf (1937) have published patterns which they believed showed such a broadening in reflection patterns as compared with that observed in transmission patterns from simultaneously prepared deposits of the same materials (gold and silver deposits 100 to 500 A. thick) on similar substrates (mica cleavage faces and collodion). Though refraction and low penetration could have been partly responsible for the greater broadening in the reflection patterns, however, the results described below in Section VI(4) show that there may nevertheless have been a real difference of crystal size in



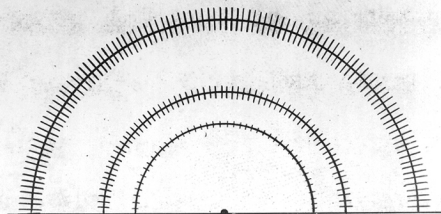
EFFECT OF LOW PENETRATION.

FIG 17_A



EFFECT OF REFRACTION.

FIG 17_B



EFFECT OF FINITE SPECIMEN SIZE
AND BEAM WIDTH.

FIG 17_C

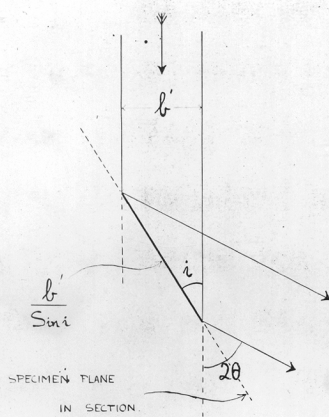


FIG 18.

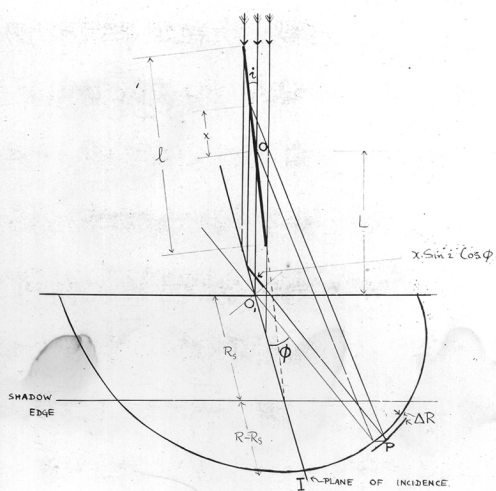


FIG 19.

their reflection and transmission specimens, resulting from appreciably different heating of the thick reflection and thin transmission substrates by radiation from the hot source of metal vapour during the deposition. Their observations cannot therefore be accepted as an argument against the possibility of deriving valid estimates of crystal size from reflection patterns, and indeed such estimates appear to be obtainable in the following way to a moderate and useful accuracy.

First and inspection and measurement of the pattern radii and ring breadths will show whether appreciable refraction or low penetration broadening displacement is present in only certain groups of rings due to definite crystal habit. If these selective effects are absent there may still be a possibility of a general broadening of all the rings due to low penetration into a relatively smooth deposit surface, and refractive displacement of mainly the inner rings towards the shadow edge. But both these effects broaden the rings in a direction normal to the shadow edge as shown in Fig.17, where the circles represent the undisturbed ring positions.

It is clear that low penetration broadens a ring on both sides practically symmetrically and scarcely at all near the shadow edge in rings of not too small radius; refraction on the other hand causes a displacement of the ring towards the shadow edge by an amount which decreases rapidly with increasing distance from the shadow edge, thus resulting in a

roughly elliptical shape of particularly the inner rings. In practice cases of clear cut refractive displacement are rare and most often if refraction is appreciable it leads to a unilateral shading off inside the more intense "transmission" type of rings having their normal ring positions, towards the position of maximum refraction. If such a unilateral broadening or displacement is detected it is necessary to estimate the ring breadth by measurement across a ring of large diameter, near the shadow edge, which should be as low as possible so as to be nearly perpendicular to at least these outer rings. Measurement in this region also avoids appreciable broadening due to low penetration.

There is a third important cause of ring broadening in reflection patterns, due to the finite beam width and size of the specimen which it grazes. If the focussed beam is practically parallel and its width at the specimen is b' , and if it is incident on the plane specimen surface at a grazing angle i then from Fig.18, its section in the specimen plane is of length $b'/\sin i$ and breadth b' . If b' is about 0.5 mm. and i is 0.5° then $b'/\sin i = 6$ cms. In practice part of the beam passes over the lower edge of the specimen and forms the undeflected beam spot on the plate, but the specimen is only 1.2 cms. in diameter, and all or practically all its length l is grazed by the beam if the angle of incidence is less than 0.75 to 1° . The extent of the broadening of otherwise sharp

rings from this cause is additional to that due to the breadth b of the focussed beam (at the plate), and it may be estimated as follows. In Fig.19 let O be the centre of the diffracting part of the surface, which is inclined at i to the beam and is of length l in the plane of incidence, and let the corresponding ray of the primary beam be OO_1 , of length L , meeting the photographic plate normally at O_1 . Consider a small element of the specimen distant x above O and unbroadened diffracted beams (from large crystals) emerging at an angle of deviation 2θ from the primary beam direction, towards a point P at an azimuth ϕ from the plane of incidence. Then for the diffracting region considered the camera length is $(L+x \cos i)$ and the effective centre of its ring pattern is in the plane of incidence and $x \sin i$ behind the mean centre O_1 for the whole specimen. The radius R' of the 2θ ring associated with net planes of spacing d is now $(L+x \cos i)/d$, and the distance ΔR of the diffracted beam in azimuth ϕ , from the mean ring of radius $R = \lambda L/d$ round O_1 , is given by

$$\begin{aligned}\Delta R &= (\lambda/d)(L+x \cos i) - x \sin i \cos \phi - (\lambda L)/d \\ &= (\lambda/d)(x \cos i) - x \sin i \cos \phi\end{aligned}$$

The total radial breadth of the ring at azimuth ϕ is then

$$\begin{aligned}b_\phi &= [\Delta R]_{x=l/2} - [\Delta R]_{x=-l/2} \\ &= (\lambda/d) l \cos i - l \sin i \cos \phi\end{aligned}$$

Since i is small this is practically given by

$$\begin{aligned}b_\phi &= (\lambda L/d)(l/L) - (l/L) \cdot R_s \cos \phi \\ &= (l/L) \cdot (R - R_s \cos \phi),\end{aligned}$$

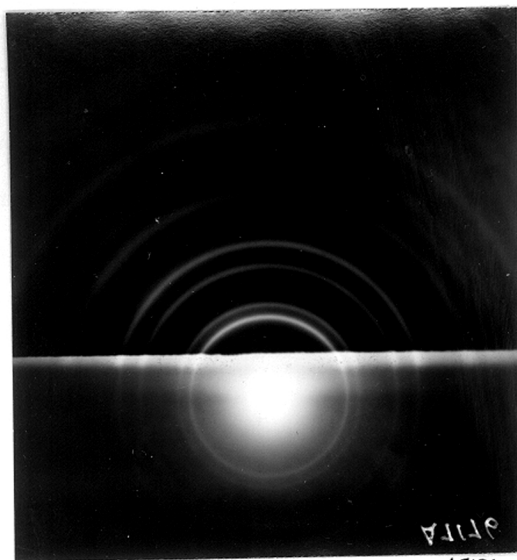


Fig 20

A7176.

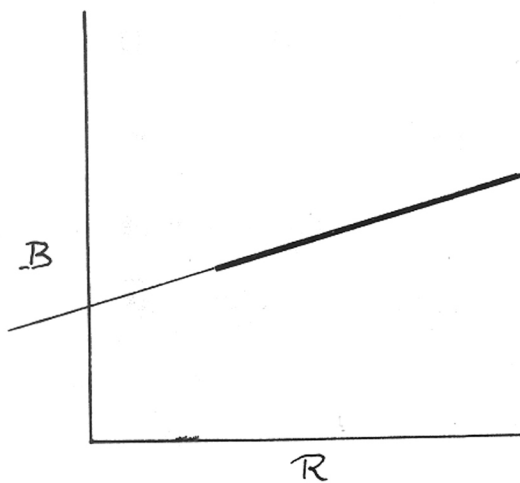


Fig 20_a

where R_s is the perpendicular distance of the shadow edge from O_1 . Thus, near the shadow edge as $\phi \rightarrow 90^\circ$ b approaches $(1/L) \cdot R$ and is proportional to the ring radius R , while in the plane of incidence where $\phi = 0^\circ$, $b_c = (1/L) \cdot (R - R_s)$.

Figure 20, from a 500 Å. thick silver layer on fused quartz, shows this kind of ring broadening clearly, since besides the reflection pattern of broad rings above the shadow edge, there is an unusually strong transmission ring system visible below the shadow edge round the central spot. The transmission rings are much sharper than the reflection rings except in the inner rings (111, 200) and occur opposite the inner part of the reflection rings in agreement with their origin being from the lower edge of the 2 cm. diameter specimen, with correspondingly shorter mean camera length.

To estimate the mean crystal diameter D from a ring breadth B the expression valid to a moderate approximation, when B is measured near the shadow edge may then be stated as

$$\frac{0.9 \lambda L}{D} = \beta = \sqrt{\left[B - \left(\frac{1}{L}\right) (R - R_s \cos \phi)\right]^2 - b^2}$$

The relation between B and R is thus linear and given by

$$B = (1/L)R + \left[(1/L) R_s \cos \phi + \sqrt{B^2 + b^2}\right],$$

and since in practice it is not always certain that the full length of the specimen is grazed by the electron beam, which may not be adjusted so as to impinge to the same extent on

the specimen for all photographs, it is best to measure the breadth B of several rings along the same radius with $\phi \sim 70^\circ$ or 80° and plot B against R (as in Fig. 2Q). The slope of the straight line through these points gives $1/L$ and it cuts off an ordinate along the B axis which after subtracting $(1/L)R_s \cos \phi$ gives $\sqrt{\beta^2 + b^2}$ directly whence β and D .

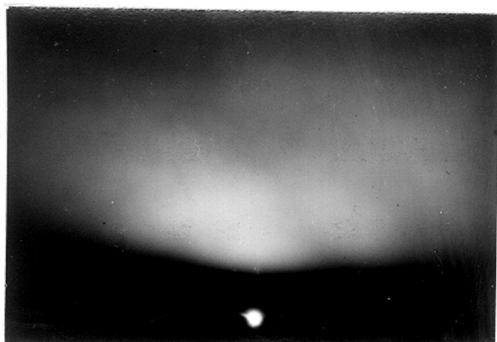


Fig 21

A7502.

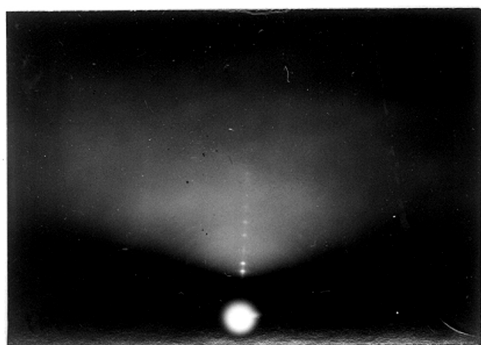


Fig 22

A8013.

III. THE STRUCTURE OF FUSED QUARTZ GLASS SUBSTRATE SURFACES.

1. Initial Polished Fused Quartz Surfaces.

Twelve photographs taken from the surfaces of three different specimens, freshly cleaned as described above in II, all showed two broad halos like Fig.21. One of these photographs was from the substrate surface of a silver deposit which had been heated for half an hour in air at 300°C., but the other two had only been cleaned in alcohol and nitric acid after receipt from the makers. Seven plates were suitable for measurement and gave Bragg plane spacings varying from 2.13Å. to 2.45Å. for the inner halo and from 1.18Å. to 1.28Å. for the outer one, as shown in Table IV.

Table IV.

Net plane spacings from fused quartz.

R_1 = radius inner halo

R_2 = radius outer halo

Camera length = 47.5 cms.

R_1 cms.	R_2 cms.	d_1 Å.	d_2 Å.
1.16	2.21	2.32	1.22
0.99	1.96	2.45	1.24
1.16	2.00	2.22	1.28
1.21	2.00	2.13	1.28
1.05	2.05	2.30	1.18
1.19	2.13	2.26	1.26
1.05	2.13	2.41	1.19
		Mean =	Mean =
		2.31Å.	1.24Å.

2. The Effect of Heat on the Surface Structure of Fused Quartz.

Heating a specimen for half an hour in air at 400°C. caused a change from the initial halo pattern to one of faint sharp arced rings, with strong spots in the plane of incidence. Fig.22 shows such a pattern but from a disc which had not been used as a substrate since its receipt from the Thermal Syndicate Co.Ltd., but which had been heated three hours in air at 400°C. in the Pyrex oven. Table V gives the corresponding spacings, with X-ray powder pattern data of some normal forms of quartz for comparison though, owing to the strong orientation shown in the above pattern the intensities cannot be easily compared with the X-ray ring intensities. The pattern has some spacings near main spacings of

α -cristobalite, but does not appear to correspond well to this, nor to β -cristobalite, α -quartz, and α -tridymite, nor to a mixture of these. In view of the high purity of the discs (over 99.8% according to the makers), the most likely alternative explanations remaining are (a) it may represent a new crystalline form of silica, or (b), it may be a silicate which has segregated out in crystalline form from the amorphous polished surface layer (Beilby layer) in which a small proportion of the polishing agent ("jeweller's rouge") may have been admixed. Neither of these alternatives has

Table V.

Net-plane spacings (A.) and Intensities of Spot
and arc diffractions in pattern from fused quartz
disc heated at 400°C. in air for 3 hours.

Plate A.8028
compared with
graphite.

Plate A.8027
compared with
graphite.

Plate A.8013
referred to 3.570A. and
1.785 A. spacings assumed

		Plane of incidence	At 50° to plane of incidence	At 60° to plane of incidence
VF 3.963	VF 3.966	VF 4.090		
S 3.567*	MF 3.715*	VF 4.006		
F 3.094*	M 3.578*	F 3.745		
	VF 3.359*	S 3.570*		
	F 3.137	VF 3.363		
		S 3.080*	VF 3.087	
		VF 2.928	VF 2.948	VF 2.889
		VF 2.809		
		VF 2.722	VF 2.748	F 2.731
		F 2.544		F 2.571
		VF 2.423	MF 2.425	MF 2.430
			MF 2.310	MF 2.291
		VF 2.246	F 2.196	F 2.177
		VF 2.133	VF 2.102	
		M 2.065*	VF 2.020	F 2.045
		VF(1.914)	MF 1.936	MF 1.935
			MF 1.899	MF 1.907
		VF 1.847	F 1.840	F 1.851
		MF 1.785*	F 1.785	VF 1.780
			F 1.747	VF 1.750
			VF 1.693	F 1.703
		VF 1.654	VF 1.643	F 1.639
		VF 1.603		F 1.601
			F 1.579	1.563
		F 1.548		VF 1.528
		VF 1.508		
		VF 1.476		
		VF 1.264		
		VF 1.235		
		F 1.194		

VF(2.65)*

VF(2.573)*

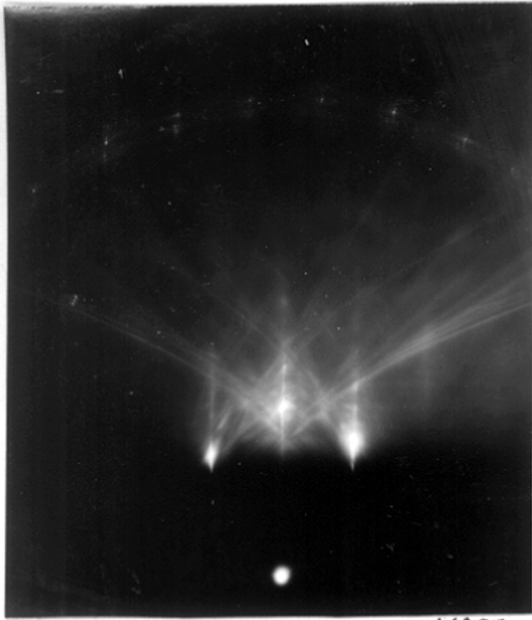
All 45° to plane
of incidence

F {2.427}
F {2.363}
F 2.235

* denotes spot in plane of incidence.

been adequately tested as yet.

In spite of the present lack of identification the above data for this pattern allow its recognition when it occurs, as it does occasionally, in patterns obtained from thin metal deposits on fused quartz substrates.



A6985.

Fig 23



A7492.

Fig 24

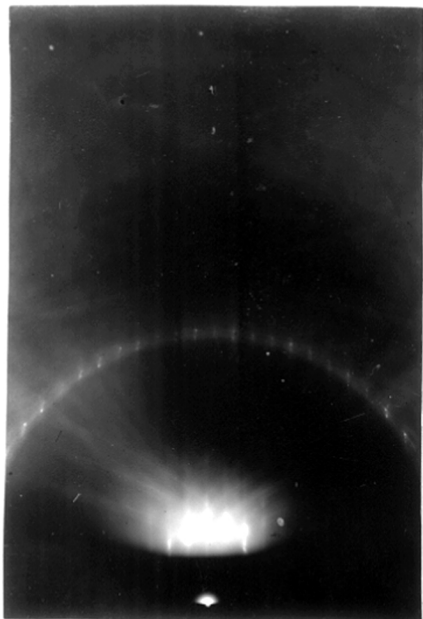


Fig 25

A7690

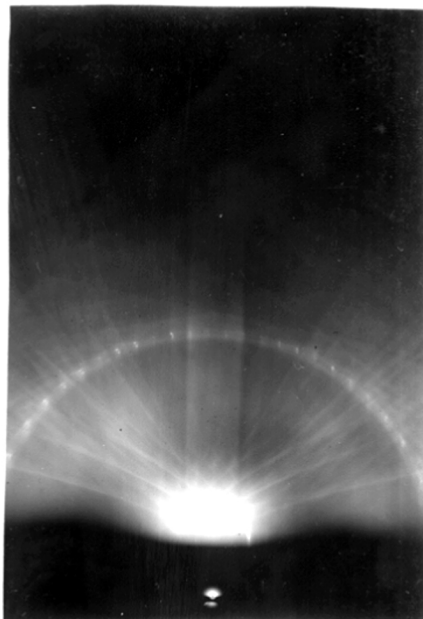


Fig 26

A7692

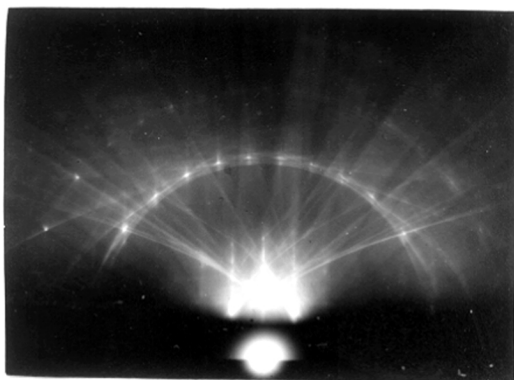


Fig 27

A7694.

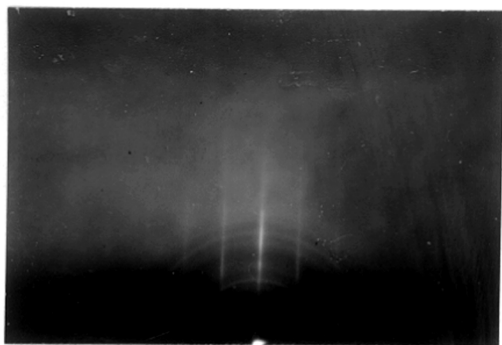


Fig 28

A6986

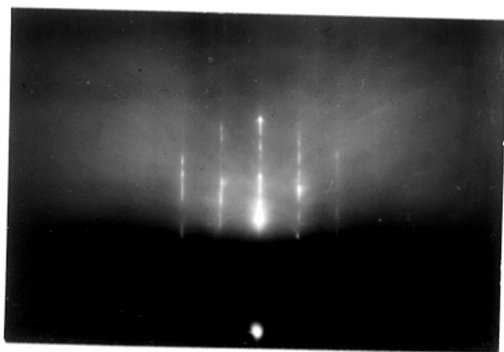


Fig 29

A7337.

IV. THE STRUCTURE OF MICA CLEAVAGE SURFACES AND THE EFFECT CAUSED BY HEAT.

IV.1. Freshly Cleaved Mica Reflection and Transmission.

Reflection patterns obtained from a cleavage plane in two azimuths at 30° to each other, with a camera length of 47.5 cms., are shown in Fig.23 and Fig.24. Fig.23 shows the spot pattern obtained with the beam along a long atom row (9.02 Å.) corresponding to the b axis in the cleavage plane and Fig.24 that with the beam along a short row (5.18 Å.) corresponding to the a axis. Spot and Kikuchi-line and band patterns obtained with a camera length of 25 cms. are shown in Figs. 25, 26, and 27, and agree with the X-ray data described above in I. The elongated 'spots' in the zero order zone of the patterns indicate the great smoothness of the mica cleavage plane. Rubbing the cleavage plane with cotton wool causes a considerable elongation of these streaks (Fig.28). This pattern also shows rings due to polycrystalline mica obtained from powder left on the surface after the polishing. The black ring from powdered mica (Finch and Wilman, 1937) is clearly seen in the plate. Distortion of the reflection specimen causes an extension of the area of the zero order zone and appearance of other sets of spots, a virtual rotation picture being obtained (Fig.29).

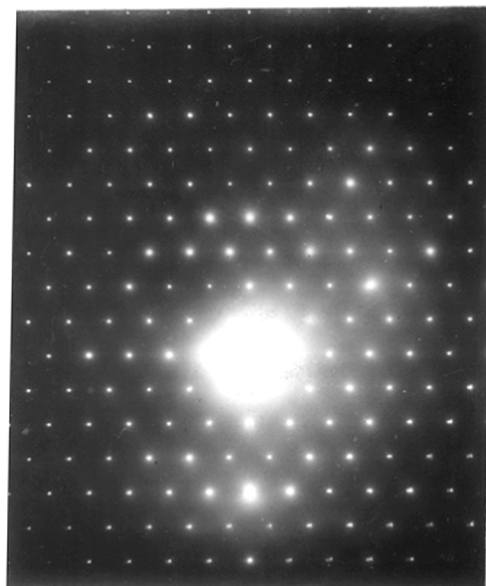


Fig 30

A7113

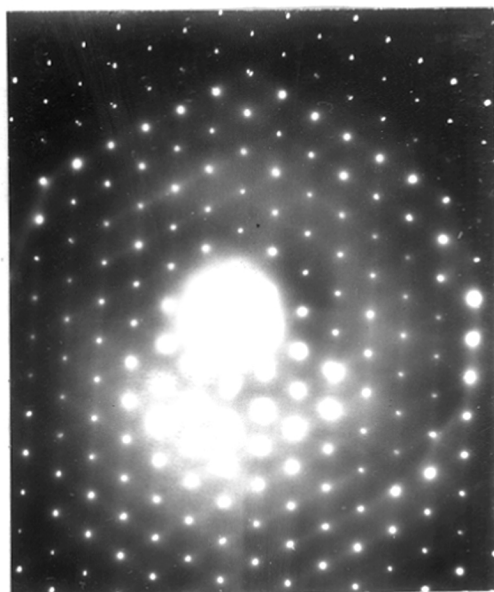


Fig 31

A7032

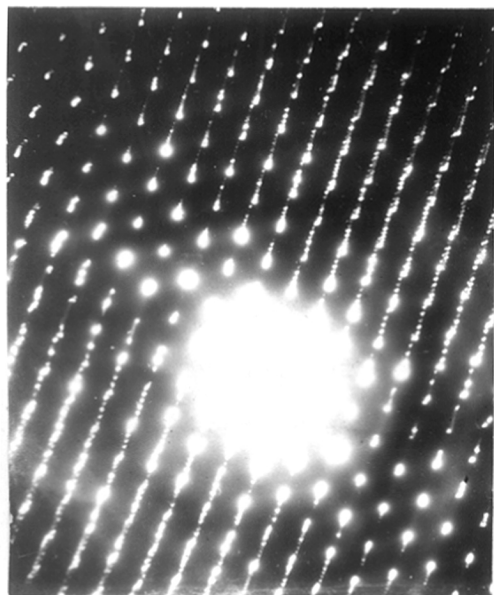


Fig 32

A7115

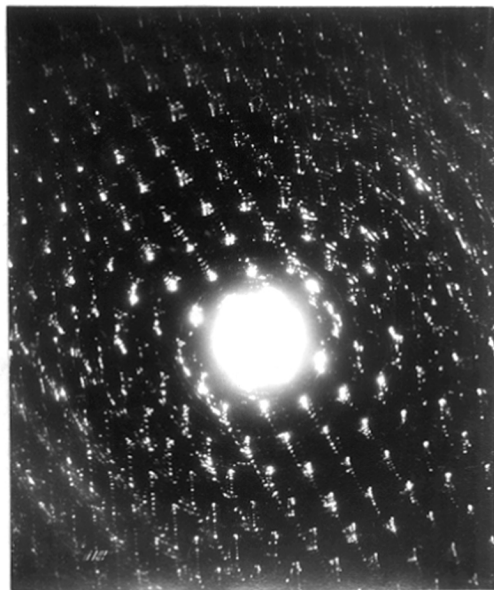


Fig 33

A7112

Transmission patterns obtained from cleavages of mica are shown in Fig.30 and Fig.31. Fig.30 obtained from a very thin cleavage shows the spots in a practically cross grating pattern and Fig.31 from a thicker specimen shows the strengthened first order circular zone. Both patterns show the normal hexagonal arrangement of spots and also diffuse lines joining the spots. These pictures were obtained from heated flakes of mica. In all, ten heated transmission specimens were examined - one heated directly in the bunsen flame, three heated at the bottom of a Pyrex beaker and six heated in the Pyrex air furnace at about 500°C. from $\frac{1}{2}$ - 13 hours. The patterns obtained show no new features different from those from unheated specimens. Fig.30 was obtained from a specimen which had a large patch of red, green, purple and yellow colours and which was heated in the beaker. Strong wrinkling of the thinner portions except for a small part in the yellow area had taken place and the pattern is probably from this yellow area of the specimen. Fig.31 is from a specimen which was heated for $\frac{1}{2}$ hour at 500°C. Figs. 32 and 33 show the effect of distortion on the pattern from such heated mica films. Fig.32 obtained from the specimen bent about a single axis shows the usual features of a rotation pattern and does not indicate any change in the lattice translation at right angles to the cleavage plane. Fig.33 indicates the great distortion that can take place in a

heated transmission specimen.

IV.2. Mica Cleavages Heated in Air.

(200, 300, 500, 550-570, 650, 850°C.).

Cleavages were heated in vacuum, air and steam.

Heating of the mica at temperatures up to 500°C. usually produced, especially at temperatures near 500°C. gaseous inclusions and occasionally brownish nuclei, which were not present in the original specimen. Specimens heated at about 650°C. when held against a dark background showed a number of translucent streaks which were more or less parallel to each other. The surface of these specimens examined in light reflected at a large angle of incidence showed splashes of colour at the streaks. Examined under a glass the streaks were found to consist of bundles of remarkably sharp parallel lines. Some of the streaks terminated sharply and this was found to occur at a 'step' in the cleavage face.

Heating at 850°C. for about 3 hours produced strong wrinkling and cleavage of the specimen and a structure consisting of approximately parallel fibres was obtained. It was found impossible to define the fibre direction as a fixed one relative to the original mica structure. Three specimens examined yielded values of 30°, 82° and 20° for this direction with respect to a long row in the cleavage face.

In the investigation of the surface structure of the muscovite cleavage faces by electron diffraction reflection patterns, described below, it is shown that muscovite begins to lose water and decompose in the surface layers at a temperature much lower than that necessary to cause the deep-seated loss of water which alone affects the X-ray diffraction pattern. Although under similar heating conditions the extent of the surface decomposition varied considerably from one specimen to another and sometimes varied noticeably over a specimen of size about 10 x 7 mm. (perhaps owing to different degrees of roughness or steeping of the surface, or to variations of composition) there was in general considerable decomposition even after a few hours heating at only 200°C. in air.

In most of the specimens examined, even those heated a few hours at 650°C. and 850°C., the mica Kikuchi lines and few elongated spots were at least faintly visible, showing that much of the mica surface (like the underlying layers) still remained highly smooth and unchanged in structure. This part of the pattern served as a useful reference in order to determine not only the orientation taken up by the crystals of the decomposition product, but also their axial lengths, which were also compared directly with those of graphite in some cases. The shape of the diffraction spots showed that the crystals of the decomposition product were in many cases

growing out from the surface in the form of projecting spikes, though often elongation of the spots normal to the shadow edge or in arrow-head form indicated that the crystals had developed relatively smooth faces parallel to the substrate or also in oblique directions. These metamorphosed surface layers remained unchanged during a few days in air at room temperature and were not appreciably soluble in water, though they dissolved in a moderate concentration of aqueous sulphuric acid.

Several well-defined decomposition product structures occurred. Below $550^{\circ}\text{C}.$, and rarely at higher temperatures, it was almost always hexagonal or very nearly so, with basal axes about $5.5 \text{ \AA}$. in length parallel to those of length $5.18 \text{ \AA}$. in the mica cleavage plane, and vertical axis (c) of length about $7.3 \text{ \AA}$.; though in one or two cases the patterns indicated a related though less symmetrical structure. At $550 - 580^{\circ}\text{C}.$ a striking change was evident in that although there were spot rows perpendicular to the shadow edge as before, showing that the crystals had a definite net plane parallel to the undecomposed mica substrate, there were usually no longer horizontal rows of spots. This structure was found to be rhombic or nearly so. Heating to $650^{\circ}\text{C}.$, however, resulted again in patterns having horizontal spot rows, and a rhombic unit cell could be chosen having a face containing two

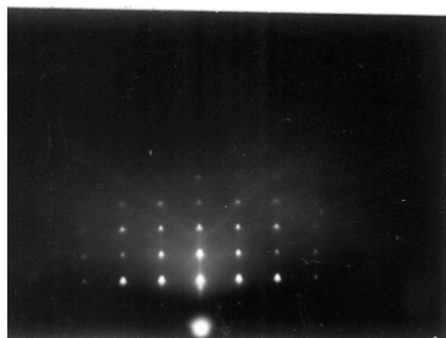


Fig 34

A7320

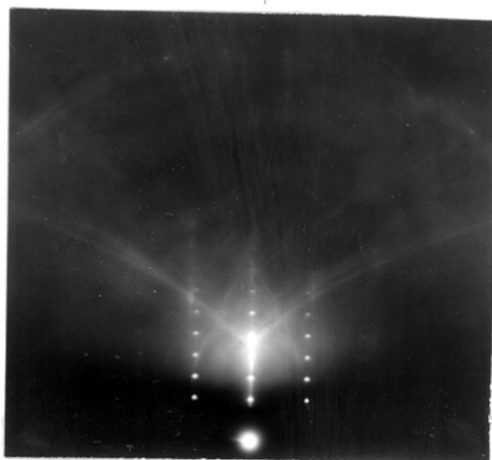


Fig 35

A7407

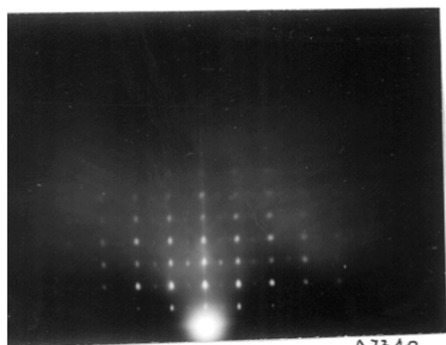


Fig 36

A7340

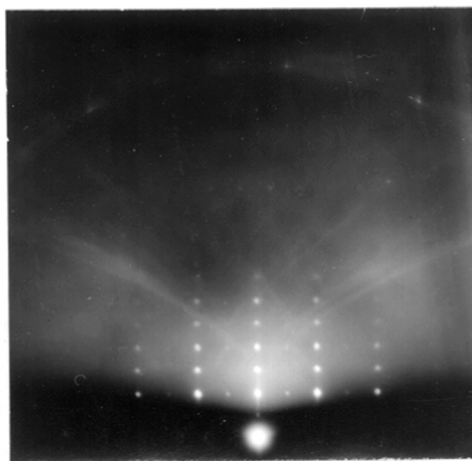


Fig 37

A7341.

of its axes parallel to the substrate. Heating specimens up to 850°C . resulted in so much wrinkling of the mica surface that the patterns were mainly of rotation type and more typical of the undecomposed lower layers than of the immediate surface layer. The lattice form, axial dimensions and orientations observed in the specimens examined are described below in detail.

(a) Mica Surfaces Heated in Air at Temperatures up to 550°C .

A simple rectangular pattern of spots was often obtained as shown in Figs.34 and 35, in the main azimuths 30° (or 90°) apart, i.e. with the beam parallel to the mica a or b type of lattice row. This was denoted by the symbol B_1 , while A was used to denote the pattern of elongated spots, and of Kikuchi lines, typical of the unchanged cleavage face. The axes a, b and c were assigned to the lattice rows parallel respectively to the a and b axes and cleavage-plane normal of the mica substrate.

Besides B_1 , a related pattern B_2 sometimes occurred usually with B_1 , and was characterised by a vertical spot spacing equal to or slightly smaller than in B_1 , and a horizontal spot spacing slightly less than half that of B_1 , though even-order vertical "row lines" were strong compared with odd row lines in the 'a' azimuth, and in the 'b' azimuth only even orders appeared in odd row lines. Figs.36 and 37

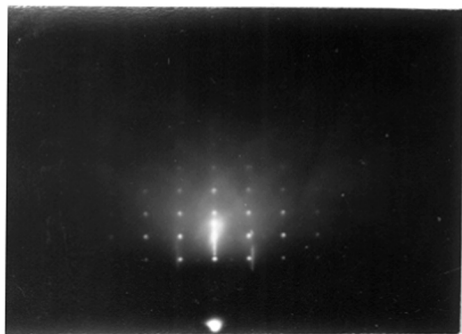


Fig 38

A7348

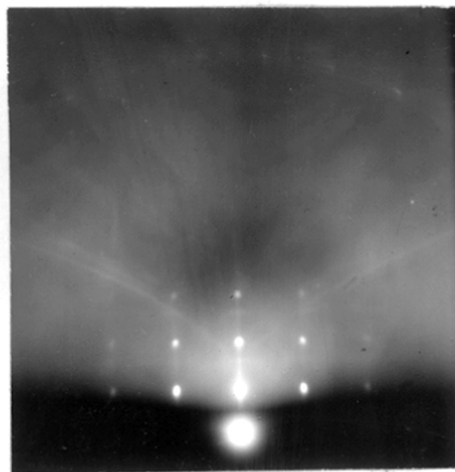


Fig 39

A7399

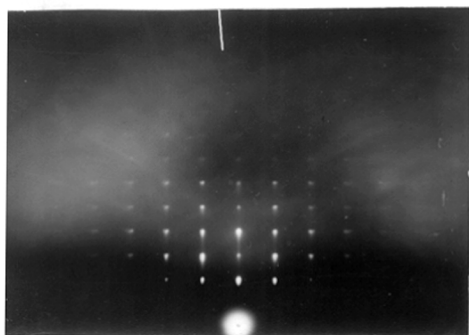


Fig 40

A7396

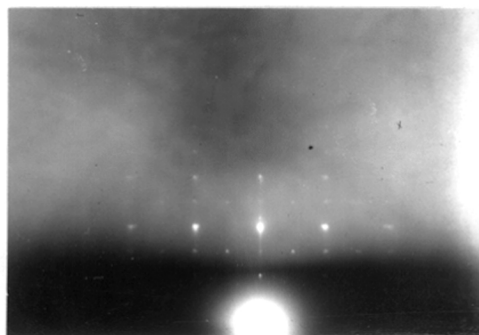


Fig 41

A7397.

show a typical example in the 'a' and 'b' azimuths. When spots were visible on a first order circular zone it was seen that in the b azimuth, as in Fig.37, ^{they} lay on vertical Laue zones halfway between those of the zero-order spots, indicating a horizontal lattice spacing of $11.6\text{\AA}$. instead of $5.8\text{\AA}$. normal to the beam.

Another product B_3 gave patterns similar to B_1 in the 'a' azimuth but showed only even order horizontal spot rows ("layer lines") in the b azimuth, as in Figs.38 and 39, where it occurs with a faint B_2 pattern. A further form B_4 gave in a 'b' azimuth a pattern, Fig.40, similar to that of B_2 except that the intermediate odd orders ^{occurred} instead of the even; and in an 'a' azimuth the pattern Fig.40 appeared to be similar to B_1 , with apparently a less uniform intensity of the spots.

Table VI shows the distribution of these patterns among the specimens prepared under various conditions of heating up to 550°C ., and the axial dimensions and ratios (with a and b parallel to the mica a and b, and c normal to them). It is useful to note that, as will be seen from the patterns of Figs. 34 to 41, the clearest identification of the type of structure of a specimen is provided by the pattern in a 'b' azimuth in general.

Table VI.

Data for Mica Cleavage Faces Heated in Air at below 550°C.

Spec. No.	Heat Treatment		Pattern type.	Lattice Constants (lengths in Å.)						Ref.
	Time	Temp		a	b	c	c/a	c/b	b/a	
102A	2½	200°	A+B ₁ +B ₂	B ₁	-	4.832*	7.32	-	1.513	M
				B ₂	2.64 ₂	-	3.47*1.313	-		
103A	3		A + B ₁	B ₁	2.79*	4.93*	7.23	2.596*(1.47)	-	M
102B	5½		A + B ₁	B ₁	2.817*	4.867*	7.29	2.585*1.498	1.73	M
103B	7		A + B ₁	B ₁	2.769*	4.850*	7.20	2.600	1.490	1.74 M
34	½	300°	A + B ₁	B ₁	-	4.984*	7.46	-	1.492	- M
106	2		A+B ₁ +B ₂ +B ₃	B ₁	2.862*	4.897*	7.36	2.595	1.497	1.71 M
				B ₂	-	10.02	7.52	-	0.746	- M
				B ₃	2.58*	4.70*	6.92	1.322	1.470	- M
107	2-1/4		A+B ₁ +B ₂	B ₁	-	4.944*	7.32	2.586	1.480	- M
				B ₂	-	10.12	7.50	-	0.741	- M
112A.	2-1/4		A + B ₁	B ₁	-	9.93	7.32	2.628	1.495	- M
107B	4½		A+B ₁ +B ₂	B ₁	5.765	9.92	7.45	1.293	1.504	1.73 M
				B ₂	5.88	10.09	7.59			M
116	5		A+B ₁ +B ₂	B ₁	2.82*	9.81	7.38	2.617	0.749	1.73 G
36	1/60	500°	A + B ₁	B ₁						
60	1/3		A + B ₁							
61	1/5		A + B ₁	B ₁	2.721*	4.652*	7.05			1.71 M
108	1		A+B ₁ +B ₂ +B ₃	B ₁	2.601*	4.482*	6.94			1.72 M
				B ₂	2.649*	-	6.94			
				B ₃	2.762*	4.741*	6.94			1.71
125	1		A + B ₁							

* these spacings probably should be doubled.

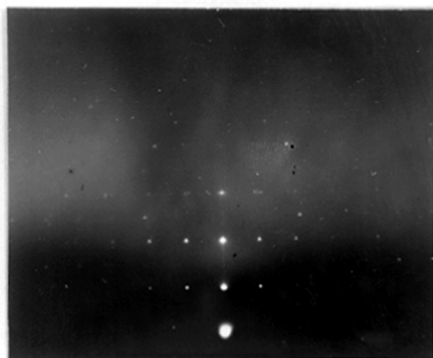


Fig 42_a A7513

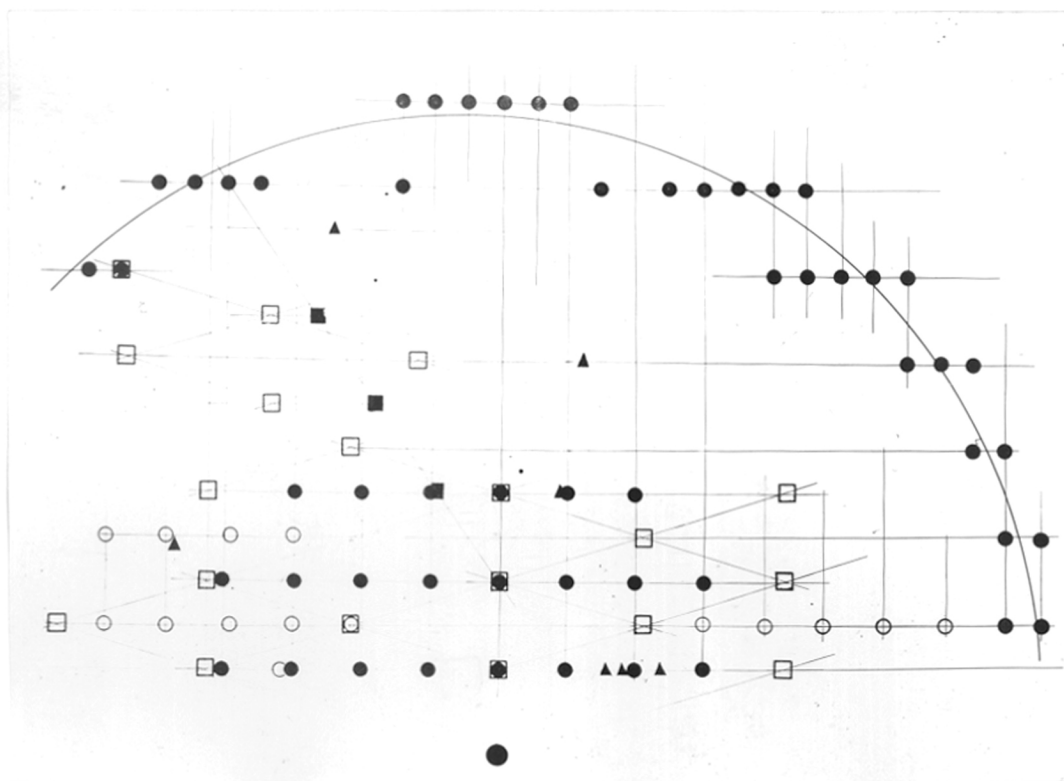


Fig 42_b.

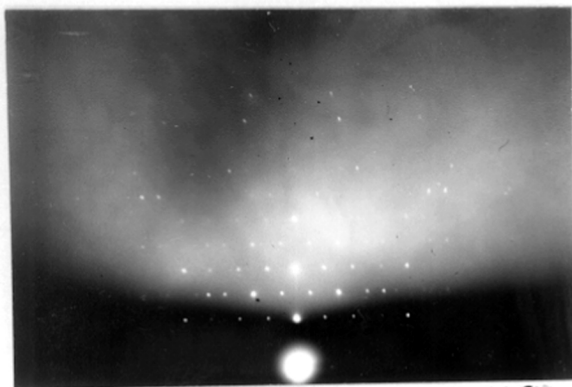


Fig 43a

A7514

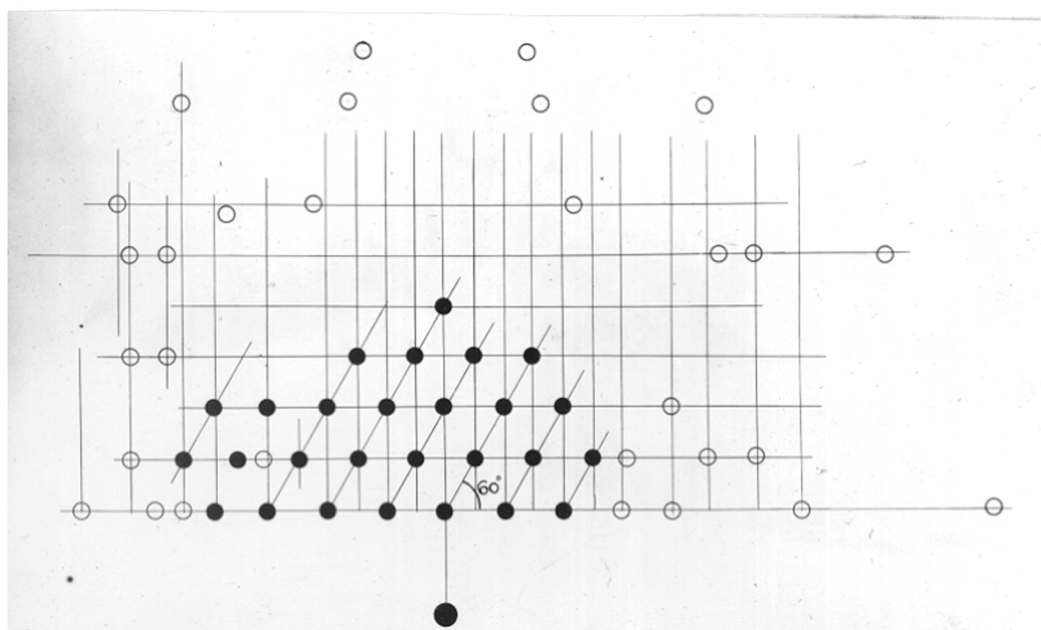


Fig 43b

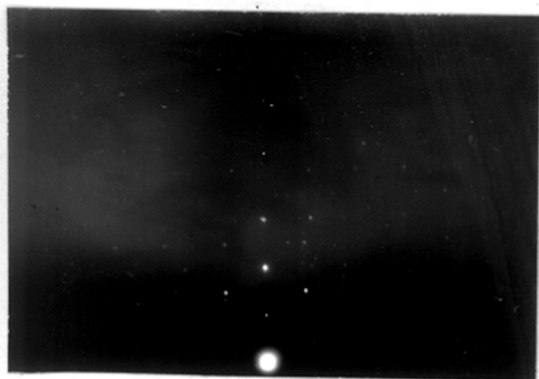


Fig 44a

A7515

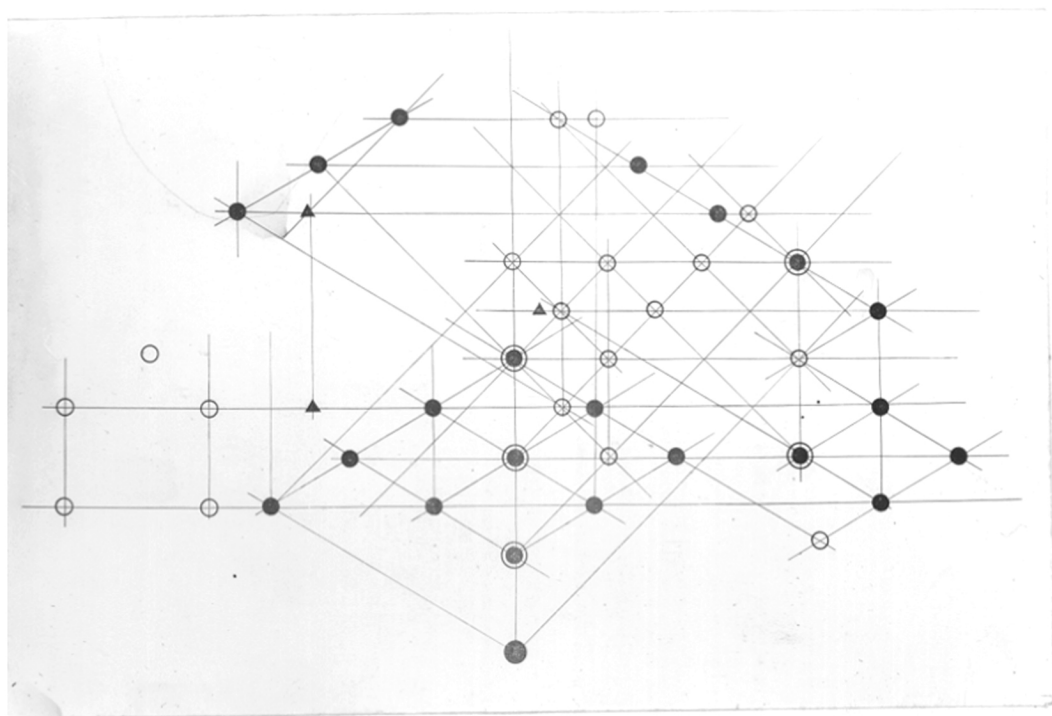


Fig 44b.

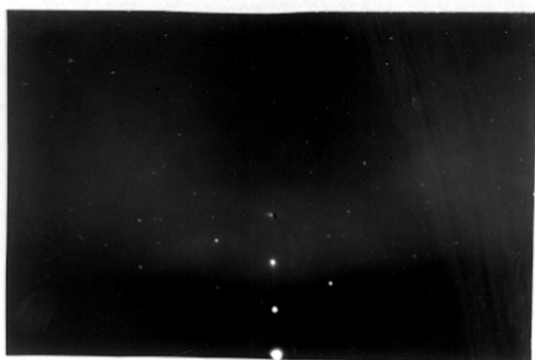


Fig 45a

A7516.

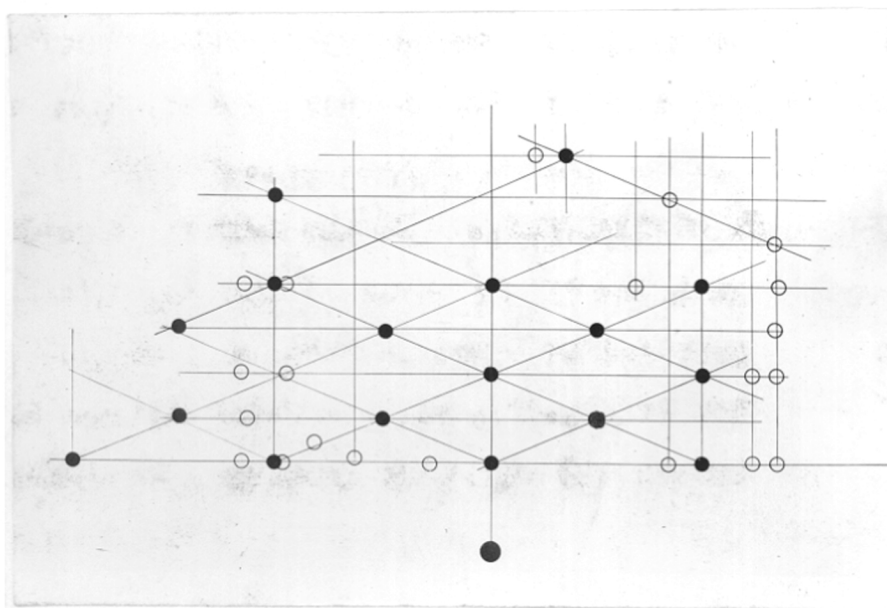


Fig 45b

(b) Mica Surfaces Heated in Air at 650°C.

The mica surfaces heated to 550-570°C. sometimes showed a component similar to the simpler 650°C. patterns, which will therefore be considered first. In the 650°C. temperature region the decomposition product^{"b"} was again rhombic with two axes in the surface parallel to the mica a and b axes and in the third vertical. Three specimens of freshly cleaved mica, heated in air at 650°C. in the silica furnace for 3, 3 and 2 hours respectively, gave consistent results, which are as follows.

Figures 42a, 43a, 44a and 45a^{were} obtained from the first specimen in azimuths 0°, 90°, 19° and 12° respectively. The relationship of these azimuths to the initial mica lattice was established accurately by presence of a well-defined 060 Kikuchi band due to the underlying undecomposed mica, normal to the shadow edge in the outer parts of Fig.43a with its median in the plane of incidence. In the case of Fig.43a the electron beam was parallel to the plane of symmetry (010) of the mica and thus parallel to a and perpendicular to b. In the original negative of Fig.42a, also, a faint diffuse trace of a first order circular Kikuchi line envelope was visible, from the radius of which it was shown independently that in this azimuth the beam was parallel to the mica b axis, since the corresponding lattice-row spacing T was estimated by the

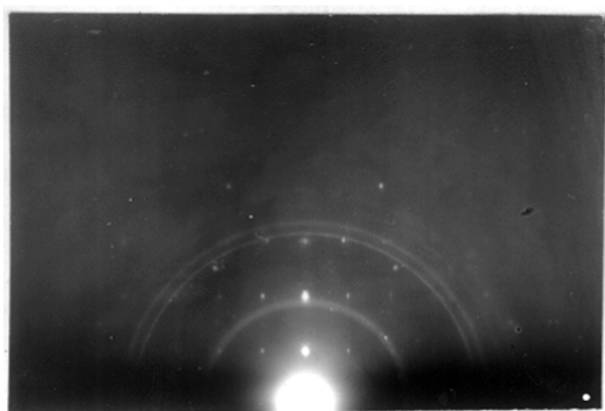


Fig 46

A7527

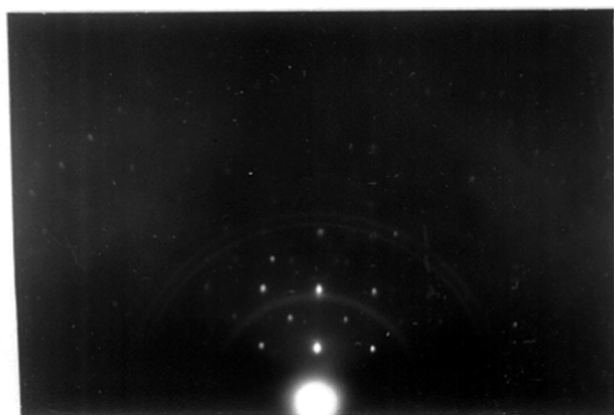


Fig 47

A7526

relation $T = 2\lambda L^2 / R_1^2 - R_0^2$, using the electron wavelength the camera length L , and the radii R_0 and R_1 of the zero and first circular zones, to be 8.96Å.

Figs 46 and 47 were obtained from the third specimen after lightly dusting it with graphite to serve as a reference for spacing determinations, and gave a value 7.68Å. for the spacing of the net plane which was parallel to the substrate surface, only the even orders from which appeared in the plane of incidence. An estimate for the first specimen relative to the mica $b = 9.02\text{Å}$. was made by comparison of the spacing of the spots in the plane of incidence with the 060 Kikuchi kin band width, and this gave a rough value 7.56Å. which agreed well with the above more accurate value, which was therefore taken as standard in estimating the lateral lattice spacings $\pm$ from other patterns such as Fig.44a and 45a. Measurements of Figs.46 and 47 also yielded the values 9.93Å. and 7.89Å. respectively for the spacings in the lattice rows which were parallel to the surface and normal to the beam at these azimuths.

The spot positions and straight-line Laue-zones from the main lattice rows normal to the beam and the circular zones due to the lattice row parallel to the beam or nearly so in Figs.42a, 43a, 44a and 45a, are shown in Figs.42b, 43b, 44b, and 45b respectively. These diagrams not only show the regularity of disposition of the spots on the Laue zones but

allow direct measurement of mean angles between the zones, and recognition of the true lattice-row periodicities by consideration of the spots lying on the circular Laue zones as well as the zero order zone which surrounds the undeflected beam spot.

From Fig.42a the horizontal lattice row spacing was calculated to be 1.285 times the vertical spacing, i.e. 9.86A., and the radius of the circular zone gave a rough estimate of 13.0A. for the lattice row at right angles to it, i.e. parallel to the beam. The corresponding axial ratio in Fig.43a, 1.740, gave a more accurate value 13.34A. for the latter spacing and showed that in this azimuth the lattice points in a plane normal to the beam were not quite in hexagonal arrangement though very nearly so, because $\tan^{-1} 1.740$ is $60^{\circ}7'$.

Figs. 42 and 43 thus indicate that this mica decomposition product ^{"D"}_K has a rhombic lattice of which the axes a,b,c have lengths 9.86, 13.34 and 6.68 A. respectively. Fig.43 shows that it is bc. face-centred so that only diffractions appear for which (k+l) is even, and from Fig.42 those of type $\{h0l\}$ only appear if h and l are both even, whereas for hkl diffractions l must be odd. This lattice is oriented with its (001) plane parallel to the mica (001) surface, its a and b axes being parallel to the mica a and b respectively.

The patterns in the other azimuths, Figs.44a and 45a confirm this unit cell, as may be seen most directly in terms

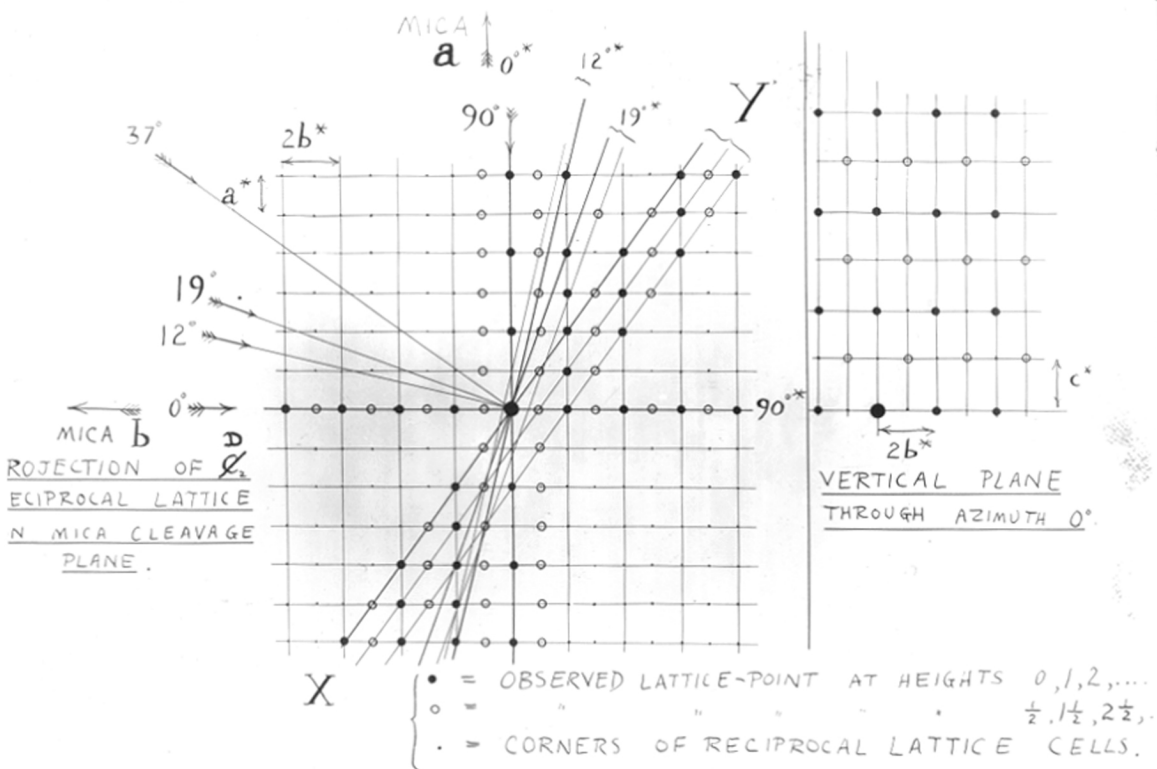


Fig 48.

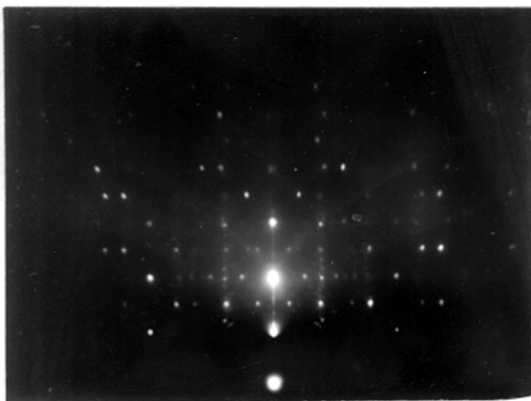


Fig 49.

A7524.

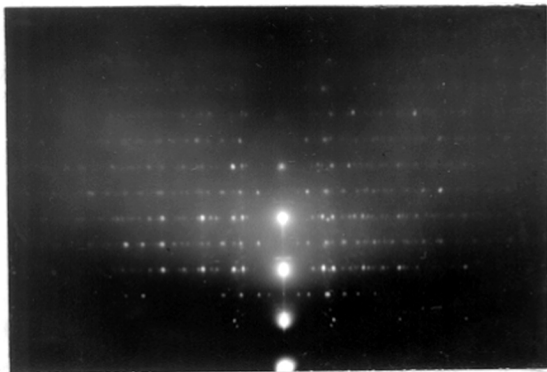


Fig 50

A 7515

of reciprocal-lattice considerations, since the patterns correspond to the λL times enlarged intersection of the Ewald sphere of reflection with the reciprocal lattice, which close to the undeflected beam spot is practically a plane normal to the beam. Thus the projection of the lattice on its (001) plane, i.e. the mica surface, is indicated in Fig.48, together with the beam directions in the 0° , 12° , 19° and 90° azimuths, and the traces of the planes perpendicular to them, represented by $0^{\circ*}$, $12^{\circ*}$ etc. The measurements of lateral spot spacings in Figs.44a and 45a agree closely with those indicated by this diagram, as also does the centred-rectangle arrangement of the spots and reciprocal lattice points in these patterns.

Although the above patterns from this first specimen show little evidence of the lattice occurring in the two other pseudo-equivalent orientations relative to the mica substrate, rotated by 60° and 120° to the above-described orientation, the occurrence of pseudo square patterns ($91\frac{1}{2}^\circ$ angle) symmetrically relative to the plane of incidence in Fig.49 from the third specimen, in addition to the hexagon pattern similar to Fig.43a, shows that here at least the three pseudo-equivalent (001) orientations occurred together.

The original of Fig.49 shows faintly the 060 band with its median in the plane of incidence, and a first order circular Kikuchi line envelope; and both of these indicate

that the beam was parallel to the mica *a* axis, in the plane of incidence (010), thus the pattern can be compared directly with that of Fig.43a in the similar azimuth. The nearly square pattern corresponds to the reciprocal lattice plane *XY* in Fig.48 and occurs when the beam is at $\pm 37^\circ$ to the *a* axis of the decomposition product. In the azimuth of Fig.49 the beam is 23° from such an azimuth, hence the square pattern occur on broad circular Laue zones centred about 7 cms. to left and right of the plane of incidence in Fig.49, owing to the presence of the other two azimuthally pseudo-equivalent (001) orientations of the decomposition product relative to the mica substrate.

In Fig.49 there can also be seen a few less prominent spots due to occurrence of a small proportion of the less symmetrical decomposition product, but Fig.50 which is a rotation pattern about the specimen normal, from 0° to 30° in azimuth measured from the mica *a*, provides in its clear horizontal layer lines and vertical row lines, still further evidence of the rhombic form of the lattice of the main decomposition product.

(c) Mica Cleavage Surfaces Heated in Air at 550-570°C.

These, as stated above, in some cases yielded patterns containing as one component a spot pattern similar to those from the 650°C. heated surfaces, but this was not present

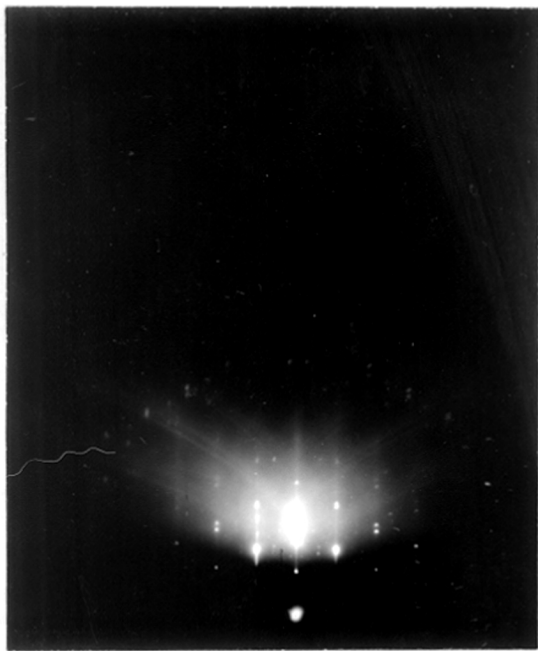


Fig 51_a

A7+38

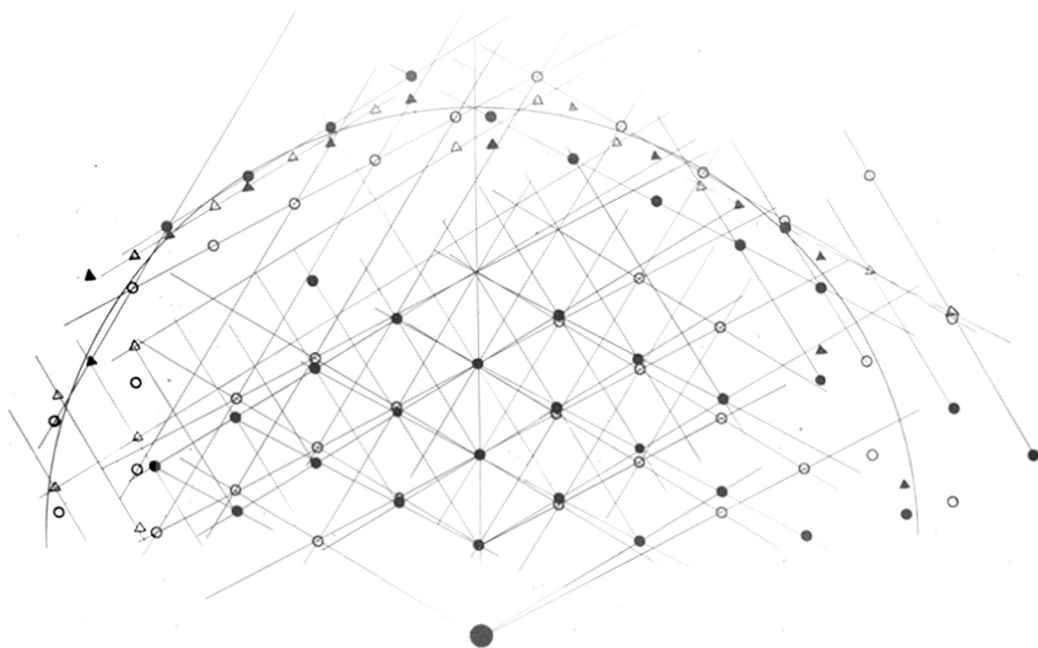


Fig 51_b

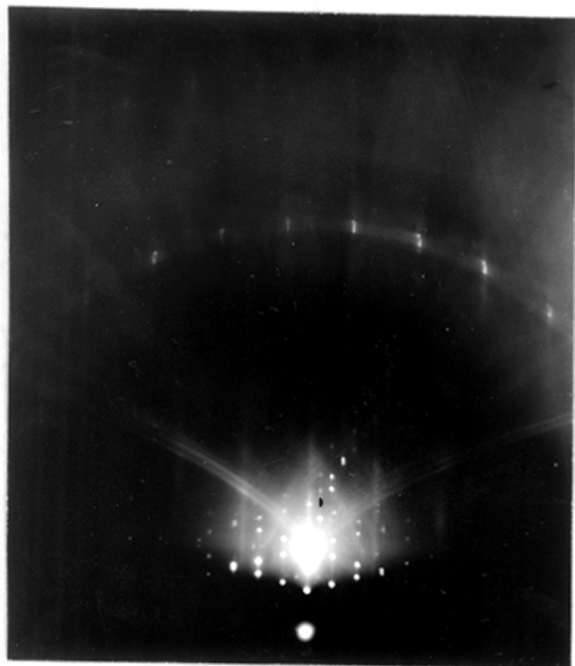


Fig 52_a

A7439.

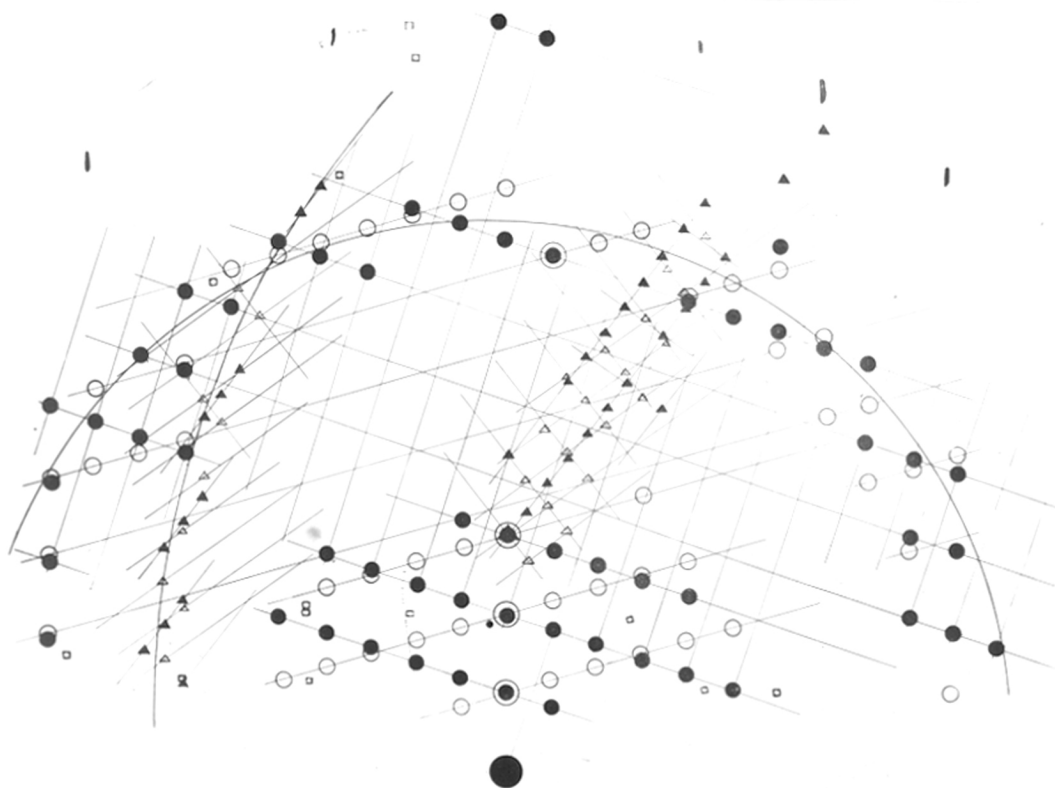


Fig 52_b

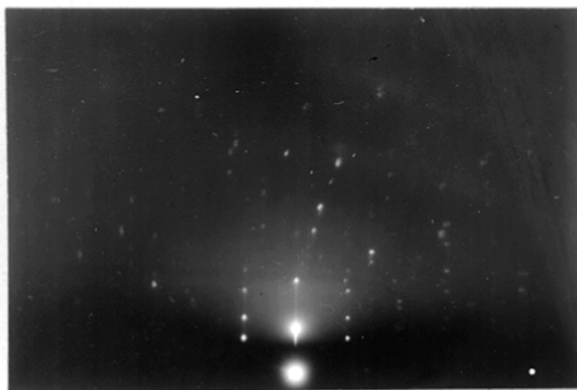


Fig 53

A7440

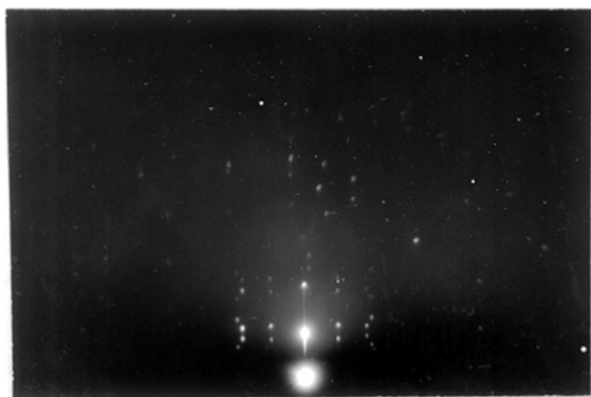


Fig 54

A7441

at all in several cases or was only represented by a few faint spots in others. The most typical patterns appear to be those shown in Figs. 51a, 52a, 53, 54 from a surface heated for 3 hours in air at $570^{\circ}\text{C}.$, and the material corresponding to these is denoted by C_2 .

In Fig. 51a the beam was parallel to the mica a axis, since the strong 060 band from the mica plane of symmetry is prominent near the plane of incidence, normal to the shadow edge. The spot positions are shown in Fig. 51b, where the spots of the component single-crystal spot patterns are distinguished by different symbols. These separate patterns are not symmetrical relative to the plane of incidence, though the mica symmetry results in two symmetrically related equivalent orientations of the decomposition product. In the zero order circular zone near the central spot in Fig. 51 the spots form a nearly hexagonal pattern, whose unit parallelogram is however representable as a centred rectangle with its diagonal vertical to the shadow edge. The first order circular zone, further out, shows the same pattern but it is displaced relative to that in the zero-order zone.

In Fig. 52a, taken at an azimuth 30° from that of Fig. 51a, the pattern shows in addition to the broad circular zones whose centre is near the plane of incidence, another set of circular zones centred on the shadow edge about 4.5 cms. from

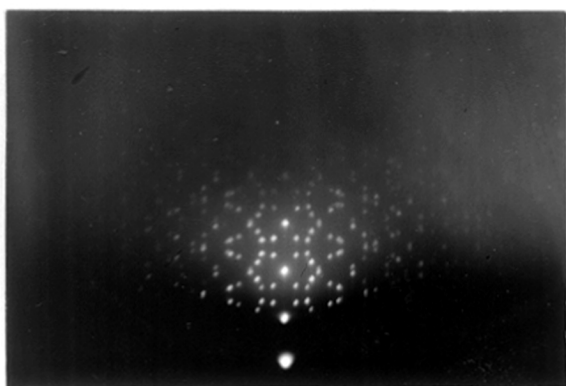


Fig 55_a

A7272

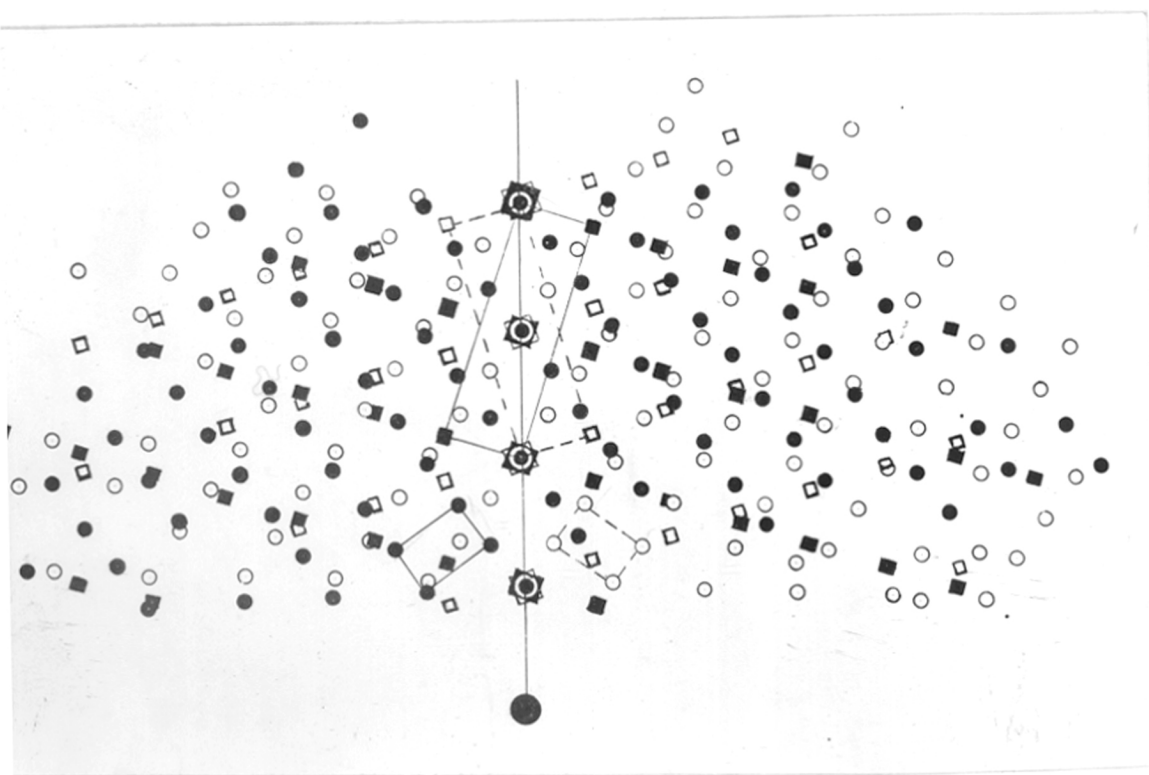


Fig 55_b.

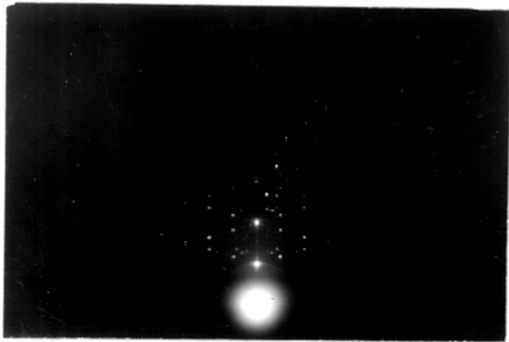


Fig 56.

A7279

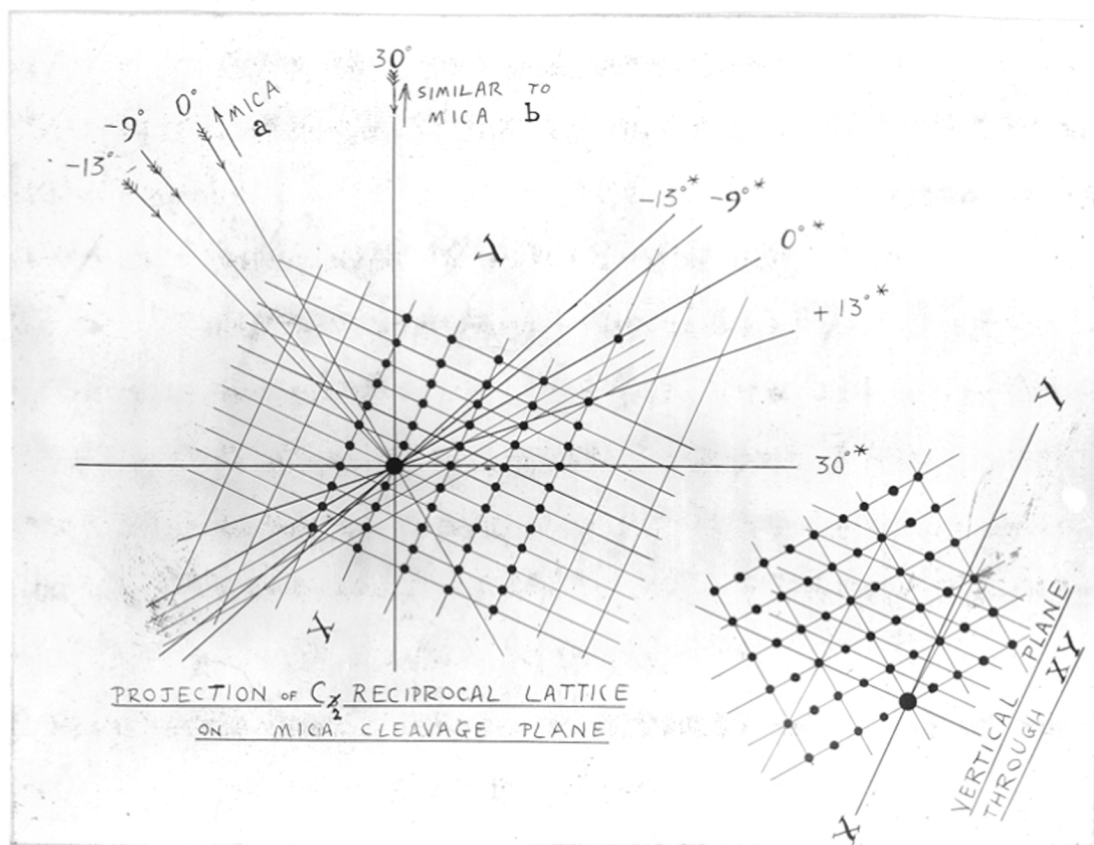


Fig 57.

the plane of incidence. Fig.52b shows the different component spot patterns which can be distinguished. Figs.55a and b and Fig.56 from two other specimens show still more clearly the four main component patterns, over the region of the zero-order circular zones.

The patterns of Figs.51 and 52 together allow a clear definition of the reciprocal lattice unit cell to be made, and Fig.57 shows the projection of the reciprocal lattice on the mica cleavage plane, the ordinates being marked as fractions of the spacing in the rows normal to this plane (corresponding to the spots in the plane of incidence in Figs.51 and 52).
 (azimuths -9° and -13°)
 Comparison of Figs.53 and 54_x with the corresponding reciprocal lattice planes through the origin in Fig.57, showed that these patterns contain vertical row lines of spots at the expected lateral distances from the plane of incidence and at the correct positions along these row lines, thus confirming this reciprocal lattice form. The circular zones in Fig.52⁵ which have their centre 4.5 cms. from the plane of incidence are also now seen to arise from decomposition product lattices in equivalent azimuthal orientations on the hexagonal plane lattice of the mica cleavage surface.

The reciprocal lattice so deduced is thus rhombic with $a^*:b^*:c^* = 1.294 : 1 : 0.754$ and oriented with a $[01\bar{2}]^*$ lattice row normal to the mica surface, with the $[110]^*$ row in a plane normal to the mica cleavage plane_{at 120°} (or 0° or -120°)

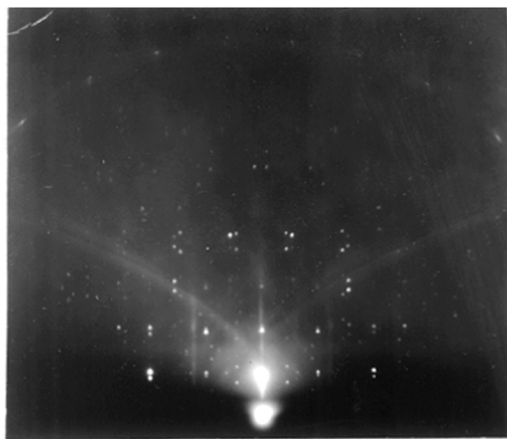


Fig 58

A7493

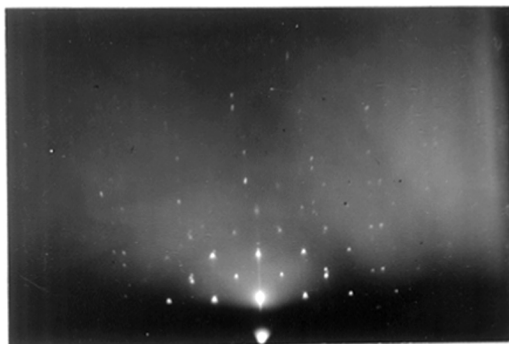


Fig 59.

A7496

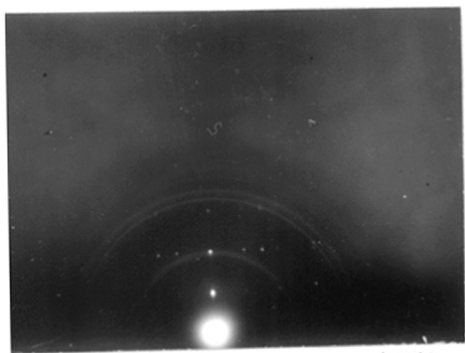


Fig 60

A7547

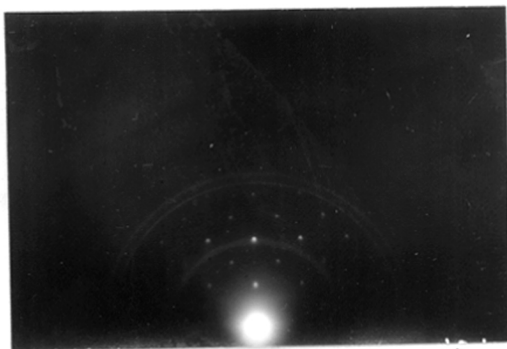


Fig 61

A.7548

to the mica a axis. The crystal lattice has thus $a:b:c = 0.773 : 1 : 1.326$ and has a $(01\bar{2})$ plane parallel to the mica cleavage face, with a  lattice row with spacing $7.74\text{\AA}$ parallel to the mica 'a' axis (or the 120° and 240° pseudo-equivalent axes), and  parallel to the mica b axis, with spacing $8.85\text{\AA}$.

Figure 58, obtained in a 'b' azimuth, from another specimen which had been heated 3 hours at 550°C . in air in a silica tube, shows a different structure denoted by C_3 . In an azimuth $34\frac{1}{2}^\circ$ from that of Fig. 58 it yielded Fig. 59, which has a prominent nearly square pattern as one component, similar to that (D) from the 650°C . specimens, but based on the same plane of incidence spot system. A further specimen dusted with graphite gave Figs. 60 and 61 at azimuths 34° apart, showing presence again of the structure $C_2 + D$, but the spacing of the net planes parallel to the mica surface was estimated from the graphite 110 ring radius to be $4.008\text{\AA}$., i.e. slightly larger than in the 650° specimens.

Table VII shows the data for the specimens of this temperature range, including the observed decomposition product types shown by the patterns.

IV. 3. Mica Cleavages Heated in Vacuum.

The results from several mica cleavage faces heated in vacuum at 300° and 500°C . (see Table VIII) were similar to those from specimens heated in air at the same temperature, and

Table VII.

Data for Mica Cleavage Faces Heated in Air at 550° - 650°C.

Spec. No.	Heat Treatment	Time hrs.	Temp °C.	Pattern type	Lattice Constants (lengths in) ^{A.}						Ref.
					a	b	c	c/a	c/b	b/a	
114A	$\frac{1}{2}$	550		A + B ₄							
114B	2-1/4			A + B ₈							
122	3			A+C ₂ +D							
119	3	570		A + C ₂	C ₂ 7.39	9.56	12.95	1.75	1.324	1.29	M
134	3	570		C ₈ + D	D	9.88	8.012				G
91	3	570		C ₂ + D					(1.30)		
92				(arcs)							
93				C ₂							
100	3	570									
117	3	570		C ₈ + D							
121	3	570		C ₂							
130	3	650		D	D 9.86	13.34	7.68	1/1.285	1/1.740	1.354	M
131	3			A + D							
133A	2			A + D	D 9.93	-	7.68	1/1.294			

Table VIII.

Data for Mica Cleavage Faces Heated in Vacuum.

Spec.	Heat Treatment		Pattern type.	Lattice Constants (lengths in A.)						Ref.
	Time hrs.	Temp °C.		a	b	c	c/a	c/b	b/a	
35	1/6	300	A+B ₄ +C							
37	1/6		A + B ₄ B ₄		4.71*	7.22		(1.538)		M
46	1/6		A + B ₁							
41	1/2		A + B ₁ B ₁	2.87*		7.50	2.67			G
44	1		A + B ₁			6.93				
45	1		A + B ₁							
48	1		A + B ₁ B ₁		4.76*	7.27				G
52	1		A + B ₁							
53	1		A + B ₁							
42	1/5	400	A + B ₁ ?							
38		500	A+B ₁ +B ₈ B ₁	2.627*	4.466*	6.94				(1.70)
			B ₈	2.790*	4.758*	6.94				(1.71) ^M
36	1/60		?							

* These spacings probably should be doubled.

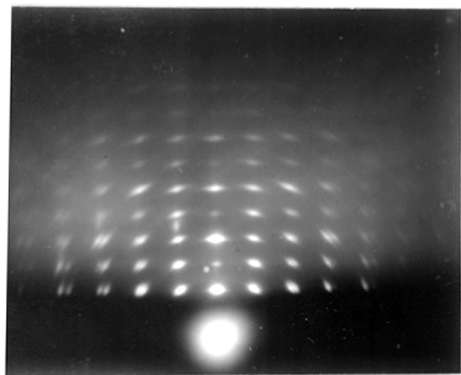


Fig 62

A 6963

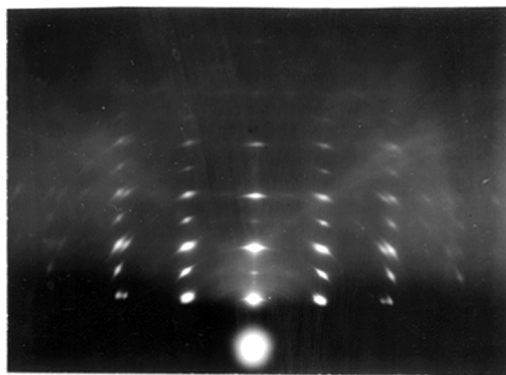


Fig 63

A 6964

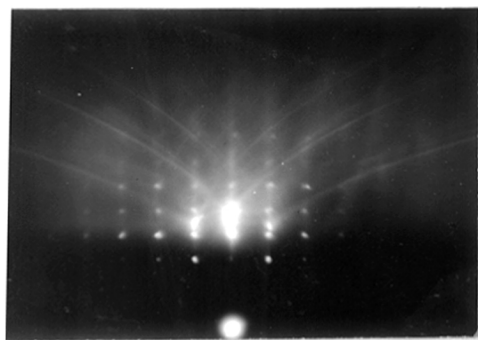


Fig 64

A 6946

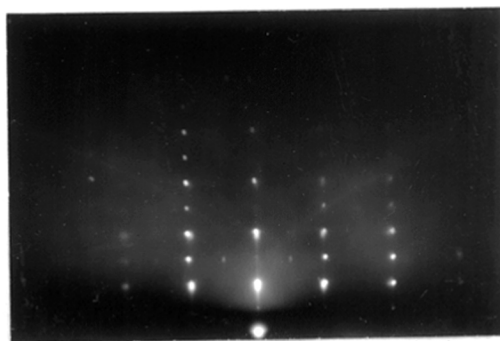


Fig 65

A. 6943

patterns of type (B_1+B_3) and (B_1+B_4) are illustrated for the 'a' and 'b' azimuths in Figs. 62 and 63 and 64 and 65 respectively. A pattern "C₁" having slightly inclined spot rows was observed in one case together with a B₄ pattern, but this has not as yet been investigated in detail. Since there was much variation in the apparent extent of the decomposition in the various specimens, as estimated from the relative intensities of the decomposition-product pattern and that still remaining of normal mica-cleavage type, it was not possible to compare effectively the rates of decomposition in vacuum and in air, though it seemed there was no pronounced systematic difference.

IV. 4. Mica Cleavages Heated in Air Saturated with Steam.

A mica cleavage face heated for $1\frac{1}{2}$ hours at 300°C. in air saturated with steam yielded a pattern characteristic of presence of a considerable amount of B₁ and B₃ products together. A second cleavage face after heating at 450°C. for 1 hour showed hardly any decomposition.

V. STRUCTURE OF SILVER LAYERS DEPOSITED ON FUSED QUARTZ AND GLASS.

As a preliminary to investigating the structure of silver deposits on fused quartz and mica it was considered desirable first to determine (1) to what extent, if any, tungsten oxide was deposited along with the silver; (2) whether bombardment of the specimen by the main beam and the electrons of the decharger beam caused appreciable changes in the deposit structure; (3) at what rate the deposit structure and colour changed, if at all, during standing in air after deposition. Following these experiments some results were obtained on the dependence of the deposit structure, especially particle size, on thickness of the deposit, gas pressure, and rate of deposition, and these are described below.

V.1. Deposition of Tungsten Oxide.

Deposition of tungsten oxide was found to occur from a filament heated to white heat for a considerable time (compared with the time of deposition of silver in the case of the silver deposits) in a vacuum of the order of 10^{-3} mm. of mercury. A well-used filament, which was further cleaned immediately prior to the experiment by heating strongly for 20 mins. in a vacuum, when heated at yellow heat for an hour in air at 3×10^{-3} mm. produced a visible deposit on a substrate placed

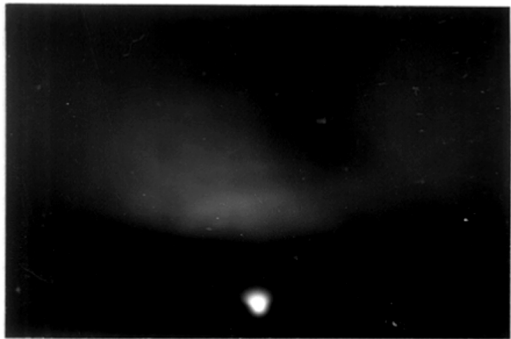


Fig 66

A 7175

2 cms. away. The deposit, which was pale blue by transmitted light and was probably due to tungsten oxide, yielded an electron diffraction pattern (Fig.66) corresponding to an amorphous substance.

Heating the filament for an hour at much lower temperatures, comparable with those used in the silver deposition experiments, gave no visible deposit but the same type of electron diffraction pattern was obtained from the substrate surface. A filament heated at 970°C. (i.e. at the melting point of silver) for an hour, however, showed a loss in weight of about 0.5 mg. The halo pattern is thus evidently from a real deposit and not the glass substrate.

The colour of the blue deposit on standing in air for about 12 hours was less noticeable than immediately after production and in reflected light it had then a pale greenish-yellow colour. The deposit was not removed by concentrated nitric acid nor a mixture of alcohol and nitric acid.

From these experiments it was concluded that the amount of tungsten oxide deposited relative to the amount of silver during normal preparation of the silver deposits was small and in effect was negligible.

V.2. The Effect of the Decharger on the Silver Deposit Structure and the Structural Changes Involved in Spontaneous Changes in Colour of Silver Films.

Changes in colour of silver deposits were often seen to

have occurred during their examination in the camera. The changes are most marked in the case of unheated deposits of yellow colour. These turned pink in the camera. No such change was observed in the case of heated deposits (see below VII) which had turned yellow on heating. To determine the effect of the decharger a pattern was obtained from a deposit 3 A. thick on silica glass, the pattern being photographed (using the decharger) almost immediately, and also a few minutes after turning on the decharger. The colour of the film on removal from the camera was distinctly pink but no marked change in the ring definition in the photographs or the production of any new orientations was found.

Colour changes, which are spontaneous, also occurred while the films were standing in air. Yellow films showed little or no change but red-purple films showed the effect distinctly. Photographs of a purple film, 15A. thick, taken soon after production showed that the crystal size was 77 A., and $1\frac{1}{2}$ days later, when it had a bluish purple colour, the crystal size was estimated to be 116 A., indicating that crystal growth had occurred. A freshly prepared yellow film 12A. thick showed only a slight increase of crystal size from 59 A. to 67 A. on standing for about a day in air. In these and other particle size estimations stated below, the breadths B of the rings were measured to a sufficient approximation for present purposes by setting the microscope

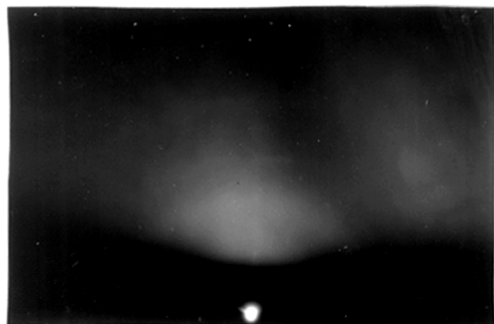


Fig 67

A7424

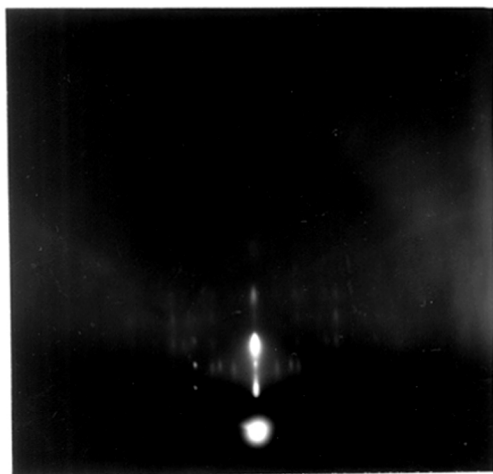


Fig 68

A7445

cross wire at each side of the ring where the steepest fall off in intensity occurred, the measurement being only made on strong well-resolved rings, for which the B values so obtained will be practically correct.

From these results it was clear that the specimens should be examined soon after preparation and the pattern recorded as soon as possible after commencing to examine the specimen by means of the electron beam and decharger.

V. 3. The Effect of Deposit Thickness on the Structure.

The size of the crystallites was found to increase with the thickness of the deposit, other conditions being closely similar. Deposits of thickness only 2.5A. on fused quartz were found to yield coherent electron-diffraction ring patterns. The crystal size in a film of this thickness evaporated on to a previously heated quartz substrate at room temperature was small enough to permit the pattern from the substrate also to appear, i.e. the characteristic spot series in the plane of incidence. A very thin deposit on mica, whose thickness was less than 3A., as estimated from the apparently exceedingly small change in the masses of filament and bead before and after evaporation, yielded a halo pattern, Fig.67, and the pattern from the smooth mica substrate was blotted out almost completely. Since this specimen, when heated for 30 mins. at 300°C., showed an aggregation into silver crystallites (in

the form of flat plates with very smooth surfaces, Fig.68) the initial halo pattern was in fact produced by the silver deposit. This observation, that such a thin and apparently continuous amorphous silver layer on the atomically smooth mica cleavage surface, so highly absorbs the electron beam at low grazing incidence, is interesting and agrees with the order of effective penetration of 20A. estimated by Finch and Wilman (1937)' in the case of hydrocarbon layers, when account is taken of the high atomic weight of silver.

The effect of the increase of crystal size with thickness was observed in films evaporated in an air pressure of 10^{-3} mm and in argon at about 10^{-1} mm. Table IX shows the crystal sizes estimated in deposits of thicknesses from 3 - 34 A., together with the conditions of these depositions. In the thicker of these films the crystal size was larger than in the thinner deposits.

Table IX.

Specimen	Thickness A.	Pressure mms.	Time of Deposition secs.	Substrate Distance cms.	Crystal Size A.
120a	3	10^{-3}	20	5	25
138	15	10^{-3}	15	5	77
152a	23	10^{-1}	7	9.5	230
155	34	10^{-1}	7	9.5	350

V.4. The Effect of Gas Pressure on the Structure and Colour of Silver Deposits.

Silver deposits of different thicknesses prepared on clean glass substrates were blue, purple, red or yellow in colour when seen by transmission in white light. At an air pressure near 10^{-3} mm. of mercury and under the conditions of deposition set down in Table X, the colours of the films were well defined, but it was not possible to correlate the estimated mean deposit thickness with the colour with any definiteness. The results of 23 evaporations performed with this purpose in view are given in Table X, and may be regarded as showing that the colour of a deposit, estimated in a broad visual sense, is not a very accurate measure of the deposit thickness, rather than that the colour is strongly dependent on the gas pressure near 10^{-3} mm. of mercury. The mean thicknesses calculated from these results agree fairly well with those stated by Goos (1937).

Simultaneous deposition on various substrates was found to yield films of different colours. Films on collodion on wire gauze generally showed no colour and only a 'silvery' reflection of white light, but films condensed on collodion layers on glass substrates and on fused quartz had widely different colours. The films on collodion seemed to transmit more light than those on glass and yielded films of blue or a lighter shade of it when those on glass had bluish-purple, purple or yellowish-red colour. This seems to indicate a

Table X.

Deposition No.	Mass of Ag evaporated mg.	Average radius of bead during evaporation cms. $\times 10^{-2}$.	Time of evaporation.	Distance between substrate and Ag bead. cms.	Filament current amps.
1	3.0	5.54	3 mins.	3.9	2.5
2	5.2	3.95	10 secs.	4.0	3.4
3	3.3	5.72	15 secs.	4.0	2.8
4	2.6	4.94	12 secs.	4.1	2.7
5	2.6	3.89	20 secs.	5.2	2.6
6	1.5	1.62	2 mins.	5.1	2.0
7	1.6	6.81	45 secs.	5.1, 7.0	2.2
8	2.7	6.43	75 secs.	5.1, 7.0	2.2
9	3.4	5.75	75 secs.	5.1, 7.0	2.2
10	3.0	4.89	75 secs.	5.0, 7.0	2.2
11	2.7	3.67	75 secs.	5.0, 7.0	2.2
12	1.1	1.46	*	5.1, 7.0	2.2
13	2.0	6.94	75 secs.	4.9, 7.0	2.2
14	2.4	6.57	75 secs.	5.0, 7.0	2.2
15	4.1	5.91	75 secs.	4.9, 7.0	2.2
16	4.9	4.61	75 secs.	5.0, 7.0	2.2
17	2.3	1.87	*	5.0, 7.0	2.2
18	3.8	6.69	75 secs.	4.9, 7.0	2.2
19	2.1	7.18	75 secs.	4.8, 7.0	2.2
20	3.7	6.39	75 secs.	4.9, 7.0	2.2
21	4.3	5.50	75 secs.	5.0, 7.0	2.2
22	3.3	2.97	75 secs.	5.1, 7.0	2.2
23	2.1	1.81	*	5.0, 7.0	2.2

*Ag bead evaporated completely

Table X. (continued)

Thickness in A. of Films.

Deposition No.	Blue	Purple	Red	Yellow
1	76	53	40	32
2	67	53	39	-
3	53	37	-	-
4	55	39	30	20
5	52	31	24	19
6	-	-	44	29
7	-	47	35,25	22,23
8	64	44,42	31,34	20,22
9	72,53	38,43	27,31	-,23
10	76	46,47	30,40	22,33
11	67	41,42	29,30	20,21
12	-	32	24	16,17
13	56	40,31	26,28	17,23
14	59	38,37	24,31	18,23
15	83,63	49,60	32,46	25,41
16	109,76	54,61	38,50	-,43
17	69	56	27,36	19,30
18	87,76	54,59	33,41	25,31
19	67,64	51,	30,32	20,24
20	82,70	56,57	36,39	29,31
21	70,70	52,66	40,43	32,38
22	76	50,51	44,40	24,33
23	58	41	26,32	20,27
Mean thickness	70	45	30	20

larger crystal size in films on collodion and is probably due to the potential barrier hindering the migration of silver atoms on the surface of collodion being less than on glass. The results of Picard and Duffendack (1943) appear to indicate this is the case for zinc and cadmium also.

Deposits made in comparatively high pressures (10^{-3} - 10^{-1} mm. Hg.) of air or argon were found to have dull colours and at the higher pressures black or greyish colours were observed. The adhesion of these deposits to the substrate was poor and in the case of very thick films a porous deposit was obtained, a part of which was removeable merely by currents of air or blowing.

The definition of the shadow cast by an obstacle and the contrast in colour of the deposit within the shadow and outside it, for evaporations in different gas pressures was very marked. A piece of nickel foil was arranged symmetrically with respect to the evaporating source midway between (2.5 cm. from) a large glass substrate and the source. Evaporations at air pressures of 3.1×10^{-3} , 1.8×10^{-2} , 9.5×10^{-2} and 1 mm of mercury were performed on four different glass substrates, in each case about 6 cms. of silver wire being evaporated with the same current through the evaporating filament. A shadow, which was however not sharp, was obtained in the case of evaporation at 3.1×10^{-3} , 1.8×10^{-2} and 9.5×10^{-2} mm.

At 3.1×10^{-3} and 1.8×10^{-2} there was a visible deposit with clear yellow, red and purple colours within the shadow edge and outside it the colour was a vivid purple. In 9.5×10^{-2} mm. of air, the contrast in colour between the two portions was not marked. It was a blue within the shadow and bluish grey in the thick part of the deposit. The contrast and definition of the shadow in the case of the evaporation in 1 mm. of air was good; a thick 'sooty' deposit outside and no visible deposit within the shadow was obtained. In this black deposit there was a large clear area free round the tip of a thermocouple which rested on the substrate, but in the case of the evaporations in better vacua (10^{-1} - 10^{-3} mm. Hg.) this clear area of the deposit round the thermocouple, though present, was much less noticeable.

An opaque black silver film, about 500A. thick, evaporated on silica glass (Fig.20) at an air pressure of about 1 mm. Hg. showed numerous well-resolved complete rings, indicating projection of the crystallites far out from the substrate surface, that part of the pattern below the shadow edge being produced by a transmission effect. The photograph shows clearly the ring broadening effect due to specimen length in reflection patterns and in the case of a specimen of this type the broadening is radial, the sharp transmission rings coinciding with the inner edge of the more diffuse reflection rings, corresponding to the smaller effective

camera length of the region contributing to this part of the pattern.

In order to observe the effect of the increasing gas pressure on the deposit structure several deposits were prepared in argon at gas pressures between 10^{-1} and 10^{-4} mms. of mercury under otherwise closely similar conditions. Since argon is of higher atomic weight than the oxygen or the nitrogen of the air and also because it is inert chemically it is a specially suitable gas for the present purpose. The diffraction pattern from the deposits which were mostly about 20A. thick, showed that though the crystals had not developed any preferred orientation relative to the fused quartz substrate there was a marked increase of mean crystal diameter with increasing gas pressure, as shown in Table XI. Fig.93 represents the pattern from the 16A. thick deposit.

Table XI.

Mean Film Thickness A.	Distance of Substrate. cms.	Time of Deposition secs.	Argon Pressure mms.Hg.	Crystal Diameter in A.
34	9.5	7	1.1×10^{-1}	350
23	9.5	7	1.3×10^{-1}	230
21	9.5	7	1.7×10^{-2}	98
16	9.5	7	10^{-4}	77

V.5. The Effect of Rate of Deposition.

Although a general impression was obtained that a slower rate of deposition resulted usually in an increase in the mean

crystal diameter no quantitative confirmation from deposits made under otherwise strictly similar conditions has yet been obtained. Of two films deposited during $\frac{1}{2}$ minute and 5 minutes respectively, other conditions being similar (12 A. thickness, 10^{-4} mm. Hg. air pressure, 9.5 cms. from filament), if the $\frac{1}{2}$ minute deposit was estimated to have mean crystal size 84A. and the 5 minute one 60A., but since the $\frac{1}{2}$ minute deposit showed the presence of a considerable proportion of hexagonal silver the crystal size estimate was less certain and also the validity of the comparison was impaired by this evidence of a difference in the conditions.

VI. THE STRUCTURE OF SILVER LAYERS DEPOSITED ON MICA.

1. Layers on Fresh and Old Cleavages of Mica.

Preliminary experiments on simultaneous deposition on mica cleavages freshly prepared and four days exposed to air indicated that there was little difference in the orientating influence of the mica, nor was there any marked difference in the crystal size. In order to avoid as far as possible variations due to differences in the amount or nature of the gas adsorbed on the surface of the mica substrates, however, fresh cleavages were used throughout the main experiments.

2. The Effect of Substrate Temperature on the Orientation in Deposits.

Thirty silver layers of between 10 and 60A. mean thickness were deposited on freshly cleaved mica in vacuo at room temperature, the gas pressure being in the region of 10^{-3} mm. of mercury for 28 and 10^{-1} Hg. for 2 of these, while the distance from filament to substrate was 5 to 10 cms. and the time of deposition was of the order of a minute. Of these 30, 2 showed two-degree (111) orientation, 6 a weak one-degree (111), and 1 (40A. thick) a weak one-degree (110), the remaining 21, including the two at the higher air pressure had randomly disposed crystals. All these deposited at the

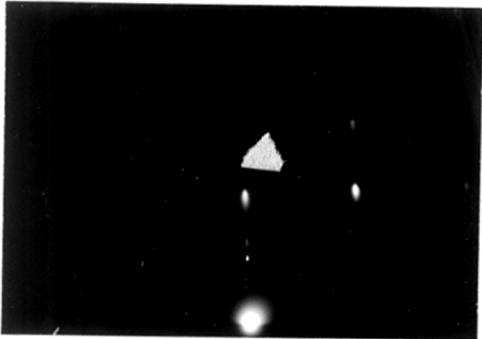


Fig 69

F. 1549

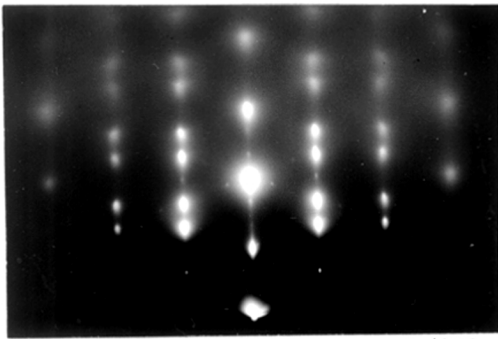


Fig 70

F. 1488

greater distance, i.e. 9-10 cms., were random, and the greater tendency to orientation on the 5 cms. distant substrates is probably evidence of the greater heating of the surface by radiation from the hot source. The mean crystal diameter was mostly of the order of 30 to 50 A. No special conditions were noted which might explain the cause of (110) instead of (111) orientation, observed in one specimen, and since the (111) orientation occurred even in deposits as thin as 14A. it must be due to the atomic mobility over the plane substrate rather than to development of preferential orientation with increasing deposit thickness.

Several deposits were prepared in vacuo on mica substrates maintained at 90°C., and the diffraction patterns were similar to Figs. 69 and 70 at azimuths 30° apart. The silver had thus grown in two azimuthally equivalent two-degree (111) orientations relative to the mica, as previously observed in this laboratory and by Rudiger (1937) in the approximate range 100 to 450°C. The indexing of these spot patterns is illustrated in Figs. 15 and 16.

A deposit ≈ 100 A. thick and of yellow colour, was prepared in vacuo on mica at 500°C., and like several similar deposits previously examined in this laboratory it was largely composed of silver crystals 200 A. or more in diameter, in strong two-degree (111) orientation on the mica, with a small proportion of (111) and (110) orientation present also.

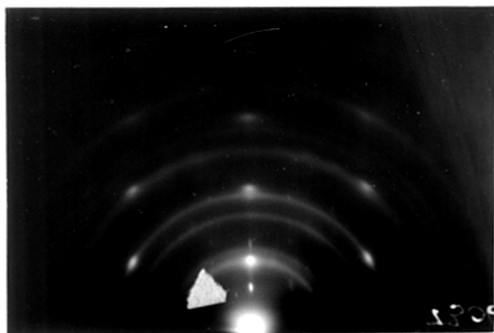


Fig 71

A. 7306

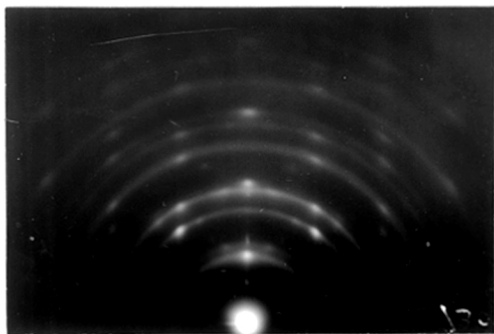


Fig 72

A. 7307

3. The Effect of Previous Thermal Decomposition on the Deposit Orientation.

A decomposed mica surface of B_1 type evidently has a stronger influence than fresh mica cleavages in promoting the two-degree (111) orientation of silver. Figs. 71 and 72 for example, were obtained in two azimuths at 30° to each other from a film deposited at room temperature on a previously decomposed at 570°C . specimen of mica. The strong pattern of spots shows good two-degree orientation in the deposit and the diffuse nature of the rings and the spots, showing the small crystal size in the deposit, indicate that the orientation is due to an intrinsic property of the decomposed surface and not a result of a reorientation resulting from the deposit being heated to more than 200°C . by radiation from the filament source. This can also be inferred by the fact that the photographs also show a feature not possessed by 'reoriented' or aggregated deposits produced by deliberate heating subsequent to deposition (cf. e.g. Figs. 81, 82 & 83), namely the two-degree (111) orientations present alone. One- or two-degree (100) and (110) orientations did not appear and also there is little trace of the other two-degree orientation of the (111) planes with the octahedral plane not symmetrically disposed with respect to the triangles in the hexagonal structure of the cleavage face. The pattern is in all respects similar to that obtained from a

deposit evaporated on to a substrate of mica at about 100° to 200°C.

This greater orientating power of the mica surfaces after their partial dehydration at not too high a temperature is thus of interest in two respects: (1) it is associated with an increase in spacing of the hexagonal lattice in the substrate surface plane (see IV, above), which fits more closely the hexagonal network in the Ag (111) planes in consequence, and it is this which accounts for the stronger orientating influence compared with unchanged mica cleavage faces; (2) it makes possible the production of two-degree (111) oriented silver layers having smaller crystal diameter than in the layers formed on mica at higher temperatures.

From the above experiment it also appears that the weak two-degree (111) orientation observed in some deposits produced by a fast evaporation on to the substrate at room temperature (see (2) above) may be in part assisted by slight dehydration of the surface layers, as well as by the increased orientating influence of the unchanged part of the mica surface when it becomes heated by radiation from the hot filament.

4. The Effect of Rate of Deposition on the Deposit Structure.

The rate of deposition affects the structure in two main ways, (1) by the correspondingly varying heating of the

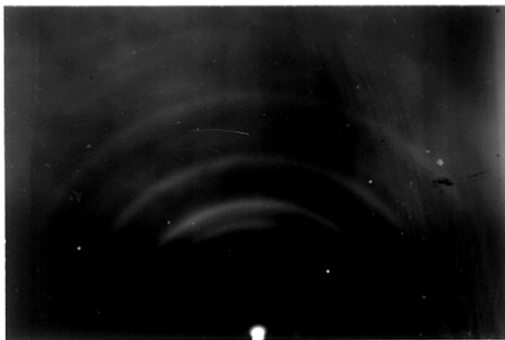


Fig 73

A 6897

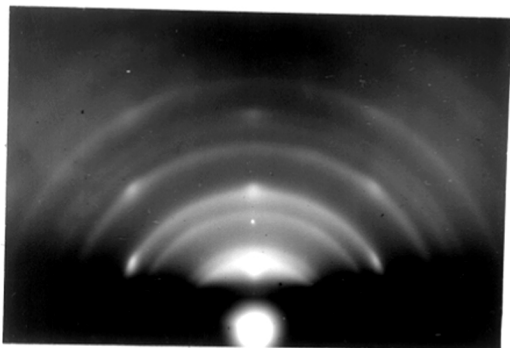


Fig 74

A 7582

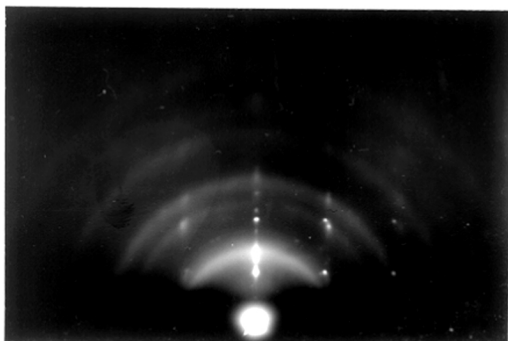


Fig 75

A 6911.

substrate by the filament, and silver globules affecting the crystal size and orientation; (2) the higher the number of atoms arriving on the surface per sq.cm. per sec., the greater will be the number of crystal nuclei formed per sec. per sq.cm. and the more rapid their growth, so that the mean crystal size in otherwise similarly prepared deposits of a definite mean film thickness is likely to be affected from this cause as well as from the different heating of the substrate surface.

Deposits formed on a substrate 5 cms. away from the source exhibited small crystal size and either a random disposition of weak one-degree or two-degree (111) orientation, and no orientation was observed with the substrate at distances greater than 5 cms. Thus the intensity of heat radiation on the deposit and substrate appears to affect the deposit structure to an important extent.

Figs. 73, 74 and 75 show the effect of the rate of deposition on the pattern type, with the substrate at 5 cms. and the residual air pressure near 10^{-3} mm. Hg. Table XII shows the conditions of deposition of these films. It will be seen that rapid evaporation of the silver produced a random disposition while slower rates yielded deposits with two-degree (111) orientation. With a very slow rate of deposition, the effect of heat radiation on the substrate is proportionally greater in causing dehydration, and in Fig. 75

Table XII.

Fig.	Thickness A.	Time of Deposition	Rate of Deposition mgs/sec/ sq.cm.	Mean Diameter of Random Crystals	Orientation
73	18	30 secs.	63.7×10^{-6}	78A	Random
74	25	1 min.	42.4×10^{-6}	60A	40%, 2-degree (111)
75	27	45 mins.	1.1×10^{-6}	55A	30% 2-degree (111)

the pattern due to the mica decomposition product (B) appears together with the silver pattern. The formation of the B decomposition product indicates that the temperature of the substrate surface in such an experiment can be as high as 200 or 300°C. and that much decomposition of the mica takes place. The two-degree (111) orientation produced is therefore in this case partly increased by the modification in the crystalline forces between substrate and deposit.

The (111) orientation of the silver relative to that of the decomposition product is shown by Fig.75 to be such that the equilateral triangles of the silver (111) planes have edges normal to those of the equilateral triangles in the surface net plane of the hexagonal mica B product. Thus, from the lattice constants of the B products stated above, this orientation is seen now to afford a closer fit of the

silver and B hexagonal planes than that where the triangles are in parallel orientation.

The crystal diameter of the random crystallites in the deposits in Table XII was small and of the order of 50A. The crystal size in deposits of this type heated to 300°C. for 10 minutes after deposition was about 350A. (cf. e.g. Figs. 75 and 82). This might indicate that although the effect of radiation on the substrate is considerable, its direct effect on the deposit structure is small or negligible, but the rate and degree of heating of the mica and the silver crystals initially formed on it are not easily estimated and the above conclusion cannot be considered to be necessarily correct.

With the substrate at 9.5 cms. the effects of heat radiation may be considered to be negligible. Deposits made at this distance showed a slight increase in the particle size in the case of low rates of condensation.

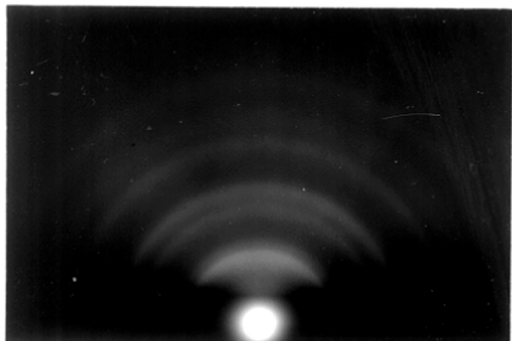


Fig 76

A7536

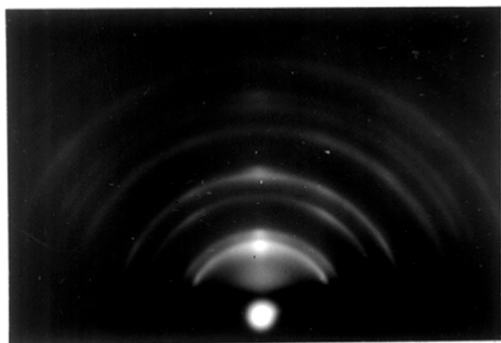


Fig 77

A7539

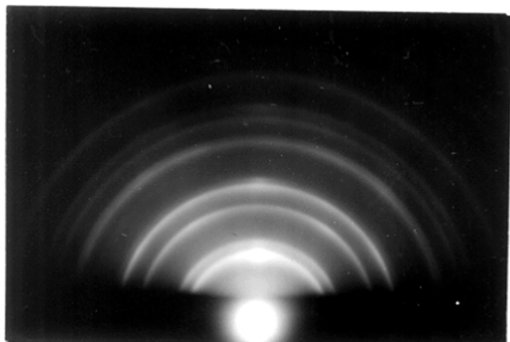


Fig 78

A7544

VII. THE EFFECT OF SUBSEQUENT HEAT TREATMENT
ON THE SILVER DEPOSIT STRUCTURE.

1. Crystal Growth in Deposits on Fused Quartz.

Heating a blue film 88A. thick on a microscope cover glass for 3 minutes at 50°C. in air, or $\frac{1}{2}$ hour at 50°C. produced no change in ring sharpening or colour. Heating the same specimen for a further 5 minutes at 150°C. caused an increase in crystal size but no change in the colour. Heating for a further 15 minutes at 150°C. changed the colour to very light blue with little further increase in crystal size. Heating similar deposits at higher temperatures for shorter periods produced a large increase in crystal size.

On fused quartz a red-purple film 28 A. thick gave diffuse rings with no orientation and having a mean crystal diameter about 128 A. (Fig.76). This became bright yellow after heating for 3 minutes at 300°C. The film after heating showed strong one-degree (111) orientation, weak one-degree (100) orientation and a crystal diameter about 150 A. (Fig.77). Heating the same film at 300°C. for a further 6, and then 18 minutes produced little change in ring sharpening or orientation. After a total time of heating of about 45 minutes there was a further increase in crystal size (to 350 A.) and less one-degree (100) orientation (Fig.78). The same type of growth was observed in a transparent grey film evaporated in

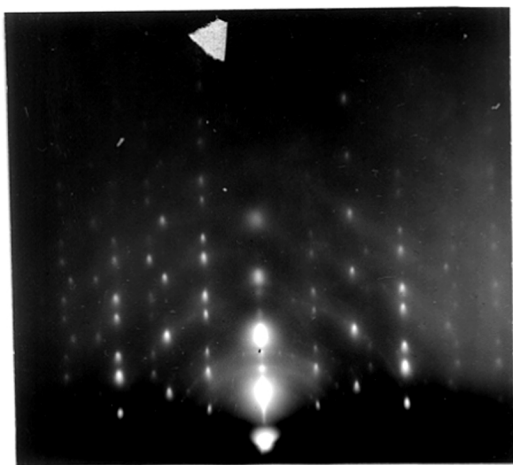


Fig 79

A6914

about 10^{-1} mm. of argon, and composed initially of random crystals 230 Å. in diameter. The colour of the film changed to weak yellow after heating for $\frac{1}{2}$ hour at 300°C. in air, the crystal diameter increased to >350 Å. and the film had a weak (111) orientation.

These results thus show that the rate of increase of crystal size of the silver, and therefore the mobility of the atoms, was very small at 50°C. but is appreciable even at 150°C. and relatively rapid at 300°C. The appearance of the (100) as well as (111) orientation observed in one case, followed by decrease of the (100) orientation on further heating is probably further evidence of the (111) orientation being the state of least potential energy on a quartz surface at 300°C., though (100) orientation is only slightly less favourable.

2. The Reorientation of Initially Random Deposits on Mica.

In agreement with the orientation of silver on mica at between 90°C. and 480°C. in strong two-degree 111 orientation as described in Section VI, it was found that deposits initially consisting of silver crystals which were mainly in this orientation, showed practically no development of other new orientation when heated in air for 5 minutes at 500°C. Fig.79 was obtained from the specimen which yielded Fig.75 after heating in air at 500°C. for 5 minutes, and several other specimens behaved in the same way. Though the (111)

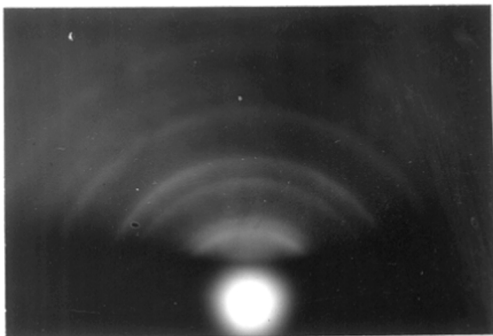


Fig 80

A7232

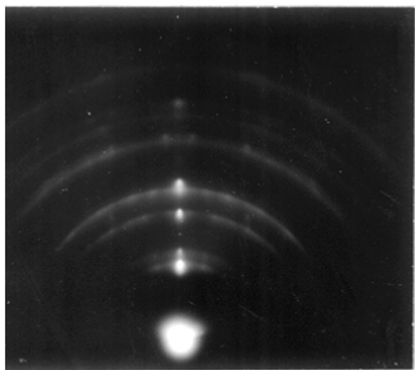


Fig 81

A 7233

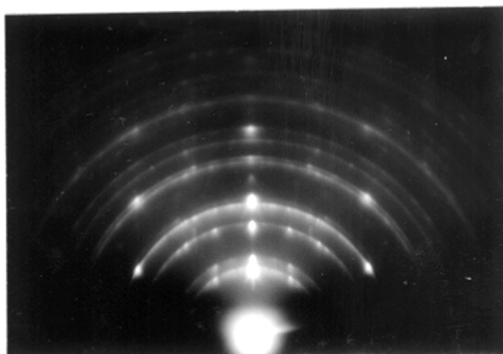


Fig 82

A 7244

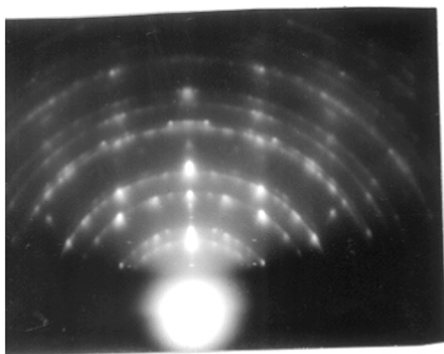


Fig 83

A 7239

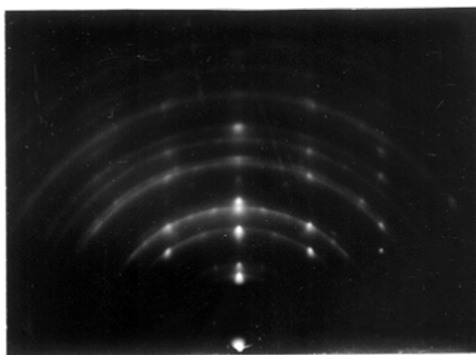


Fig 84.

A 7242

orientation remains unchanged it had grown much larger, to well over 200 Å. in diameter, and the crystals had relatively smooth (111) surfaces parallel to the substrate.

When the initial deposit was random crystals, however, crystal growth occurring when the specimen was heated in air or vacuum was also accompanied by prominent development of other orientations together with the normal two-degree (111) orientation. Fig.80, for example, was obtained from a 40 Å. thick, reddish-purple silver film deposited on mica at room temperature during $\frac{1}{2}$ minute at a distance of 5 cms. from the source, the air pressure being about 10^{-3} mm. of mercury. On heating for 10 minutes in air at 300°C. it yielded Fig.81, which shows a large increase in crystal size, though it is not at a main azimuth it shows the strong two-degree orientation partly of (111), but partly also (100) and (110) types. Fig.82 for comparison was obtained from another piece of the initial deposit after 10 minutes in vacuum at 300°C. It also shows the same types of orientation and larger crystal size than in the initial film. Heating new pieces of the original random deposit for half an hour in air and vacuum respectively yielded Figs.83 and 84, which show again (at an azimuth 30° from Fig.82) the same orientations as the specimens heated for 10 minutes, Figs.81 and 82.

A piece of the same specimen which yielded Fig.80 when heated in vacuum for 10 minutes at 500°C. gave Fig.85, which

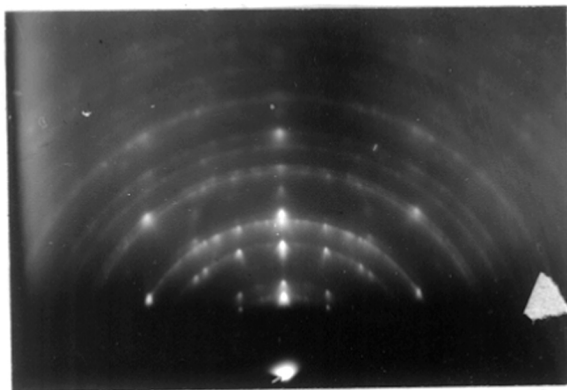


Fig 85

A7265

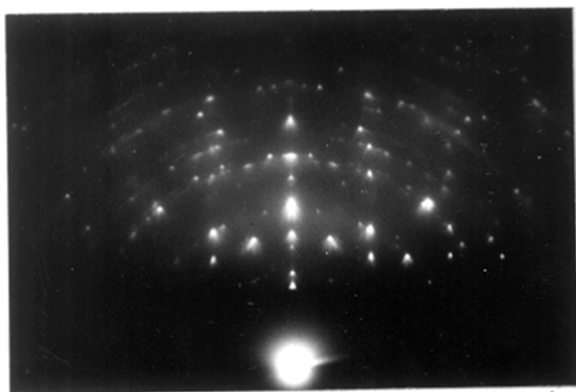


Fig 86

A7246

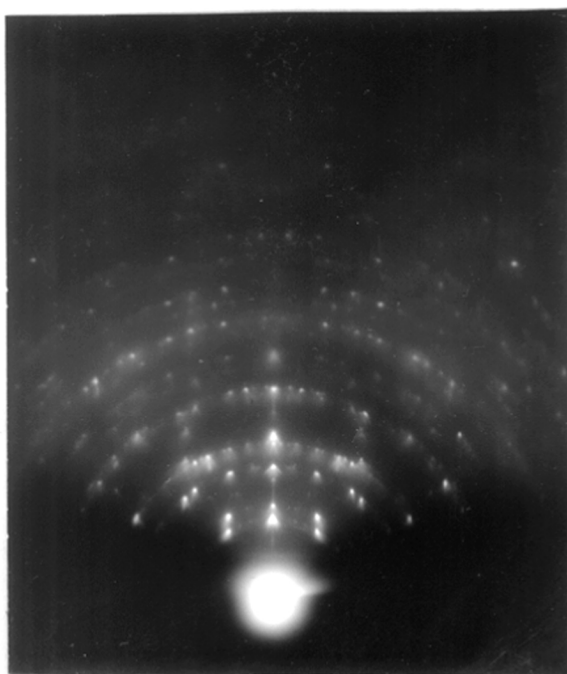


Fig 87

A7248

is again similar to those from the 300°C. specimen apart from the still larger increase in crystal size and the still stronger development of boundary faces as shown by the spots being elongated by refraction. Figs. 86 and 87 at two azimuths 30° apart were from an initially random deposit when heated for 5 minutes at 550°C. in air, and these are similar in type to the 500°C. vacuum results.

While the azimuthal positions of the crystals in the (100) and (110) orientations have not as yet been fully determined it is clear that in the (111) orientation some crystals have the equilateral triangles in the (111) planes parallel to the mica a axis while others are rotated by 30° in azimuth to this. Fig. 83 for example shows faint sharp mica decomposition spots of B₁ type which establish the azimuth is parallel to the mica b axis, while Fig. 87 correspond to the a azimuth or the equivalent 60° apart directions. In this respect there is a peculiar difference from silver deposited on freshly cleaved mica, or on previously decomposed mica (Section VI). Rudiger (1937) observed both these sets of azimuthal orientations together in deposits prepared at 380°C. but it is clear that the surface decomposition of the mica exerts a change of 30° in the azimuthal orientations of the silver relative to the mica and that the reason both types occur together is that some parts are decomposed into a B₁ type product while others are not.

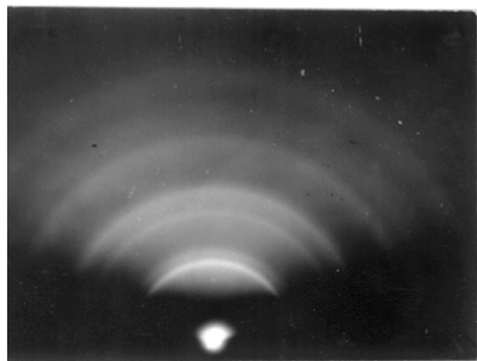


Fig 88

A7292

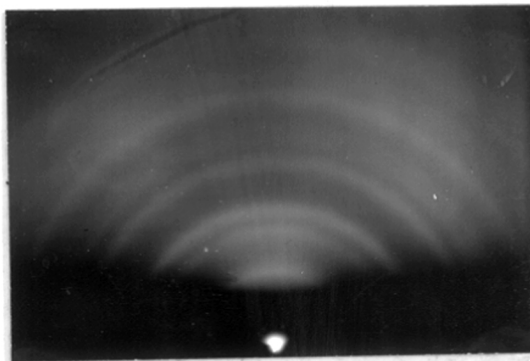


Fig 89

A7295

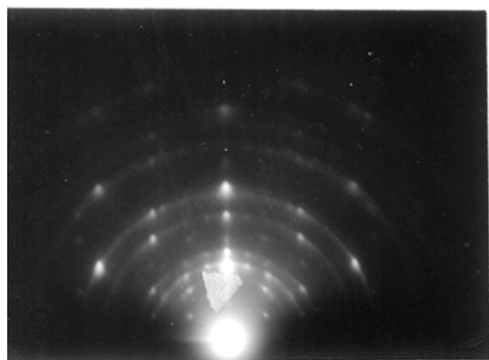


Fig 90

A7296

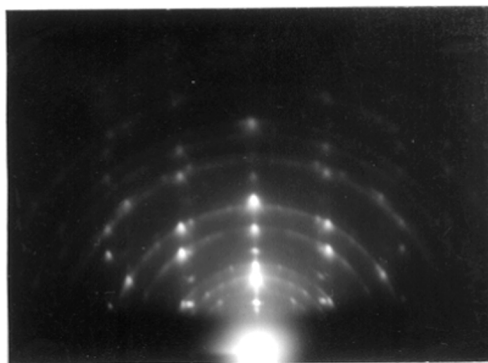


Fig 91

A7297

For comparison with these results a random blue deposit of gold 28A. thick was prepared on mica at room temperature in a vacuum of about 10^{-3} mm. and it gave Fig.88. Heating for half an hour in air at $300^{\circ}\text{C}.$, unlike in the case of silver, caused no change in colour or pattern features, Fig.89, but 5 minutes in air at $550^{\circ}\text{C}.$ caused it to become pink (by transmitted white light) and it then gave Fig.90 and 91 in azimuths 30° apart. In Fig.90, a B_1 mica decomposition pattern is present which establishes the azimuth as parallel to the mica a axis and shows that extensive surface dehydration had occurred, the gold (111) orientated crystals corresponding being in the same two sets of azimuths relative to the mica as occurred with silver. The (110) and (100) orientations also occurred exactly similar to those of similar silver specimens.

These results show that gold behaves in a closely similar way to silver in respect to the orientations it takes up on mica but its atomic mobility is less than that of silver at the same temperature.

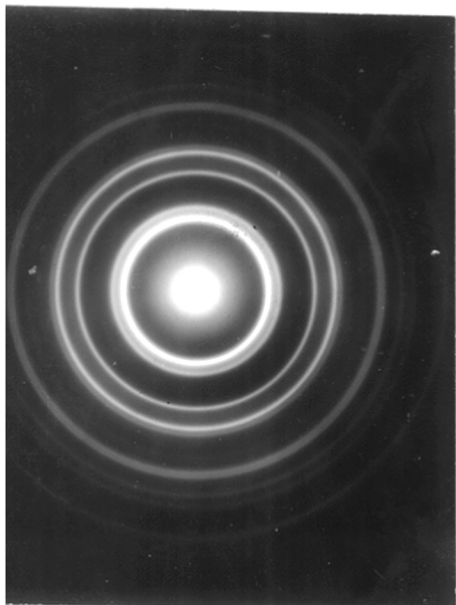


Fig 92

A7015

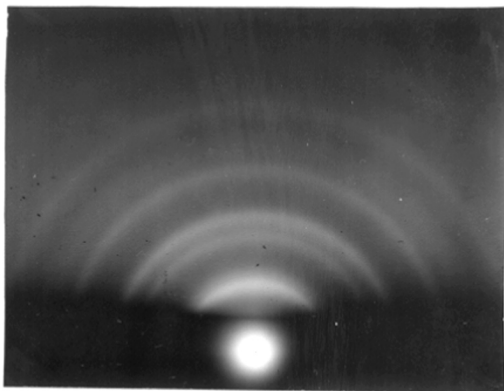


Fig 93

A8034

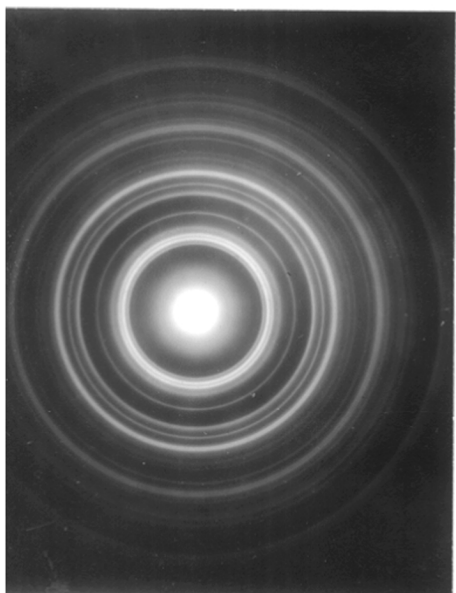


Fig 94

A7014

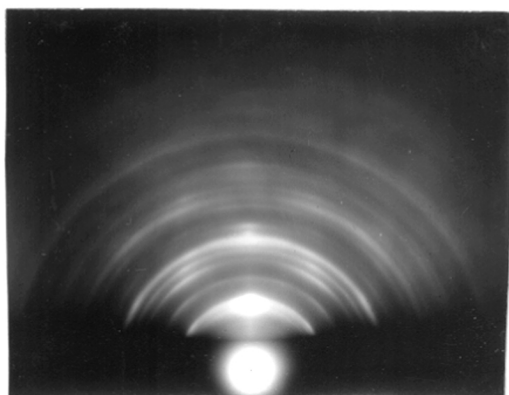


Fig 95

A8039

VIII. THE FORMATION OF HEXAGONAL SILVER
AND THE CONTAMINATION OF FILMS IN
THE LABORATORY ATMOSPHERE.

The normal and hexagonal modifications of silver were observed together in films evaporated on to transmission substrates of collodion and on to reflection substrates of silica glass. Fig.92 and Table XIII show the normal transmission pattern and its analysis and Fig.93 the normal reflection pattern.

Table XIII.

Analysis of the pattern of Fig.92, from Normal Cubic Silver - a 28A. thick Silver deposit on Collodion.

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

Intensity	Ring Radii	Indices hkl	d in A.	d in A. from X-ray data.
VS	1.046	111	2.336	2.355
M	1.203	200	2.031	2.039
S	1.709	220	1.430	1.442
S	2.000	311	1.222	1.229
F	2.092	222	1.168	1.177
VF	2.417	400	1.011	1.020
S	2.630	331	0.929	0.935
S	2.708	420	0.902	0.912
F	2.968	422	0.823	0.832
F	3.138	333	0.779	0.785

The Bragg plane spacings shown in the last column are calculated from the X-ray result of 4.077 A. for a_{Ag}

Table XV

Analysis of Pattern of Fig. 94 - Mixture of Cubic and
Hexagonal Forms of Silver.
73A. of Silver on Collodion.

Normal Silver $a = 4.077A$. used as Reference.

Intensity	Ring Radii cms.	d_A	Hexagonal Indices	Cubic Indices	Hexagonal Form a_A	c/a
M	0.976	2.508	100		2.896	
S	1.042	2.349	002	111		1.62 ₃
MS	1.106	2.214	101			1.63 ₈
MF	1.203	2.034		200		
M	1.419	1.726	102			1.64 ₄
M	1.693	1.445	110	220	2.89 ₀	
MF	1.715	1.427	-			
M	1.833	1.336	103			1.63 ₆
VF	1.900	1.288	-			
F	1.949	1.256	200		2.90 ₀	
S	1.984	1.234	112	311		1.63 ₀
MS	2.017	1.213	201			
VF	2.082	1.176	004	222		1.62 ₅
VF	2.099	1.166	-			
MF	2.200	1.113	202			(1.67 ₀)
F	2.291	1.069	113			
			104			
M	2.491	0.983	203			1.64 ₀
VF	2.576	0.950	210		2.90 ₂	
M	2.627	0.932	211	331		
M	2.674	0.915	114	420		1.63 ₀
VF	2.722	0.899	105			(1.66 ₈)
MF	2.771	0.883	212			
F	2.847	0.859	204			1.62 ₉
F	2.930	0.836	300	422	2.89 ₆	
MF	3.012	0.813	213			
F	3.099	0.789	006			
			302			
F	3.241	0.755	106			1.64 ₀
F	3.308	0.740	214			
VF	3.396	0.721	220		2.88 ₄	
VF	3.446	0.710	221			
MF	3.540	0.692	222			
			116			
F	3.593	0.681	007	442		
MF	3.662	0.668	312			

Mean $a_{\text{hexl}} = 2.895 A$. Mean $c/a = 1.63_8$; thus $c = 4.72_9 A$.

The values in brackets were not used in taking the means. The 202 hexagonal ring was a broad one.

Table XV

Analysis of pattern of Fig. 95 Mixture of Cubic and
Hexagonal forms of Ag.
14 A. of Ag on Silica Glass.

Normal Silver $a = 4.077$ A. used as Reference.

Intensity	Ring Radii cms.	d_A	Hexagonal indices	Cubic indices	Hexagonal Form a A. c/a
S	0.920	2.564	100		2.96 ₁
VS	0.995	2.345	002	111	1.60
S	1.058	2.206	101		1.55 ₈
M	1.359	1.718	102		1.58 ₉
MF	1.610	1.450	110	220	2.90 ₀
M	1.747	1.336	103		1.61 ₉
S	1.852	1.260	200		2.91 ₀
S	1.922	1.214	201		
MF	1.986	1.175	004	222	1.61 ₁
M	2.102	1.110	202		1.59 ₆
F	2.200	1.060	104		1.60 ₂
	2.387	0.977	203		1.58 ₇
F	2.512	0.929	211	331	
VF	2.553	0.914	114	420	1.60 ₇
MF	2.652	0.880	105 213		
MF	2.790	0.836	300	422	2.89 ₆
VF	2.826	0.826	213		
M	2.976	0.784	006 302	333	

Mean $a_{\text{hexl}} = 2.917$ A. ; Mean $c/a = 1.597$; thus $c = 4.658$

The transmission pattern from a mixture of the cubic and hexagonal forms in a film 73A. thick deposited in 90 secs. on a substrate 6.3 cms. away in an air pressure of 4.4×10^{-3} mm. of mercury is shown in Fig.94 and the corresponding reflection pattern from a film 14 A. thick deposited in 30 secs. on a substrate 9.5 cms. away at 10^{-4} mm. Hg in Fig.95. The transmission picture, having over 33 well resolved rings in the negative, shows a slight broadening of the cubic circles relative to the hexagonal ones.

Analysis of these patterns, given in Tables XIV and XV using the cubic silver rings as reference yields for the transmission case $a_{\text{hexl}} = 2.895$ A., $c/a = 1.633$ $c = 4.729$ A. and with less accuracy for the reflection one $a_{\text{hexl}} = 2.917$ A., $c/a = 1.597$ and $c = 4.658$ A. The silver in the reflection pattern is in several different orientations, sharply defined (111) cubic and the equivalent (001) hexagonal and only slightly less strongly in hexagonal (100) and (101) orientations.

In one of the observed cases it was noticed that a visible amount of tap grease (vaseline-rubber mixture) was present accidentally near to the evaporating filament during the deposition. This observation suggests that the hydrocarbon vapour in the region of the depositing silver was responsible for the formation of the hexagonal silver crystals.

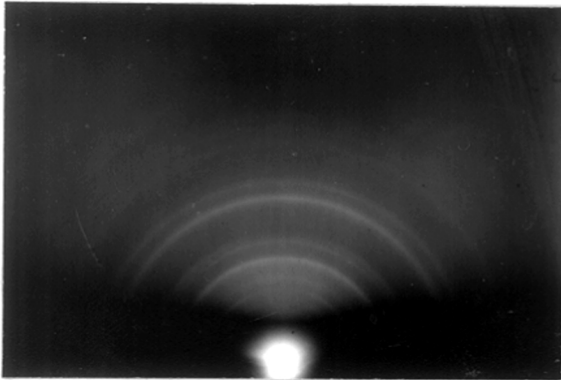


Fig 96

A7584.

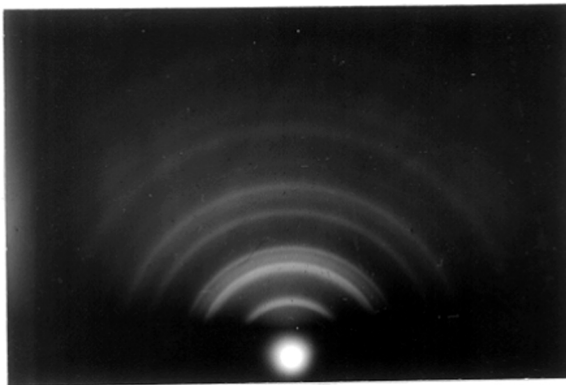


Fig 97

A8031

This hexagonal structure caused by the gaseous atmosphere in this type of deposition is analogous to the similar formation of hexagonal nickel (Thomson, 1929, Ogawa, 1937) sputtered in hydrogen, and cobalt layers electrodeposited under certain conditions.

The Contamination of Films in the Laboratory Atmosphere.

Silver films of the range of thickness used in these investigations were found to be easily contaminated in the atmosphere. Figs. 96 and 97 show patterns obtained from films of thickness 15A. and 34A. respectively which had evidently reacted with chlorine and iodine respectively. Analysis of these patterns is given in Tables XVI and XVII. Fig. 96 is almost entirely due to silver chloride. The faint extra ring with Bragg plane spacing of about 2.35A. observed in this and other 'contaminated' patterns is probably the 111 ring of Ag.

Table XVI.

Analysis of pattern of Fig. 96 from Silver Chloride.

Camera Length = 47.5 cms. Voltage = 46KV.

Intensity	Radius cms.	d in A.	Indices hkl	a A.
F	0.838	3.172	111	5.494
MF	0.981	2.709	200	5.418
F	1.136	2.340	-	
S	1.378	1.929	220	5.45
MF	1.604	1.657	311	5.49
MF	1.688	1.574	222	5.45
S	2.167	1.227	420	5.48
MS	2.375	1.119	422	5.48
F	2.919	0.911	442	5.46
VF	3.058	0.869	620	5.49

Table XVII

Mixture of Cubic and Hexagonal Forms of AgI
 formed from a 34A. thick Silver Layer
 Evaporated in Argon at 1.1×10^{-1} mm. of Hg.
 Camera Length = 47.5 cms.
 Voltage = 45 KV.

		Silver Silver Iodide Diffractions						
		Cubic form			Hexagonal form			
Intens.	Radius cms.	d(A)	Indices hkl	Indices hkl	a in A.	Indices hkl	a in A.	c/a
M	0.707	3.802				100	4.39 ₀	
M	0.747	3.598		111	6.23 ₂	002		1.63 ₀
F	0.800	3.359				101		
M	1.166	2.305	111					
S	1.219	2.205		220	6.23 ₆	110	4.41 ₁	
MF	1.326	2.027				103		1.62 ₅
S	1.423	1.889		311	6.26 ₆	112		
VF	1.491	1.803		222	6.24 ₆	004		1.63 ₃
VVF	1.544	1.741				202		
VF	1.607	1.673				113		
M	1.895	1.418	220					
F	2.094	1.283		422	6.28 ₅	300	4.49 ₄	
M	2.231	1.205		333 511	6.26 ₂	006 302		1.63 ₈
F	2.548	1.055	400					
MF	2.909	0.924	331 420					
MF	2.990	0.899				403		
F	3.247	0.828				412		
F	3.505	0.767				414		

Mean a = 6.25₄ A.

Mean a = 4.43₂ A.

Mean c/a = 1.63₂

Wilman { a = 6.489 A.
 (1940) { a = 4.583 A.
 { c/a = 1.640 ± 0.003

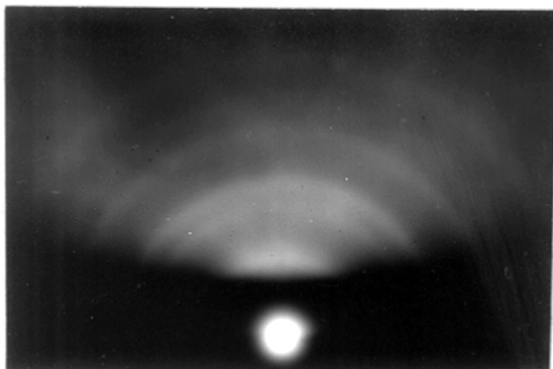


Fig 98

A7459

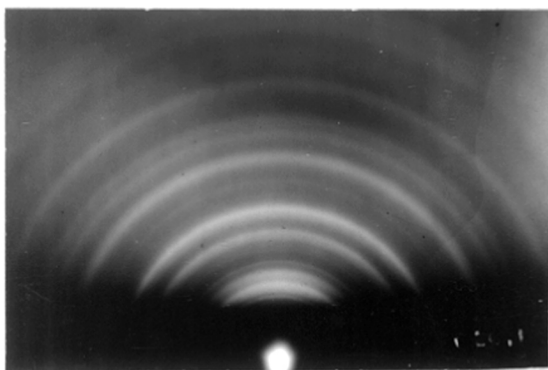


Fig 99

A7461

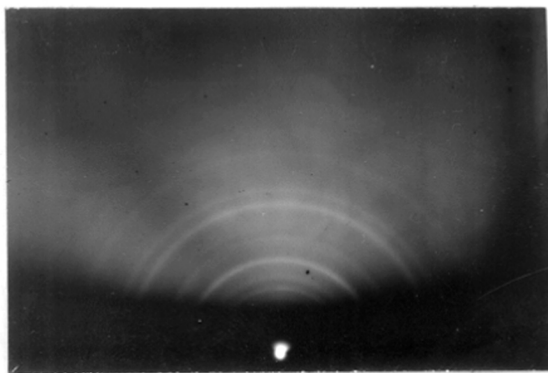


Fig 100

A7464

It is of interest to note that the silver chloride in the pattern of Fig.96 is in (311) orientation. This orientation does not seem to have been observed before in the chloride. The value for $a_{\text{AgCl}} = 5.418$ A. calculated from the estimated λL values agrees within the limits of the error of the experiment with that of 5.547 A. obtained by Wilman (1940).

The chloride has only been observed in heated silver films and this seems to indicate a ready reaction of the film with chlorine during or after the heat treatment. With a film 3A. thick on silica glass it was found possible to follow the progress of the reaction. Figs.98, 99 and 100 show the patterns from the unheated film and after heating for $\frac{1}{2}$ hour at 300°C. and 5 mins. at 550°C. The heating at 300°C. gives a mixture of Ag and AgCl while at 500°C. only AgCl (and the faint extra ring) is present.

In one case where a two-degree (111) orientated silver layer on mica had partly reacted with chlorine the AgCl took up a two-degree (111) orientation, but in a 30° rotated azimuthal relationship to that of the silver.

The pattern of Fig.97 is from a mixture of the unchanged silver and the cubic and hexagonal forms of silver iodide. The rings due to the unchanged Ag are broad compared with the iodide pattern and these cannot therefore be used as reference for the iodide pattern. There is, however, good agreement

between the values obtained for a_{hexl} , a_{cubic} and c/a calculated from the camera length and voltage and those of Wilman (1940). The agreement of the intensity of the iodide pattern is also good.

IX. SUMMARY.

An investigation has been made of the influences of some of the most important factors which determine the structure and properties of metal deposits condensed from the vapour in vacuum or low pressure gas. Silver deposited on fused quartz and muscovite mica cleavage faces was studied mainly and also gold to a less extent for comparison. In these experiments the evaporation of the metal was carried out under conditions which allowed the various factors to be studied as far as possible separately and under simple conditions.

Heat radiation from the hot metal source was found to be one important factor, resulting not only in a rise of temperature in the substrate surface by about 200-300°C. above the mass of the main substrate, but also in the case of mica cleavage faces it led to much dehydration of the surface layers which again caused a marked change in their orientating power. The changes occurring in heated mica cleavage faces in air and vacuum were therefore investigated using the reflection method and a remarkable series of crystalline dehydration products were found to occur, of different types in the three main temperature regions - 20°-550°C., 550°- 600°C. and in the neighbourhood of 650°C. Up to near 800°C. there was usually evidence that part of

the mica cleavage surface remained atomically smooth and practically unaffected and at near 850°C. the surface break up began to be serious. The decomposition of the mica when heated in vacuo up to 500°C. was similar to that in the case of air.

Below 550°C. the dehydration products were usually hexagonal and layer lattices like the initial mica. The basal axes were parallel to the pseudo-hexagonal axes in the mica cleavage face and about 6% larger, while the c axis, i.e. the layer plane spacing, was about 7.2 - 7.5 Å. However, two or sometimes three such similar materials with slightly different lattice constants often occurred in the same specimen. Between 550° and 600°C. rhombic lattices also occurred but with only one axis parallel to the surface although the orientation conformed epitaxially to the substrate. Towards 600°C. a related closely similar rhombic structure tended also to be present orientated with two of its axes parallel to the mica a and b axes, and at about 650°C. this material with slightly decreased lattice spacing occurred practically alone. A search of the literature has not yet led to definite identification of these materials and their composition, but the 20-550°C. hexagonal structures are evidently related to those of one group of clays, the chlorites; and the higher temperature forms appear to have

affinity with the potassium feldspars (Adular, Orthoclase, Sanidine and Microcline, all KAlSi_3O_8 ; and Leucite, KAlSi_2O_6).

Transmission electron diffraction patterns from thin heated mica films did not provide any indication of decomposition, perhaps because when the decomposition was slight the product materials were small in amount compared with that of the diffracting region of the mica, and when the decomposition was extensive the products tended to grow out from the surface in large crystals having low coherent diffracting power compared with the diffuse secondary scattering. The failure hitherto of X ray diffraction experiments to show a decomposition of the mica about 500°C . suggests that the former explanation is the more correct.

The effect of heat on the polished fused quartz was to produce a strongly orientated product as shown by a characteristic array of spots in the plane of incidence of the pattern. It was found not possible to identify the product with any of the known forms of quartz and it is indicated that the substance is attributable to recrystallisation into a hitherto unknown form of silica or a silicate formed as a result of the polishing agent (jeweller's rouge) being incorporated in the Beilby layer.

In the case of thin silver layers deposited on mica the degree of heating of the surface layers by radiation from the filament was indicated by the appearance of a prominent mica decomposition pattern when the rate of deposition was slow; and the silver crystals developed strong two-degree (111) orientation instead of the random disposition characteristic of more rapid deposition. The strong orientation of the silver was evidently, at least in part, caused by the presence of the decomposition product whose lattice was larger than that of the mica so that the silver (111) layer conformed more accurately to its (001) surface plane. This hypothesis was confirmed by Strong two-degree (111) orientation of the silver occurring when the silver was deposited at room temperature on a mica cleavage face whose surface had been previously partially dehydrated by heating, even though the rate of deposition of the silver was similar to that which normally yielded random layers on freshly cleaved mica.

Silver deposits on mica which were initially random were found not only to develop larger crystal size when heated in air or vacuo at temperatures as low as 300°C. but to develop also strong two-degree orientations at (111), (100), (110) and occasionally (311) types. This is in marked contrast to the normal two degree (111) orientation which

when deposited on freshly cleaved mica at 200-300°C. occurs alone and is not changed appreciably by subsequent heating after deposition. The (100), (110) and other orientations arising when random deposits on mica are heated did not appear to be associated with appreciable decomposition of the mica substrate and is probably to be attributed to the relative epitaxial stability of crystals occurring in contact with the mica in such orientation among the random deposit. Gold was also shown to behave in the same way as silver in this respect as might be expected from its closely similar lattice constant.

Silver deposits on fused quartz at room temperature generally showed no orientation. On heating the deposits in air, a crystal growth was observed at 150°C and at 300°C. the development of orientation, usually strong (111) occurred. In one case simultaneous presence of (100) was observed.

The presence of a gaseous atmosphere (air or argon) was found to increase the crystal size in the deposit. Both air and argon at pressures above about 10^{-1} mm. of mercury were found to produce a greyish deposit in films of about 50 Å. and sooty black in 500 Å. thick. Hydrocarbon vapours appear to be responsible for growths of silver in the hexagonal modification and the easy contamination of silver films by chlorine and iodine in the atmosphere to form AgCl and AgI

respectively has been observed indicating the special need for care to avoid such surface attack.

The method of estimating the mean crystal diameter in a deposit has been examined and the conditions under which reliable estimates can be made have been stated. The crystal diameter in deposits of about 15 A. thick is of the order of 75 A.

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REFERENCES.

- Andrade, E.N.daC., and Martindale, J.G., 1936, Phil.Trans., 235, 69.
- Appleyard, B.T.S., 1937, Proc.Phys.Soc., 49, extra part, 118.
- Appleyard, B.T.S., and Lovell, A.C.B., 1937, Proc.Roy.Soc., A.158, 718.
- Aron, A., 1946, Annales de Physique, 1, 25.
- Barth, T.W.F., 1932, Am.J.Sci., 23, 350.
- Barth, T.W.F., 1932, Am.J.Sci., 24, 102.
- Bartlett, H., 1928, Phil.Mag., 5, 848.
- Beeching, R., 1936, Phil.Mag., 22, 938.
- Beilby, Sir George, 1921, 'Aggregation and Flow of Solids'
Macmillan, London.
- Bragg, W.L., 1930, Zeit.f.Krist., 74, 237.
- Bragg, W.L., 1937, 'Atomic Structure of Minerals'
Univ.Press, Cornell Univ.
- Bragg, W.H., and Gibbs, R.B., 1925, Proc.Roy.Soc., A.109, 405.
- Bredig, G., and Allolio, R., 1927, Zeits phys.Chem., 126A., 41
- Bresler, S., Strauff, E., and Zelmanoff, I., 1933, Phys.Zeits.
Sowjet., 4, 909.
- Brindley, G.W., and Robinson, K., 1946, Min.Mag., 27, 242.
- Brindley, G.W., and Robinson, K., 1946, Trans.Farad.Soc., 42B.,
198.
- Bruck, L., 1936, Ann.Phys.Lpzg., 26, 233.
- Burgers, W.G., and Dippel, G.J., 1934, Physica, 1, 549.
- Burgers, W.G., and Ploos van Amstel, J2J.A., 1936, Physica,
3, 1057.

- Caldwell, W.C., 1941, J.Appl.Phys., 12, 779.
- Cockcroft, J.D., 1928, Proc.Roy.Soc., 141, 399.
- Colombani, A., 1942, Compt.Rend., 215, 17.
- Countryman, M.A., 1937, J.Appl.Phys., 8, 432.
- Darbyshire, J.A., 1933, Zeits.f.Krist., 86, 313.
- Darbyshire, J.A., and Cooper, E.R. 1935, Proc.Roy.Soc., A.152, 104.
- Eisenhut, O., and Kaupp, E., 1931, Z.Elektrochem., 37, 466.
- Eitel, W., Muller, H.O., and Radczewski, O.E., 1939, J.Appl. Phys., 10, 61.
- Essig, S., 1939, Phys.Rev., 55, 229.
- Estermann, I., 1923, Z.Phys.Chem., 106, 399.
- Finch, G.I., 1937, Proc.Phys.Soc., 49, 113.
- Finch, G.I., and Fordham, S., 1936, Proc.Phys.Soc., 48, 85.
- Finch, G.I., and Fordham, S., 1937, J.Soc.Chem.Ind., 56, 632.
- Finch, G.I., Murison, C.A., Stuart, N, and Thomson, G.P.,
1933, Proc.Roy.Soc., A.141, 414.
- Finch, G.I., and Quarrell, A.G., 1933, Proc.Roy.Soc., A.141, 399.
- Finch, G.I., Quarrell, A.G., and Wilman, H., 1935, Trans.Farad. Soc., 31, 1051.
- Finch, G.I., and Wilman, H., 1936, Trans.Farad.Soc., 32, 1539.
- Finch, G.I., and Wilman, H., 1936, Proc.Roy.Soc., A.155, 345.
- Finch, G.I., and Wilman, H., 1937, Trans.Farad.Soc., 33, 337.
- Finch, G.I., and Wilman, H., 1937, Ergeb.exakt.Naturwiss.,
16, 353.
- Fritz, H., 1915, Ann.d.Physik, 47, 763.

- Fukuroi, T., 1936, Bull.Inst.Phys.Chem.Res., Jap., 15, 663.
- Fukuroi, T., 1937, Sci.Pap.Inst.Phys.Chem.Res.Tokyo., 32,
157, 172.
- Gen, M.I., Zelmanoff, I., and Schalnikoff, A.I., 1933,
Phys.Zeits.Sowjet., 4, 825
- Gibbs, R.E., 1926, Proc.Roy.Soc., A.110, 443.
- Gibbs, R.E., 1926, Proc.Roy.Soc., A.113, 351.
- Goche, O., and Wilman, H., 1939, Proc.Phys.Soc., 51, 625.
- Goos, F., 1936, Z.Physik, 100, 95.
- Goos, F., 1937, Z.Physik, 106, 606.
- Gruner, J.W., 1939, Amer.Min., 24, 624.
- Hamburger, L., 1931, Ann.Phys., 10, 789.
- Haringhuizen, P.J., Was, D.A., and Kruithoff, A.M., 1937,
Physica, 4, 695.
- Hass, G., 1937, Naturwiss., 25, 232.
- Hass, G., 1942, Kolloid Z., 100, 230.
- Hendricks, S.B., 1929, Zeits.f.Krist., 71, 269.
- Insley, H., and Ewell, R.H., 1935, J.Res.Nat.Bur.Stand., 14,
615.
- Jackson, W.W., and West, J., 1930, Zeits.f.Krist., 76, 211.
- Jackson, W.W., and West, J., 1933, Zeits.f.Krist., 85, 160.
- Jagersberger, A., and Schmid, F., 1934, Zeits Phys., 88, 264.
- Jones, F.W., 1938, Proc.Roy.Soc., A.166, 16.
- Kamogawa, H., 1938, Phys.Rev., 54, 91.
- Kamogawa, H., 1940, Phys.Rev., 58, 660.
- Kikuchi, S., 1928, Jap.J.Physics, 5, 83.
- Kikuchi, S., 1935, Sci.Pap.Inst.Phys.Chem.Res.Tokyo, 26, 225.

- Kikuchi, S., and Nishikawa, S., 1928, Proc.Imp.Jap.Acad.,
4, 475;
Nature, 121, 1019.
- Kindinger, M., and Koller, K., 1938, Mikrochim Acta., 3, 317.
- Kirchner, F., 1932, Ergel. exakt. Naturwiss 11, 64.
- Kirchner, F., 1937, Ann.Phys., 28, 21.
- Kirchner, F., and Lassen, H., 1935, Ann.Phys., 24, 173.
- Kramer, J., 1934, Ann.Phys., 19, 37.
- Krautkramer, J., 1938, Ann.Phys., 32, 537.
- Lapparent, J.de., 1937, Zeits.f.Krist., 98, 233.
- Lassen, H., 1934, Phys.Zeits., 35, 172.
- Lassen, H., and Bruck, L., 1935, Ann.Phys., 22, 65.
- Laue, M.von., 1926, Zeits.f.Krist., 64, 115.
- Lennard Jones, J.E., 1932, Trans.Farad.Soc., 38, 333.
- Linnik, W., 1929, Nature, 123, 604.
- Lovell, A.C.B., 1936, Proc.Roy.Soc., A.157, 311.
- Lubzynski, K., and McGee, I., 1939, J.I.E.E., 84, 468.
- Marton, L., and Schiff, L.I., 1941, J.Appl.Phys., 12, 763.
- Mangin, C., 1927, Compt.Rend., 185, 288.
- Mangin, C., 1928, Compt.Rend., 186, 879, 1131.
- Maxwell, L.R., and Mosley, V.M., 1935, Phys.Rev., 47, 331.
- Mitchell, H.R., 1938, Phys.Rev., 53, 250.
- Nakai, T., and Fukami, Y., 1933, J.Soc.Chem.Ind.Jap., 36, 434.
- Nelson, J.B., and Riley, D.P., 1945, Proc.Phys.Soc., 57, 477.
- Ogawa, K., 1937, Tohoku Univ.Sci.Rep., 26, 92.

- Olsen, L.O., Smith, C.S., and Crittenden, E.C., 1945,
J.Appl.Phys., 16, 425.
- Papsdorf, W., 1937, Dissertation, Köln.
- Pauling, L., 1930, Proc.Nat.Acad.Sci., 16, 123.
- Picard, R.G., and Duffendack, O.S., 1943, J.Appl.Phys., 14, 291.
- Powell, R.W., Griffiths, E., and Wood, W.A., 1937, Proc.Roy.,
Soc., A.163, 189.
- Preston, G.D. and Bircumshaw, L.L., 1936, Phil.Mag., 21, 713.
- Pringheim, P., and Pohl, R., 1912, Deutsch.Phys.Ges.Verh.,
14, 506.
- RamaSwamy, S., 1934, Proc.Phys.Soc., 46, 739.
- RamaSwamy, S., 1936, Proc.Ind.Acad.Sci., 4A, 656.
- Randall, J.T., Rooksby, H.P., and Cooper, B.S., 1930,
Zeits.f.Krist., 75,
196.
- Reinders, W., and Hamburger, L., 1931, Rec.Trav.Chim.Pays-Bas,
50, 441.
- Ritschl, R., 1931, Zeits Physik, 69, 578.
- Rouard, P., 1937, Ann.de Physique, 7, 291.
- Rudiger, O., 1937, Ann.Phys., 30, 505.
- Scherrer, P., 1920, R.Zsigmondy's "Kolloidchemie", 3rd Edn.,
p. 387, Spamer, Leipzig.
- Schoon, Th., 1938, Nature, 142, 263.
- Shinohara, K., 1930, Proc.Jap.Phys.Math.Soc., 12, 171.
- Steinheil, A., 1934, Z.Physik, 89, 50.
- Stern, O., 1920, Z.Physik, 2, 49.
- Strong, J., 1945, "Modern Physical Laboratory Practice",
Blackie and Son, Ltd.

- Suhrmann, R., and Barth, G., 1934, Phys.Zeits., 35, 971.
- Suhrmann, R., and Barth, G., 1936, Z.Physik., 103, 133.
- Suhrmann, R., and Schnackenberg, H., 1941, Z.Elektrochem.,
47, 271.
- Suhrmann, R., and Schnackenberg, H., 1942, Z.Physik, 119, 289.
- Taylor, A., 1941, Phil.Mag., 31, 339.
- Taylor, A., 1945, "An Introduction to X Ray Metallography",
p.223, Chapman and Hall, London.
- Thomson, J.J., 1901, Proc.Camb.Phil.Soc., 11, 119.
- Thomson, G.P., 1929, Proc.Roy.Soc., A.125, 352.
- Thomson, G.P., 1930, Proc.Roy.Soc., A.128, 641.
- Thomson, G.P. and Cochrane, W., 1939, "Theory and Practice of
Electron Diffraction",
(Macmillan and Co.).
- Trillat, J.J., and Oketani, S., 1937, Journ.de Phys., 8, 59.
- Trzebiatowski, W., 1937, Roczn.Chem., 17, 73.
- Tschermak, W., 1884, Traite de Mineralogie, (1st Edn., p.504).
- Vand, V., 1936, Z.Physik, 104, 48.
- Volmer, M., 1925, Z.Physik, 35, 170.
- Warren, B.F., 1933, Zeits.f.Krist., 86, 349.
- Warren, B.F., 1934, Phys.Rev., 45, 657.
- Warren, B.F., 1938, Zeits.f.Krist., 92, 448.
- Was, D.A., 1939, Physica, 6, 390.
- Was, D.A., and Tol, T., 1940, Physica, 7, 253.
- Weinhart and Wehe, 1947, ex Heising - Quartz Crystals for
Electrical Circuits - D.Van Nostrand
Company, Inc. New York.

llman, H., 1940, Proc.Phys.Soc., 52, 323.

bod, R.W., 1919, Phil.Mag., 38, 98.

yckoff, R.W.G., 1925, Am.J.Sci., 9, 448.

yckoff, R.W.G., 1925, Zeits.f.Krist., 62, 189.

ahn, H., and Kramer, J., 1932, Naturwiss., 20, 792.