

and O(2) at the positions given in Table 1, the distances across the twofold axis are: O(1)–O(1'), 2.76 Å; O(2)–O(2'), 4.00 Å; and O(1)–O(2'), 3.38 Å. The distances from these sites to the nucleoside atoms where hydrogen bonding might occur are: O(1)–AN(6), 3.04 Å; O(2)–AN(6), 3.00 Å; O(1)–UO(2), 2.98 Å; and O(2)–UO(2), 2.72 Å. These results possibly explain why the water lattice site may not be uniquely fixed. Position 1 would give favorable O–H···O interaction between water molecules (assuming the hydrogen atoms do not satisfy the twofold symmetry), whereas position 2 is more favorable for O–H···O hydrogen bonding with the carbonyl oxygen O(2) of bromouridine. For both positions the interaction with the available proton on the amino nitrogen N(6) of the adenine ring is approximately the same.

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The Epitaxial Growth of Selenium

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Films of selenium have been deposited in vacuo on certain faces of NaCl, KBr, BaF₂, CaF₂ and MgO. Under certain conditions, epitaxial growth of the selenium was observed. The orientations obtained are discussed in relation to the substrate configuration and it appears as if the orientation may be governed by misfit considerations. Anomalies were observed in the film structure, which was found to differ slightly from that quoted for bulk selenium.

1. Introduction

An extensive literature exists on the physical properties of films of amorphous selenium and also of films which have been made polycrystalline by heat treatment. These have been generally found to consist of randomly oriented crystallites, although Semiletov

(1960) observed fibre orientation, the crystallites lying with their basal faces (0001) parallel to the substrate. Although film growth has been studied on amorphous substrates, few experiments appear to have been carried out with single-crystal substrates at elevated temperatures. Chihaya (1955) condensed selenium on cleavage faces of rocksalt at tempera-

tures between 100 °C and 200 °C, obtaining films showing a higher degree of crystallinity than those deposited on formvar. However, no signs of epitaxial growth were observed. Schlossberger & Ticulka (1961) studied the growth of selenium on the cleavage face of magnesium oxide at room temperature, but obtained very little crystalline material. When substrate and film were annealed at 150 °C some preferential orientation resulted, with the (10 $\bar{1}$ 0) plane of selenium parallel to the substrate. Deposition on the substrate at 112 °C resulted in some hexagonal material together with an unrecognized phase.

In the experiments of Andrievski, Nabitovich & Kripykevich (1959), evidence was obtained of four further types of structure. At low temperatures, two complex monoclinic forms were observed, whereas at high temperatures cubic structures were obtained. For a temperature range of 160–170 °C, a face-centred form with $a=5.750 \pm 0.007$ Å is reported, although it is possible that this may in fact be Cu₂Se (f.c.c., $a=5.840$ Å), which could be formed by reaction between the selenium and the copper microscope grid.

Although very many cases of epitaxial growth are known, there are few examples of such growth for structures of the type normally exhibited by selenium, which is hexagonal, belonging to the space group $P3_121$ (or $P3_221$), with selenium atoms located at the following fractional coordinates:

$$P3_121: (u, 0, 0), (\bar{u}, \bar{u}, \frac{1}{3}), (0, u, \frac{2}{3})$$

$$P3_221: (u, 0, 0), (\bar{u}, \bar{u}, \frac{2}{3}), (0, u, \frac{1}{3})$$

where $u=0.217$ (Wyckoff, 1948). The lattice parameters are $a=4.34$, $c=4.94$ Å. In this structure, covalent-bonded chains of selenium lie parallel to one another in the c direction and are held together by relatively weak van der Waals forces.

The absence of a satisfactory theory of epitaxial growth makes difficult the choice of substrate for a given deposit material. There are many examples of epitaxial growth for which the misfit between the lattice dimensions of substrate and deposit are very large, showing that epitaxial growth does not always require a close correspondence in lattice spacings. In certain cases, however, the extent of register appears to play some part. This is the case with selenium, as is discussed in § 4 below.

In the experiments described here, selenium films have been deposited on substrates of sodium chloride, potassium bromide, barium fluoride, calcium fluoride and magnesium oxide. The highest degree of orientation was obtained on potassium bromide substrates and the growth on this material has been most extensively studied.

2. Preparation of films

Spectrographic and chemical analysis of the selenium used in these experiments indicated the following impurities: Te, 0.7 p.p.m., Ca, 0.04 p.p.m., Cl, 5 p.p.m.,

with no other elements within the detection limits. The selenium was evaporated from glazed porcelain boats, used as lining for the usual tungsten boat which served as the heater. The selenium charge was out-gassed by prolonged heating below the evaporation temperature. The working pressure in the evaporation system was 2×10^{-5} torr.

The crystal surfaces were prepared by cleaving or cutting followed by grinding and polishing. The disordered layers produced by polishing were removed by annealing at a temperature just insufficient to cause etching. For potassium bromide, heating for one hour at 370 °C produced the surface shown in Fig. 1. The surface contains extensive smooth, flat areas. Multiple-beam interferometry indicated a reasonable degree of flatness, with gross irregularities about 200 Å in height.

The selenium specimens were removed from the preparation chamber and allowed to cool in a desiccator. As would be expected for a material such as selenium, very slow cooling resulted in a considerable degree of agglomeration of the films.

The films were removed from the alkali halides by solution of the substrates in water. For barium fluoride, calcium fluoride and magnesium oxide, 35% hydrochloric acid solution was used. For the thinner films, a carbon film of thickness ~ 200 Å was deposited on the specimen before removal from the substrate.

The usual method of determining the thickness of films, by multiple-beam interference (Tolansky, 1948) cannot be used for selenium, which reacts with the deposited silver or aluminum layers to produce a non-reflective surface. The masses of the films were therefore determined fluorimetrically (Watkinson, 1960). The film and substrate were digested in nitric acid, evaporated to dryness and diluted with water. The pH was adjusted to 2.5 by the addition of ammonium hydroxide or formic acid and the solution reacted with 3,3'-diaminobenzidine. The selenadiazole produced was extracted with toluene and irradiated with the 4046 and 4358 Å lines in a Hilger & Watts Fluorimeter. In this method, due allowance must be made for the interfering effects of the potassium nitrate present in the solution. In the subsequent sections, the thickness quoted is that which would be obtained if the film were uniformly distributed.

3. General features of the film structure on various substrates

(a) Growth on sodium chloride

Micrographs and diffraction patterns were obtained from films deposited at rates from 200 to 1000 Å.min⁻¹ on rocksalt surfaces maintained at temperatures up to 115 °C. Film thicknesses were in the range 500–2000 Å. At temperatures up to ~ 70 °C amorphous films resulted: no deposition was obtained if the rocksalt was held at temperatures above 115 °C.

In the temperature range 80–115 °C polycrystalline films were obtained. The diffraction patterns obtained from deposits on all three faces — (100), (110) and (111) — showed a mainly random polycrystalline form, characteristic of the normal hexagonal selenium structure. The relative intensities of the rings agreed reasonably well with the values calculated for the normal selenium structure. In certain cases a faint sign of a diffraction ring in the position corresponding to a 0001 reflexion was observed. This reflexion should be absent in the selenium structure: this point is further discussed in § 4.

The crystallite sizes observed tended to be largest for films grown on the (100) face and smallest on the (111) face. The form of deposit was as shown in Fig. 2. The regular growth of needles from the individual crystallite regions occurred in random directions, indicating random orientation of the seed crystals. The growth of the needles themselves was probably not influenced by the substrate.

(b) Growth on calcium and barium fluorides

Films of selenium grown on annealed cleavage (111) faces of calcium fluoride showed similar general behaviour to those formed on sodium chloride, except for a substantially larger crystallite size. For a rate of deposition of 500 Å.min⁻¹ on calcium fluoride held at 92 °C a selenium film 700 Å thick covered only about two-thirds of the crystal surface. The mean crystallite size was ~ 10 Å. The same behaviour was observed on barium fluoride (Fig. 3) except that the temperature above which no deposition occurred was low for this material (88 °C). Some signs of orientation were in evidence from the diffraction pattern, suggestive of a deposit with the (11 $\bar{2}$ 1) planes parallel to the substrate with two orientations inclined at about 70° to one another. This type of behaviour was clearly shown in growth on potassium bromide and is discussed in § 4(c) below.

(c) Growth on cleaved magnesium oxide

Totally different results were obtained on annealed cleavage planes of magnesium oxide (Fig. 4). With the temperature of the crystal maintained at 88 °C a completely amorphous layer resulted, the individual crystallites exhibiting a drop-like form. In view of the readiness with which the selenium recrystallized on the other substrates examined, it appears that magnesium oxide imposes a strong inhibiting effect on crystallization. It should, however, be noted that the appearance of 'droplets' in the micrograph does not necessarily imply an amorphous structure. (See § 4(b).)

4. Growth of selenium on potassium bromide

(a) Cleaved (100) surfaces

In contrast to the behaviour discussed above, marked epitaxial growth of selenium was observed on

certain faces of potassium bromide. Such growth was observed over a temperature range of 83–102 °C. Below this range amorphous films formed, whereas above 102 °C the rate of deposition was extremely low (no observed film in five minutes at 1000 Å.min⁻¹). Fig. 5 shows the results obtained for a film 1500 Å thick deposited on cleaved (100) potassium bromide. The needle-like crystals were orientated in two perpendicular directions and the main diffraction spots indicated that the (10 $\bar{1}$ 0) planes of the selenium were parallel to the substrate with the *c* axes of the crystallites pointing in two perpendicular directions. The direction of the *c* axes relative to the axes of the substrate were determined by cleaving the substrate, so as to produce a selenium film with an edge in a known direction, mounting the film with its edge parallel to the bars of the specimen grid and reducing the power of the objective lens when the diffraction pattern was being observed. The resulting pattern (Fig. 6) shows clearly the orientation of the diffraction pattern with respect to the (defocused) grid lines and hence establishes the relation between the directions of the axes of deposit and substrate. This avoids the difficulties associated with specimen charging which arise in reflexion micrography with a non-conducting specimen and substrate.

Variation of the temperature of the cleaved potassium bromide surface over the range 83–100 °C produced little variation either of crystallite form or of diffraction pattern. The best conditions for orientation entailed a deposition rate of about 200 Å.min⁻¹ to an equivalent film thickness of ~ 240 Å. Under these conditions misorientation in the film (Fig. 7) was less than ~ 2°. Complete coverage of the surface required a thickness of the order 3000 Å. Orientation persisted to this thickness but with a somewhat larger range of misorientation (~ 8°). The crystallite form of a rapidly deposited (1200 Å.min⁻¹) film showed the formation of large crystallites of circular cross-section (Fig. 8). Such films were well orientated, however, with a range of misorientation less than 6°.

It is immediately clear from Fig. 7 that the selenium does not possess its normal hexagonal structure. The spots closest to the centre lie in the position of 0001 reflexions, which should be absent for the *P*3₁21 space group. There is also a reflexion in the 0002 position. The allowed 0003 reflexion is strong, but less so relative to the remaining diffractions than would be so for the normal structure. In the diffraction patterns of hexagonal selenium given by Semiletov (1960) it is difficult to decide whether a 0001 reflexion occurs since there appears to be some amorphous material present, giving scattering which would obscure the low-angle diffraction. (It should be noted that Semiletov's Fig. 2 was obtained with the specimen at an angle of 45° to the beam, although this is not stated.)

Whilst it may appear that the abnormal structure described above may arise from the influence of the



Fig. 1. Polished (100) face of potassium bromide, annealed at 370 °C for one hour. ($\times 200$).

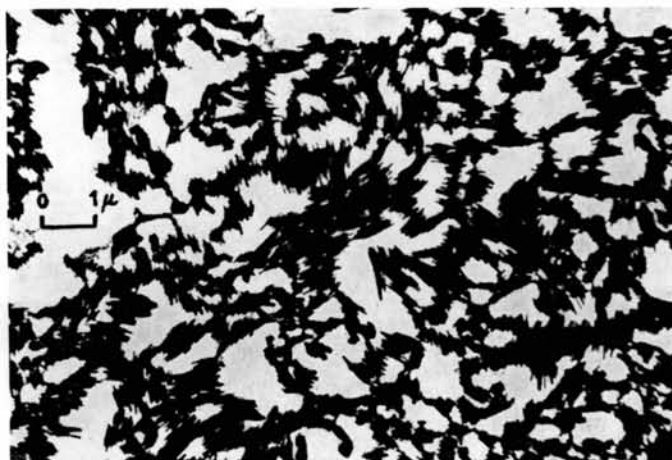
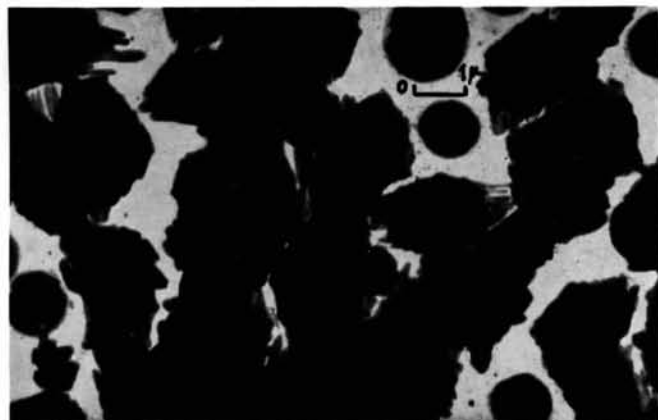
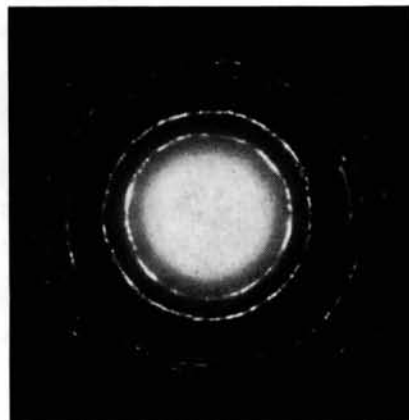


Fig. 2. Selenium film grown on annealed (111) face of sodium chloride. Film thickness 50 nm.



(a)



(b)

Fig. 3. (a) Micrograph of selenium film (70 nm thick) deposited on (111) barium fluoride at 88 °C.
(b) Diffraction pattern of the same film.

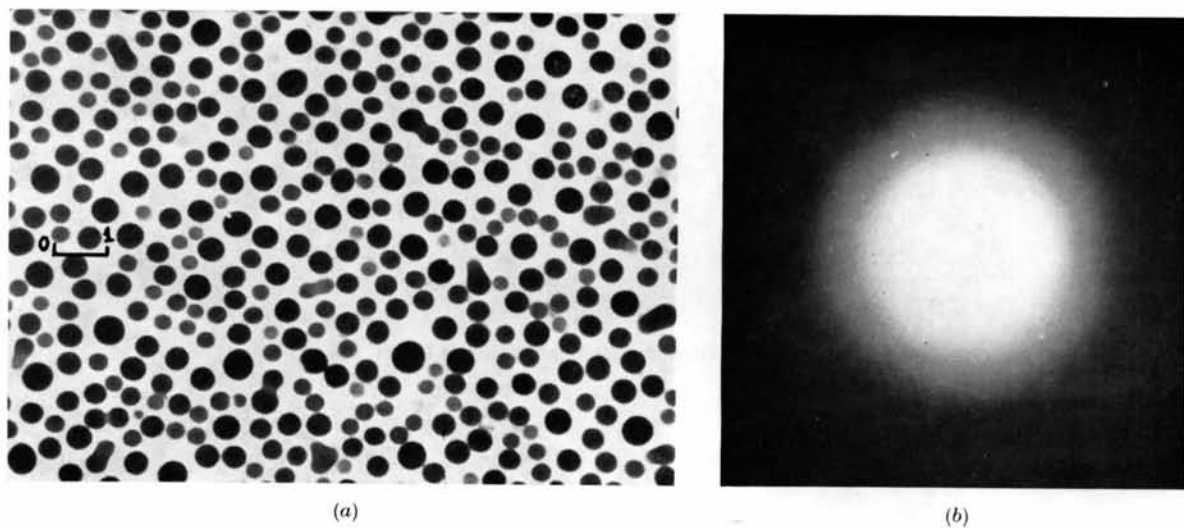


Fig. 4. (a) Selenium film grown on (111) magnesium oxide at 88 °C. (b) Diffraction pattern of the same film.

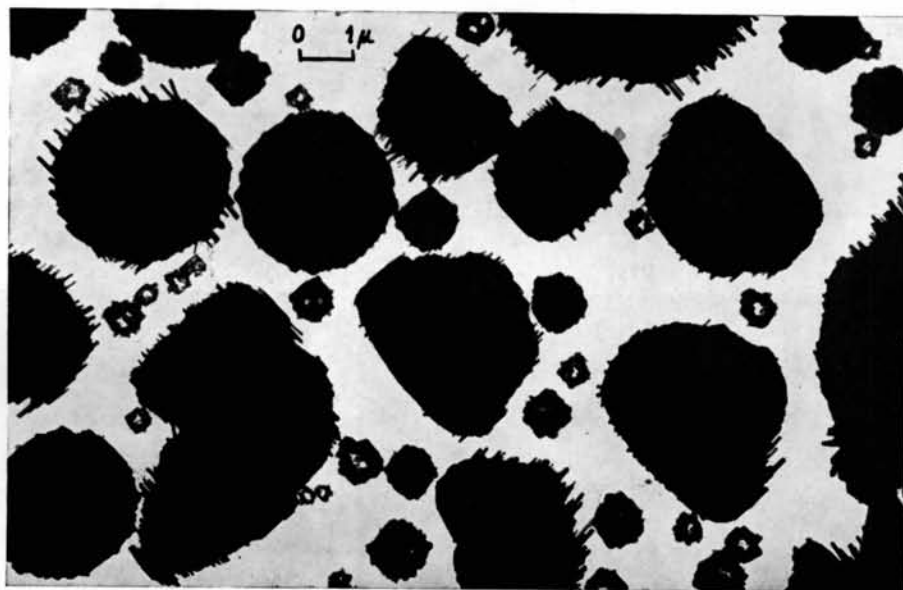


Fig. 5. Micrograph of selenium film (150 nm thick) deposited on (100) potassium bromide at 95 °C.



Fig. 6. Appearance of diffraction pattern with defocused objective lens.

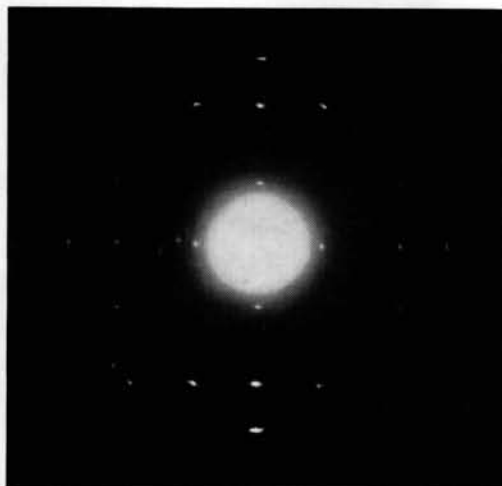


Fig. 7. Diffraction pattern of well-oriented Se film (23 nm thick) on (100) KBr.

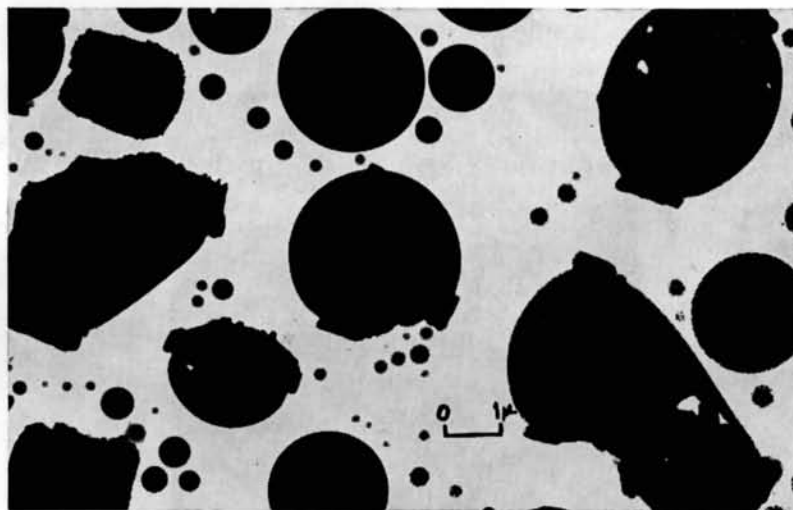


Fig. 8. Micrograph of rapidly deposited ($120 \text{ nm}\cdot\text{min}^{-1}$) Se film.

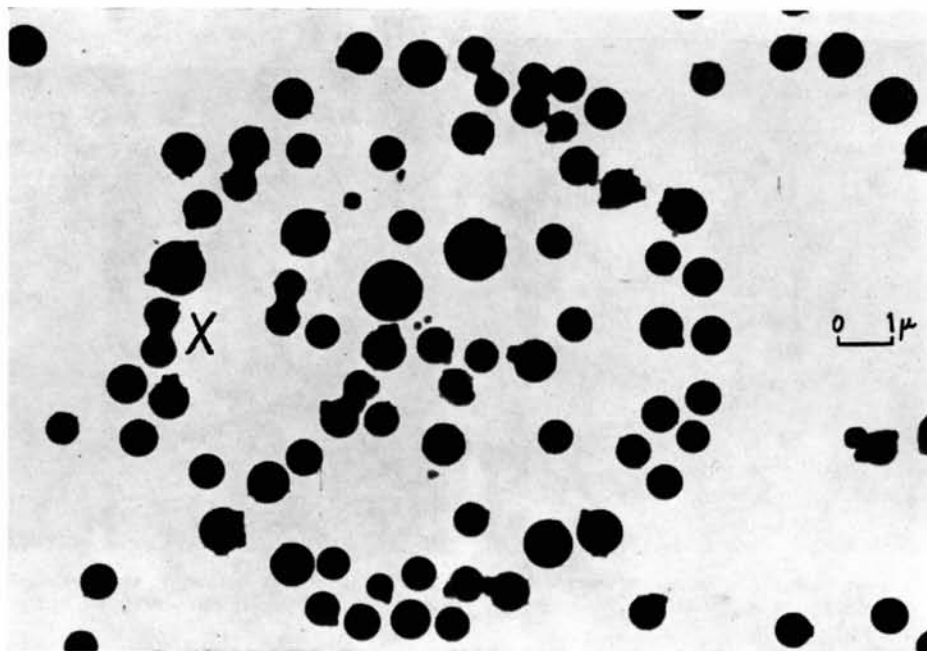


Fig. 9. Micrograph of selenium on polished and etched (100) potassium bromide. Deposition at 93 °C. Film thickness 32 nm. Rate of deposition 20 nm.min⁻¹.

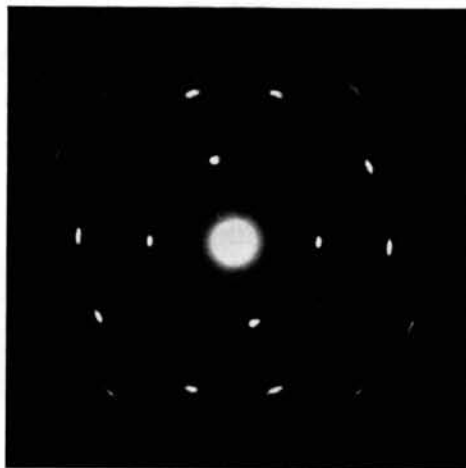
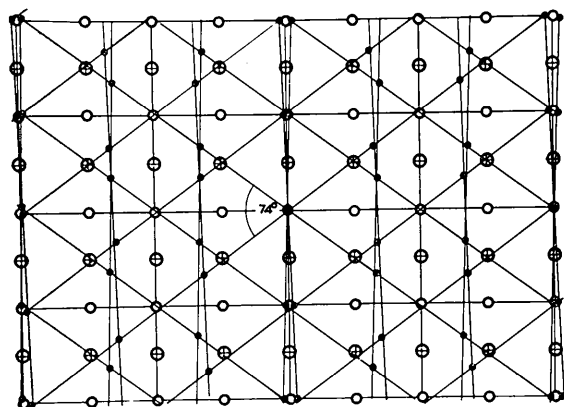


Fig. 10. Diffraction pattern of selenium film on (110) potassium bromide at 96 °C.: 33 nm.min⁻¹.

substrate, we note that similar forbidden reflexions are observed in the diffraction patterns obtained by Furuta (1960), for specimens grown on a grid. The portions examined grow freely as ribbons across the grid apertures. It is clearly necessary to determine the precise form of the abnormal structure, but this cannot be done with certainty by the techniques at present used owing to the limited number of reflexions which can be obtained. The observed patterns are not inconsistent with a slightly distorted chain structure in which the threefold screw axis is not present.

(b) *Polished (100) surfaces*

Film growth was studied on faces which had been cleaved, polished and etched, as described in § 2. Diffraction patterns were similar to those obtained from specimens grown on cleaved surfaces. The micrographs exhibited decoration effects, the selenium forming spherical crystallites lying along well-defined circular features. As is seen from Fig. 9, the individual crystallites show a marked liquid-like behaviour, to the point of showing (at \times) the shape characteristic of two droplets in the process of coalescing. This suggests that fairly rapid quenching of the liquid state occurs although it is surprising that such deposits yielded diffraction patterns showing that the crystallite consisted of perfectly oriented single crystals. The selenium will pass through a liquid state during the formation of the crystallites, since vitreous selenium has a softening point around 35 °C. The formation of such well-defined oriented crystals therefore suggests an extremely rapid rate of crystallization.



- ⊕ Bromine ion sites in (110) KBr plane
- Potassium ion sites in (110) KBr plane
- Selenium atom sites in the two orientations of the $(11\bar{2}1)$ se plane

Fig. 11. Relative positions of Se atoms in $(11\bar{2}1)$ planes inclined at 74° and K, Br ions in (110) planes.

(c) *Polished (110) surfaces*

Suitable (110) faces could be produced by heating for one hour at 365 °C. Deposition at a rate of 330 Å.min⁻¹ on surfaces maintained at 96 °C yielded very well-oriented deposits (Fig. 10), showing that the selenium film formed with the $(11\bar{2}1)$ planes parallel to the substrate, in two orientations in which the $[1\bar{1}0]$ directions inclined at 74°. Examination of the relative positions of the K, Br, and Se atoms for crystallites in these orientations reveals that there is a small lattice misfit under these conditions (Fig. 11). Although there are many examples of epitaxial growth in which the misfit is unimportant, the orientations observed in these experiments are those for which a small misfit obtains. In this connection, it may be remarked that a similar small misfit exists for the growth orientation observed on the (100) face of potassium bromide.

(d) *Polished (111) surfaces*

No evidence of epitaxial growth on the octahedral faces of potassium bromide was obtained for the ranges of substrate temperature and rate of deposition used in the studies of the (100) and (110) faces. The results obtained were very similar to those obtained on (111) sodium chloride (see § 3(a).)

5. Conclusions

The mode of growth of selenium on various crystal substrates indicates that, for this material, epitaxial growth is favoured by the existence of a small misfit between the substrate and deposit lattice. Of the several substrates studied, well-ordered single-crystal films were obtained only on faces of potassium bromide for which a small misfit exists. On the cube and dodecahedral faces of potassium bromide, double orientation of selenium occurred, in each case in the directions of small misfit. The orientations of the selenium deposits appeared to be correlated with directions in the underlying crystal for which a small misfit occurs. The structure observed in films grown under these conditions differed slightly from that generally quoted for selenium. The unit-cell dimensions were found, however, to correspond closely to those of bulk selenium.

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The Crystal Structure of Heteratisine Hydrobromide Monohydrate*

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The space group of heteratisine hydrobromide monohydrate, $C_{22}H_{33}O_5N \cdot HBr \cdot H_2O$ is $P2_1$ and the unit-cell dimensions are: $a = 8.96$, $b = 14.54$, $c = 8.55$ Å, $\beta = 90^\circ 40'$, $Z = 2$. The structure was solved from a three-dimensional Fourier synthesis by the heavy-atom method. No chemical assumptions have been made, except that the nitrogen atom was identified by comparison of the skeleton with that of lycocotinine. Refinement was carried out by the least-squares method.

Introduction

In the course of isolation of atisine from the roots of *Aconitum heterophyllum*, Jacobs & Craig (1942) obtained small amounts of alkaloids, which they called heteratisine and hetisine. They assigned the empirical formula $C_{22}H_{33}O_5N$ to heteratisine and discovered that it contained a lactone group, one methoxyl group, two hydroxyl groups and an *N*-alkyl group, which they presumed to be methyl. No unsaturated linkage could be detected by hydrogenation.

The solution of the molecular structure of heteratisine presented an interesting problem, especially as it is the only known base from aconite and delphinium species to contain a lactone ring; and since only a very limited amount of the substance was available, Dr Edwards suggested a detailed X-ray analysis.

The preliminary account of this study which described the molecular structure has been published (Przybylska, 1963).

Edwards & Ferrari (1964) have described chemical and physical evidence which is fully consistent with our results.

Considerable chemical and spectroscopic studies leading to the same structural conclusion have recently been reported by Aneja & Pelletier (1964*a*).

Experimental

The hydrobromide derivative of heteratisine was prepared by Dr O. E. Edwards. Large colourless prisms of the monohydrate, $C_{22}H_{33}O_5N \cdot HBr \cdot H_2O$, were obtained on crystallization from water.

The chemical analysis carried out by Mr R. H. Séguin confirmed the presence of one molecule of water of crystallization. The density measured by the

flotation method in a mixture of carbon tetrachloride and toluene is 1.459 g.cm^{-3} and the calculated value for the monohydrate is 1.462 g.cm^{-3} .

The space group and unit-cell dimensions were determined with Cu $K\alpha$ radiation and a precession camera. They are:

$$a = 8.96 \pm 0.02, \quad b = 14.54 \pm 0.03, \quad c = 8.55 \pm 0.02 \text{ Å};$$

$$\beta = 90^\circ 40' \pm 10', \quad V = 1114 \text{ Å}^3.$$

$0k0$ reflexions for k odd are absent, and since the compound is optically active the space group is $P2_1$.

The number of electrons per unit cell, $F(000)$, is 516.

The data were collected for thirteen b -axis levels with Mo $K\alpha$ radiation with a Hilger and Watts automatic linear diffractometer designed by U. W. Arndt and D. C. Phillips (1961). The output was in the form of cards punched by the 26 IBM machine connected to the diffractometer.

The data was supplemented with measurements for the $0kl$, $1kl$ and $2kl$ levels. 1345 reflexions were obtained with a count higher than 20, after the two background readings were subtracted. They constituted about 52% of all intensities theoretically available with copper radiation.

All the crystals used were of either square or circular cross section, varying from 0.27 to 0.35 mm in thickness and the absorption corrections were not applied.

Structure analysis

A Patterson synthesis for the $h0l$ data indicated four different positions for the bromine atom. The interpretation of two additional syntheses for the $hk0$ and $0kl$ zones reduced the number of possible locations to two. To find the position of the heavy atom unambiguously, it was necessary to carry out a summa-

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