

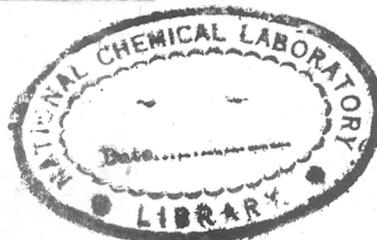
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EPITAXIAL CRYSTAL GROWTH AND FORCE FIELD

DISTRIBUTION AT SINGLE CRYSTAL SURFACES.

by

M. Levy.

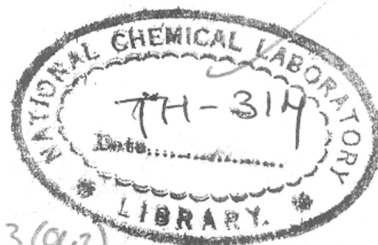


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Abstract of Thesis.EPIAXIAL CRYSTAL GROWTH AND FORCE FIELD
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Deposits were prepared and examined in situ of KBr, NaCl, LiF, and TlBr on rocksalt cleavage faces, and of NaF and NaCl on rocksalt cleavage faces, (110) and (111) faces, and of NaBr and KCl on sylvine cleavage faces. Deposits of TlBr and NaCl on glass were prepared and examined in the camera. Parallel growth was observed in all deposits on ionic substrates, and sometimes a second type of two degree orientation of the deposit ions was also observed.

There were only nine deposits prepared in the external evaporator, and these were of NaF onto rocksalt cleavage faces. Forty percent of these experiments gave diffraction patterns corresponding to a NaF-NaCl superlattice unit cell of dimensions 9.24 Angstroms, which is twice that of the normal NaF unit cell. A structure for this superlattice unit cell was suggested which had a structure amplitude corresponding to the observed intensities.

KBr deposits on rocksalt cleavage faces and NaBr deposits on sylvine cleavage faces both showed that the deposit and the substrate reacted chemically at temperatures above 150°C . to give diffraction patterns in which all four halides KBr, NaCl, NaBr,

KCl were observed to be prominent.

Deposits of NaCl prepared on rocksalt (001) cleavage, (110), and (111) faces, and KCl deposits prepared on sylvine (001) cleavage faces grew in continued growth of the substrate surface above 90°C. substrate temperature. Seventy percent of the deposits prepared thus were observed to twin on (111) planes at temperatures above or when the deposit was heated above 195°C. The twinning is probably caused by non-uniform heating of the substrate surface by the furnace, thus giving rise to strains on the surface. The effect was never observed for substrate crystals alone heated to above 195°C.

LiF and TlBr deposits prepared on rocksalt (001) cleavage faces showed their preferred second orientation of $\langle 001 \rangle$ LiF parallel to $[110]$ NaCl as well as that of the normal $\langle 110 \rangle$ LiF parallel to $[110]$ NaCl; in both cases $\{001\}$ LiF was parallel to (001) NaCl. This orientation was preferred because both LiF and TlBr have the property that $\sqrt{2} \cdot a(\text{LiF or TlBr}) = a(\text{NaCl})$, the orientation was observed in specific substrate temperature ranges. The deposits of TlBr on rocksalt cleavages and on glass showed that the halide possesses both the caesium chloride and the rocksalt type structures at room temperatures, but at temperatures above 125°C. the TlBr has a rocksalt type structure only. Lattice constants of the TlBr in these structures were found to be identical and thus in disagreement with the conclusions made by Schulz (1950).

Deposits of NaCl on glass were examined both for normal and oblique incidence of the deposit atoms; cube face orientation was observed.

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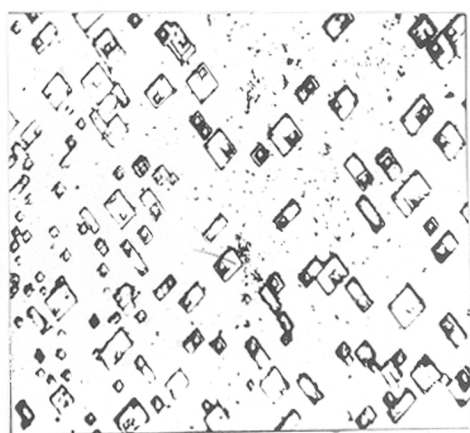


Fig. 1.

I INTRODUCTION.

1. General Introduction.

Epitaxy is the name given by Royer to the phenomenon of the oriented growth, in a definite relationship, of crystals of one kind of material upon a crystal of another kind. A well known example of epitaxy is the growth of NaNO_3 from aqueous solution onto a calcite cleavage face (Frankenheim 1836). Figure 1 illustrates this parallel arrangement of the NaNO_3 crystals with their edges parallel to those of the calcite cleavage rhombs. Many cases of epitaxy have been recorded, largely in minerals (Hügge 1903), although also in the cases of various isomorphous chemical compounds as studied for example by Barker (1908), who suggested that the condition for epitaxy was that the molecular volumes of the two materials should be similar in magnitude.

Microscopy, X-ray, and particularly electron diffraction are now increasingly useful techniques for the crystallographer. After the discovery of X-ray diffraction in 1912 by Laue, Friedrich, and Knipping, the atomic arrangements of many kinds of materials were elucidated, and in a classical work, in which the optical microscope was used to study epitaxy, (Royer (1928) discussed epitaxy for the first time in terms of the atomic arrangements of the substrate and deposit crystals. Electron diffraction was discovered in 1927 by Davisson and Germer for electrons accelerated through several hundred electron volts, and independently by Thomson and Reid for electrons accelerated through several hundred about 30KV. The diffraction of slow electrons involves using a Faraday ^{cylinder} to

explore the field of diffraction, and this is slow and laborious. On the other hand, for fast electrons, the wide field of diffracted beams can be recorded simultaneously on a photographic plate or film. Owing to this and the less exacting vacuum technique, most electron diffraction is now carried out with fast electrons.

Finch and Quarrell (1955) first applied the principle of the co-axial electro-magnetic focussing coil to increase the resolution of the diffraction pattern, also enabling the focussed beam to be moved at will over a wide area of the specimen by tilting the coil.

Electrons, because of their charge, are more easily scattered by the intense localised electrostatic charge of the atomic nucleus, and since they can only penetrate into solid matter a few hundred or a thousand Angstroms in the beam direction before losing energy, they are exceedingly useful for studying thin surface regions or films on massive materials. Consequently, they can be used for studying the structure near the interface between the substrate and the deposit, whereas X-rays, which are not so strongly scattered and therefore have a higher power of penetration, only give information about the internal structure of the material.

The present studies have utilised electron diffraction to determine the structures of exceedingly thin deposits near the interface. This study has been restricted to the growth of many halides on rock salt and sylvine, and in the light of the results obtained, some interesting aspects of crystal growth are discussed.

2. Historical Survey.

(a) Royer's conditions for epitaxy.

Royer (1928) proposed the word "epitaxy" for substrate continued crystal overgrowth, and in his experiments using the optical microscope, he systematically explained the growth of the alkali halides and some other salts from their solutions onto cleavage faces of some rocksalt type structures and onto mica. He concluded that the following conditions were necessary for epitaxy to occur.

- (i) At the interface, the two dimensional networks of the substrate and deposit must not differ in size by more than fifteen percent.
- (ii) The ions in the first layer of the deposit should occupy positions similar to those which the ions of the substrate would occupy if the substrate were continued in free space.
- (iii) The binding forces of the constituents of the substrate and the deposit must be of the same type.
- (iv) The atomic arrangement in the third dimension plays no part.

It must be remembered, before criticising Royer's rules too strongly, that modern techniques have by now brought to light much new data; and moreover, that Royer restricted his studies to experiments which did not give a general picture of crystal growth.

Sloat and Menzies (1931) found apparent exceptions to these conditions and showed that the symmetry of the electrostatic fields of

the molecules also has an influence on orientation, particularly when the axial lengths of the deposit and the substrate crystals differ by about 15 percent. Sloat and Menzies found that this axial difference could be as great as 30 percent for complete orientation to take place. Seifert (1935) (1937), Royer (1936) and Wilman (1939) pointed out that it was the similarity in parallel lattice row spacings which was more important than the networks. Elleman and Wilman (1949) pointed out that the primary factor in determining epitaxy must be the local atomic fitting as distinct from the lattice fitting, and they illustrated this by the case of $PbCl_2$ growing on PbS .

Examples of oriented overgrowths between crystals of different types of molecular bindings have also been found, thus disproving Royer's third condition. Sloat and Menzies (1931) and Heukers (1939) respectively observed orientation of NH_4Br and $CsCl$ onto silver, and of $NaCl$ onto galena all grown from their solutions. Hocart (1933) observed that arsenolite and senaxmonite oriented on mica, Royer (1933) observed hexagonal quinol oriented on calcite, and KNO_3 and $CS(NH_2)_2$ oriented on zincblende. Kirchner and Lassen (1935) and Goche and Wilman (1939) obtained epitaxy of silver grown onto rocksalt, Bruck (1936) and Rudiger (1937) obtained epitaxy of other face-centred cubic structured metals grown onto rocksalt and similar substrates. Uyeda (1940) (1942) obtained epitaxy of silver grown onto rocksalt, molybdenite, zincblende, galena, pyrites and stibnite. Willems (1949) obtained oriented deposits of pentachlorophenol and carbon tetrabromide (polar groups), and hexamethylbenzene and dural (aromatic hydrocarbons) grown onto sugar, which is covalent.

Johnson (1950) (1950) observed in the optical microscope epitaxy of NaCl grown from solution onto electropolished polycrystalline silver, and Gharpurey (1950) observed epitaxial crystal growth of NaCl and As_4O_6 onto a pyrites cleavage face. Webb (1951) and Brå and Gharpurey (1951) observed epitaxy of As_4O_6 onto rocksalt cleavages and of silver onto (110) and (111) faces of rocksalt, respectively. Royer (1951) observed oriented growth of hydroquinone and anthraquinone from solution onto cleavage faces of rocksalt and LiF and of anthraquinone grown from solution onto (001) faces of brucite and muscovite.

(b) The effect of temperature and the physical topography of the substrate surface.

Brick (1936), Lassen (1936) and Rudiger (1937) examined metal deposits on rocksalt and established a temperature dependence for epitaxy, above a critical temperature there being complete orientation, whilst below this temperature the growth was random. Rudiger also found this critical temperature dependence for the growth of gold, silver, and platinum onto mica, calcite and fluorite faces. This shows that increase in temperature increases the likelihood of an ion or an atom settling down in a specific potential trough on the substrate surface. Ellmen (1948) observed epitaxy of PbS grown on rocksalt cleavage faces occurred as a result of an initially random PbS deposit when the temperature was raised sufficiently. Fordham and Khalsa (1959) examined deposits of palladium on rocksalt, and observed that certain orientations occurred in a specific temperature

range.

Thomson and Cochrane (1938) and Thomson (1948) thought that the steps and cracks in the substrate surface may cause orientation, the deposited atoms taking up positions in rows along a step and becoming a main lattice row direction of the deposit crystals. Brabbe (1949) showed this need not be necessarily so, because when he grew crystals of methylene blue on glass ruled with fine scratches by a diamond, he found rather that many crystals happened to grow initially in the trough of the scratches, but those having their needle axis along a scratch grew longer than the other crystals. Wilman (1951), by a consideration of rotational slip and the lattice fitting between the crystals, concluded that steps and cracks are of minor importance in determining the orientation of crystals, but that they may well determine the habit and location of the deposit crystals.

(c) Directed disorientation due to epitaxial stresses.

It has been established recently that one of the ways of relieving excess strain in atomic layers is by directed disorientation. Evans and Wilman (1950), Goswami (1950), Wilman (1951) and Brú and Charpurey (1951) have shown that a directed disorientation within a range of rotations about the normal to a densely populated net plane often occurs in epitaxial deposits. Evans' and Wilman's experiment was to heat a ZnS crystal (110) cleavage face in air to 520°C. when they obtained a film of ZnO in (105) orientation on this face. From the arcing of the spots in some azimuths and not in others, they concluded that the

observed orientation could be explained most simply by a lamellar rotational slip occurring on the ZnO (110) planes perpendicular to the substrate surface. An example of such a directed disorientation is shown in the present experiments for the growth of NaF on rocksalt.

(d) Pseudomorphism.

Referring to Royer's first rule, it may be noted that Frank and van der Merwe (1949) estimated theoretically that if the lattice misfit was less than 14 percent, then the atoms in the first atomic layer of the deposit should take up positions of minimum potential energy on the substrate surface. This effect was first indicated by Finch and Quarrell (1934) who called it "basal-plane" or "interfacial" Pseudomorphism. Finch and Quarrell (1935) (1934) reported pseudomorphism for Al on platinum and for ZnO on zinc, also Cochrane (1936) for nickel deposited on etched electropolished single crystal of copper, and Clark, Pish and Weeg (1944) in certain cases of electro-plated metals. Its infrequency of observance is presumably due to the fact that the effect is confined to the first few atomic layers.

The orientation of a deposit crystal must be determined by the arrangement of the first two or three deposit atoms of the initial nucleus, and clearly, the atomic separation must be different from that which occurs in large crystals. For example, it is known that the interatomic distance of an alkali halide vapour at about 800°C. differs by about 8 percent from that of the solid state at room temperature. If

such a diminution persisted, even at the substrate temperature, then in some cases this must favour pseudomorphism in the growth of crystals as for example KCl (K-Cl = 3.14 Angstroms solid, 2.79 Angstroms vapour) on rocksalt (Na- Cl = 2.81 Angstroms). This interatomic distance change in the vapour state is discussed in greater detail in the next section (e).

Another important fact in considering the misfit between deposit and substrate during deposition from the vapour is the thermal expansion of the two materials, for example, a one centimetre cube of rocksalt expands to a 1.01 centimetre cube on heating by about 250 degrees C. (Wooster 1949). It should be noted that if abnormal lattice constants are observed in an epitaxial deposit, this may in certain cases, such as alkali halide materials (Royer 1928), be due to solid-solution formation in the region of the interface, rather than to pseudomorphism proper.

(e) Survey of results on growth of rocksalt and caesium chloride type structures on rocksalt, sylvine and other substrates.

A classic study was made by Royer (1928); he found that in growth from solutions, mutual epitaxy occurred between two materials of rocksalt type structures when the lattice dimensions differed by not more than 15 percent. Royer was careful to distinguish between cases when solid solution occurred and when it did not. Van der Merwe (1949)

carried out a concise study of deposits of rocksalt type structures onto each other and Schulz (1952) also examined deposits of rocksalt and caesium chloride type structures on rocksalt, LiF and calcite.

In connection with the deposition of the alkali halides and similar salts from their vapours, it is important to note that the interatomic distances in the molecules of the hot vapour is less than that in the crystal solid state as the following table shows:-

TABLE I

<u>Material</u>	<u>Vapour (\AA)</u>	<u>Crystal</u>	
NaCl	2.51	2.81	
KCl	2.79	3.14	
RbCl	2.89	3.27	
CsCl	3.06	3.56	All units in Angstroms.
NaBr	2.64	2.98	
KBr	2.94	3.29	
RbBr	3.06	3.45	
CsBr	3.14	3.71	
NaI	2.90	3.25	
KI	3.23	3.53	
RbI	3.26	3.66	
CsI	3.41	3.95	
TlCl	1.54	1.92	
TlBr	1.46	1.99	

* Hendricks and Mosley (1937);+ Hendricks, Maxwell & Mosley (1937)
 † Grether (1936)

One disadvantage of the Thallium halides is that they decompose into thallium and the halogen at temperatures well below their boiling points and therefore have to be deposited at low substrate temperatures and consequently low rates of deposition.

Another observation on CsCl, CsBr, TlCl and TlBr by Schulz (1950), (1950), (1951) is that under the epitaxial forces exerted by a single crystal substrate, these may crystallise out with a rocksalt type structure instead of their normal caesium chloride type structure. Schulz investigated depositions of many halides on each other, although on cleavage faces only. He found these four halides had rocksalt type structures when deposited on NaCl, KBr, LiF, KI and CaCO₃, and in addition Pashley (1952) reported the same thing for the deposition of TlCl on mica. Schulz drew up a table of differences in interatomic spacings of the alkali and thallium halides he found to have this property.

TABLE II

<u>Halide</u>	<u>Rocksalt type</u>	<u>Caesium chloride type.</u>	<u>Difference.</u>
CsCl	3.47	3.56	0.09
CsBr	3.62	3.72	0.10
CsI	3.83	3.95	0.12
TlCl	3.15	3.32	0.17
TlBr	3.29	3.44	0.15
TlI	3.47	3.64	0.17

All units in Angstroms.

Schulz also deposited NaCl onto glass, attaching more importance to the deposit thickness for governing the orientation in general of NaCl on any amorphous substrate. Deposits thicker than 100 Angstroms were (110) orientated, and for deposits less than 100 Angstroms thick, the NaCl was (100) cube face oriented, this does not agree with the present results for the deposition of NaCl on glass. (cf. under Section III, part 6.)

Pashley (1952) condensed AgCl vapour onto a KBr cleavage face, and found a chemical reaction took place at room temperature, and all four halides as well as metallic silver were observed to be prominent in diffraction patterns at the same time. This is similar to the observations on the deposition of KBr on rock salt and NaBr on sylvine in the present studies.

3. Refractive index and potential field over a smooth crystal surface.

It is important to note that the deposition of a material onto a surface often causes this surface to become atomically smoother; this was inferred by the change in the diffraction pattern during and after deposition. This is presumably due to either the impinging deposit atoms filling up the crevices or that ~~they~~ their nuclei crystal buds are planes parallel to the substrate surface and building out from the projections of which the surface is normally composed. Such smooth substrate crystal faces and very smooth deposit crystal faces give rise to refractive effects such as were observed in many

of the present experiments. On the basis of this it was thought highly desirable to evaluate where possible, the mean "inner potentials" in important cases.

From the Schrodinger equation we may calculate the refractive index " μ " for electrons passing from a boundary of space potential zero to a boundary of space potential E inside a crystal, and this simplifies to :-

$$\mu^2 = 1 + \frac{E}{V}$$

E = mean "inner potential", V = accelerating voltage.

μ is calculated from geometrical measurements.

Laschkarew (1935) (1935) and Laschkarew and Tschaban (1935) discussed the problem from a more general point of view, and they showed how the inner potential $\mathbb{E} = f(x,y,z)$ explains systematic deviations from Bragg's Law. They evaluated $\mathbb{E}(z)$ in the special one dimensional case, both for high orders and for low orders of reflection. The most relevant aspect of Laschkarew's and Tschaban's work was to plot the potential field over a (001) cleavage face of rocksalt. The method is long and elaborate, but may be briefly outlined as follows:-

Knowing the positions of the atomic nuclei in the grating and the electron density distribution, it is possible to calculate the potential at any point by means of the X-ray scattering factor $F(\text{like})$ and a very slowly converging series.

W. E. LASCHKAREW

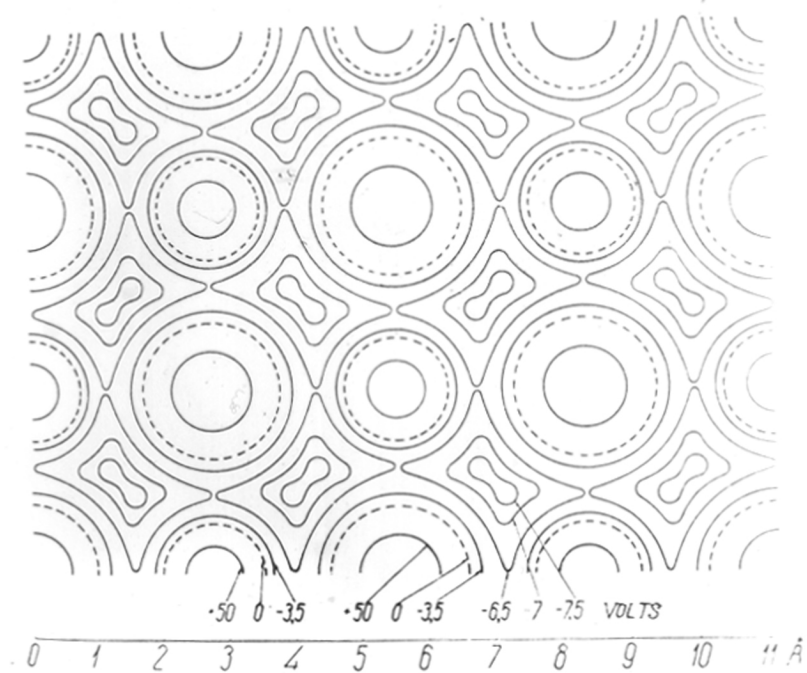


Fig. 2.

We replace the real atoms in the crystal by fictitious ones having the following properties.

- (i) The fictitious (equivalent) atom (or ion as is probably meant) possesses spherical symmetry.
- (ii) The fictitious grating has the same scattering factors as the real one.
- (iii) The centres of these equivalent ions are situated at points in the real grating.
- (iv) The electron fields of the real and imaginary sets of ions must overlap one another.

$\Phi(x,y,z)$ must be both a continuous and a regular function in any ionic crystal, and the arrival of an alien ionic crystalline deposit will tend to distort this field at the interface but in no way to make it discontinuous.

The potential field over a rocksalt (001) cleavage face is shown in Figure 2.

A deposit anion tends to take up a position over a cation of the substrate surface providing it has enough energy to move to this point, it being a position of minimum potential energy. Therefore, a deposit cation arriving in this atomic location will have a minimum distance of approach to the deposit anion, and on this basis will take up a position of minimum potential energy relative to the combined field of that part of the substrate's surface and the deposit anion. Finch and his collaborators (unpublished discussion at the Royal Society in 1951) therefore postulated

that the first two atoms of an ionic deposit on an ionic crystal determine the orientation, if any, that the deposit atoms will take up. An elementary consideration of a mechanical model representing the two crystals would show this to be so, although the proof holds only for an atomically smooth region of the substrate's surface.

From this point of view it is possible to outline a set of conditions governing oriented overgrowths.

- (a) The distance an impinging deposit atom moves before becoming "stable". This depends on the position on which it first lands, the rate of deposition, the substrate temperature and the angle subtended between the incident atoms' path and the surface.
- (b) The rate of nucleation. This case of growth of the crystal bud depends on practically the same factors as in (a).
- (c) The method of arrival of the deposit atoms, in groups or singly, and the effect on surrounding potential field.
- (d) The thermal vibration of the ions in a crystal. This amplitude is of the order of $\cdot 1$ Angstroms, but increases with increase in temperature and therefore may have a considerable effect on the growth of a deposit in an orderly form or otherwise. (cf. I. 2(b).)

4. Aim of the present work and nature of results.

The aim of the present studies was to examine in detail the crystal growth of rocksalt and caesium chloride type structure on rocksalt, sylvine and other substrates, and to correlate the results observed with the four factors listed above at the end of section 3. Hitherto, there

has not been much information available concerning the epitaxy of these materials.

Many new and interesting aspects in the present research was observed. A NaF - NaCl superlattice was discovered and a possible structure suggested; this superlattice unit cell size was 9.24 angstroms, which is twice that of the Normal NaF unit cell. A case of what was thought to be directed disorientation for a deposit of NaF grown onto rocksalt was also observed. KBr was found to react with its substrate when deposited onto rocksalt and similarly for NaBr grown onto sylvine, both these sets of experiments gave diffraction patterns in which all these four halides, NaBr, NaCl, KBr and KCl were observed to be prominent. NaCl was observed to twin when deposited onto rocksalt either in a specific temperature range or when a deposit was heated up to a temperature within this range, also beautiful secondary scattering and refractive effects were observed. LiF and TlBr both adopted identical second type of two degree orientation in a specific temperature range, and TlBr was observed in both a rocksalt type structure, and in a mixture of a rocksalt type structure and its normal caesium chloride type structures.

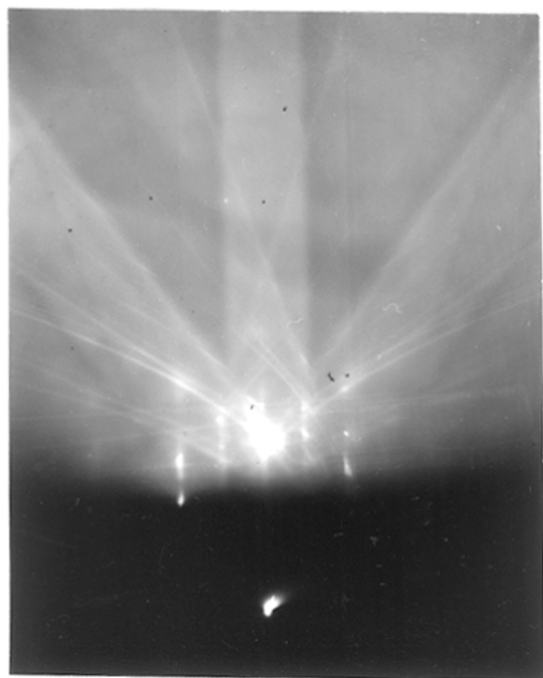
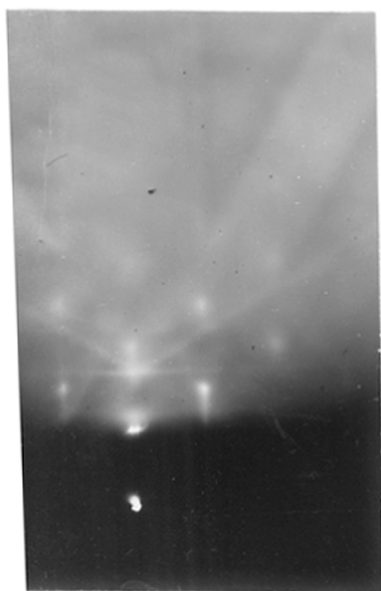


Fig. 3.

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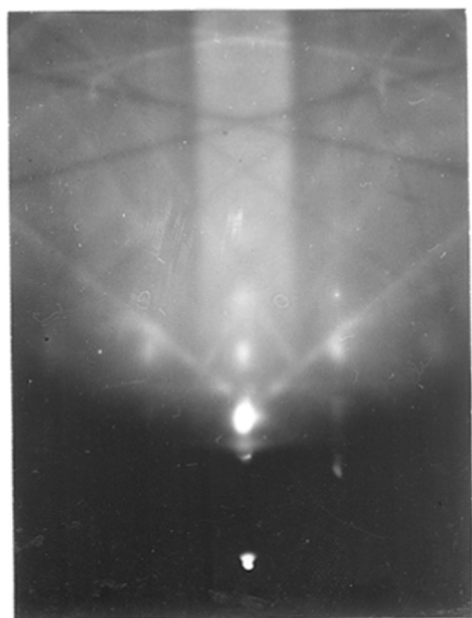


Fig. 5.

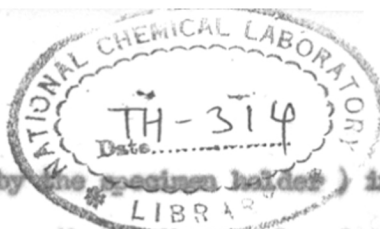
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II EXPERIMENTAL

Rocksalt and sylvine substrates were prepared by cleaving crystals 10 millimetres square by 3 millimetres thick off the main crystal blocks. Rocksalt crystals were provided by Hilger and Watts and Professor Pohl of Göttingen provided the sylvine crystals. Loose particles due to cleavage were removed by gently rubbing the edges of the freshly cleaved crystal with a clean filter paper and then brushing the surface with a dry grease-free camel hair paint brush. This treatment reduces the tendency of the substrate crystal to charge up when examined with an electron beam, and thus improves the diffraction patterns. Figure 3 illustrates the typical diffraction pattern which is obtained from such a (001) cleavage face.

(110) and (111) faces of rocksalt were prepared by grinding blocks of rocksalt about a centimetre cube on coarse emery paper on a rotating wheel, then grinding by hand in alternating $[100]$ and $[010]$ directions from 0 emery down to 0000 emery. This new face was then etched in a stream of running cold water for two seconds, plunged into absolute alcohol and then dried on filter paper. Figures 4 and 5 show typical diffraction patterns observed from (110) and (111) faces prepared in this way. All three types of crystal faces were used whilst fresh as possible.

Glass substrates were microscope slides cleaned by immersing in a solution of methyl alcohol and nitric acid, washed in distilled water and then dried on a clean filter paper. The microscope slides were about 8 centimetres long and although this meant difficulty in



inserting the glass slide (when held by the specimen holder) into the diffraction camera, the advantage was that both normal and oblique incidence of the deposit atoms beam could be examined at the same time.

For material to be deposited, TlBr was prepared by treating a strong solution of $TlNO_3$ with excess hydrobromic acid; this solution was then evaporated to small bulk and left to crystallise, the crystals were then dried on filter paper. All other chemicals used in the present studies were the normal Hopkins and Williams products.

A Finch-type electron diffraction camera (Finch and Quarrell 1934, Finch and Wilman 1937) was used in the present studies, with voltages in the range 50 to 65 KV. , a camera length of approximately 48 centimetres, and at working pressures below 10^{-5} millimetres. Examinations of state of aggregation and thickness of deposits were carried out using a Vickers Projection Microscope and magnifications between 200X and 600X. An advantage of rocksalt, sylvine and glass is that their transparency enables one to use either the reflection or the transmission methods depending on the thickness of the deposit to be examined.

The method of heating the substrate crystal was by an electrically-heated "H"-shaped molybdenum tape, insulated from the copper specimen carrier platform by a 3-millimetre thick porcelain disc. A clean sheet of mica about 2 centimetres square was placed

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between the furnace and the base of the substrate crystal to ensure uniform heat transmission as far as possible to the crystal and also to prevent the furnace, when hot, from sticking to the crystal. Rock-salt and sylvine can be heated up fairly rapidly as they are better conductors than glass; a microscope slide takes about five minutes to be heated up to 100°C . without breaking. The thermocouple rested on top of the substrate crystal and about $\frac{1}{2}$ centimetre away from the sprung specimen clip, which held it, together with the whole assembly of porcelain disc, furnace, mica sheet and crystal against the back of the specimen carrier platform. The furnace was capable of heating a normal sized cleavage crystal (10mm. square by 3mm. thick) up to about 400°C .

The junction of the thermocouple consisted of a copper-constantin welded joint each of 40 S.W.G. whose leads passed, like those of the furnace's, through the back of the specimen carrier. Both the furnace and the thermocouple leads passed through porcelain beads inset inside 5 millimetre diameter bored holes, the outside of which was placed a covar, metal-glass-metal, seal soldered onto the specimen carrier. The thermocouple leads were then connected to an engine galvanometer reading up to 350°C . and especially designed to be used with such a junction. It should be noted that the temperature of the substrate surface is higher than that which is recorded during deposition, this is due to the radiation and the energy of the incident atoms from the hot depositor filament.

A tungsten wire decharger filament, of about 200 volts accelerating voltage, was used in the majority of the present experiments, as rocksalt, sylvine and glass, being insulators, are liable to charge up when bombarded with electrons at low grazing incidence. The decharger filament was never needed after deposition was carried out on ionic substrates, although the electron diffraction pattern indicated by very strong refractive effects, that the deposit crystals had very smooth faces parallel to the substrate surface.

A tungsten wire was used for the depositor filament, its gauge and shape being adopted to the type of deposition to be carried out. The depositor lead passed through the back of the decharger to a 4volt, 2amp A. C. circuit with a rheostat in series to control the filament temperature. The depositor filament was flashed in vacuo before using, thus cleaning off any impurities (oxide, grease etc.), and at the same time the current was adjusted to maintain the required rate of deposition. The depositor filament could be moved as far as 8 centimetres away from the substrate surface and down to angles giving almost horizontal incidence of the deposit atoms' vapour stream.

III RESULTS.

1. NaF deposits on rocksalt cleavage, (110) and (111) faces.

In the present experiments of depositions of NaF from the vapour condensed onto (001) cleavages, (110) and (111) faces, parallel growth was observed in all cases where the substrate temperature varied in the range 90°C. to 220°C. In these cases of parallel growth, NaF ($a = 4.62\text{\AA}$) growing with its lattice axes parallel to those of rocksalt, has a misfit of approximately 18 percent. Depositions prepared below substrate temperatures of 90°C. were observed to give random deposits, and those prepared above substrate temperatures of 220°C. gave disoriented deposits. Twinning on octahedral faces was observed in about one in ten deposits prepared on (001) cleavage and (111) faces (see Table III), such may be expected in view of the large degree of misfit. (18 percent)

The first nine experiments on (001) cleavage faces were carried out in an external evaporator, this involves higher residual air pressures ($c 10^{-3}$ mm.) during deposition and contact with air whilst transferring the specimen to the camera for examination. After certain complications were noted, it was decided that all future depositions should be prepared in the higher vacuum of the diffraction camera and examined in situ without contact with air. It has already been stated that the residual air pressure inside the camera was less than 10^{-5} mm..

Table III shows the results observed and their proportion.

Table III

NaCl face.	No. of deposits.	NaF orientation.	Twinning in {111}	Fig.	Ref.
Depositions carried out in the external evaporator.					
(001)	7	(001) + (110)	-	-	A
(001)	4	(001)	-	8,9.	B
Depositions carried out in the camera.					
(001)	4	(001)	-	6,7	C
(001)	2	(001)	Observed.	-	D
(001)	10	(001)	-	-	E
(110)	5	(001)	-	-	-
(111)	3	(001)	Observed once	-	-

* (001) = {001} NaF parallel to (001)NaCl, <100>NaF parallel to [100]NaCl.

References: A- Substrate temperatures about 150°C.

B- Superlattice diffraction patterns observed.

C- Alleged directed disorientation.

D- Substrate temperatures about 160°C.

E- Substrate temperatures about 200°C.

Deposits prepared both in the external evaporator and in the electron diffraction camera were extremely consistent in their reproducibility at any given deposition conditions. It should be noted however, that the depositor filament was closer to the substrate surface for depositions carried out in the external evaporator than for those prepared in the camera, and therefore, not only effects due to

deposition at ~~the~~ higher residual air pressures during deposition and to the effect of air when transferring the specimen to the camera for examination have to be considered, but also the higher substrate temperature during deposition, this being due to the greater radiation effect of the depositor filament. (It has been shown, that during deposition, the temperature of the substrate surface is raised by about 200 degree C. (Murucumanara 1948)). The fact that all deposits prepared in the evaporator changed but little when left in air for a few hours, this being observed by the fact that diffraction patterns before and after leaving in air show no change, implies that although moisture may have had an effect on the deposit crystals, then this effect must have been either fairly rapid or almost instantaneous.

Deposits prepared below substrate temperatures of 90°C. were observed to be random polycrystalline; deposits prepared between substrate temperatures of 90°C. and 220°C. grew parallel to the substrate lattice rows; deposits prepared above substrate temperatures of 220°C. showed more or less a spread of orientation from the mean epitaxial growth, and at 300°C. the disorientation is almost complete and deposit crystals were observed to be in random formation. The spread of orientation was indicated by the arcing of the diffraction spot patterns. A closely similar relationship between structure and temperature was observed for deposits heated above their substrate deposit temperature, for example, if a deposit which was

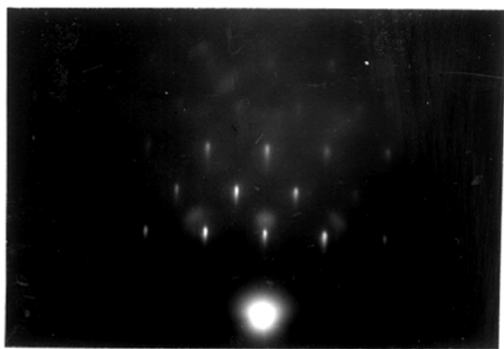


Fig. 6. 2431.

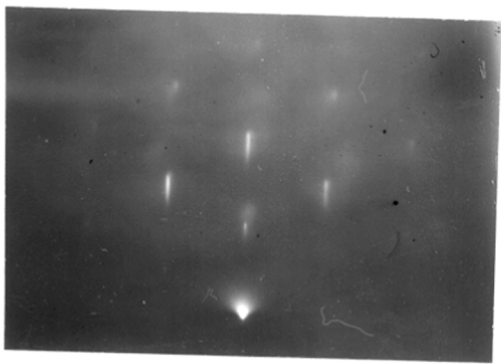


Fig. 7. 2432.

prepared at room temperature, i. e. random, were to be heated up slowly to 300° Centigrade, the following process would be observed:- The initially random deposit would be transformed into a simple spot pattern inferring parallel growth had occurred (at 90° Centigrade) and then to become disorientated at 220°C. , and when the crystal had been heated to 300°C. the deposit crystals would be observed random again. It was noted that heating a deposit which was prepared at a substrate temperature of approximately 100°C. up to about 250°C. produces the same results as leaving the same deposit without this treatment in air for about 24 hours, in both cases the diffraction patterns showed that the deposit crystals had become disorientated. It may be inferred from this that heating a deposit in vacuo or leaving a deposit of the NaF in air for about 24 hours has the same effect. Moreover, since (110) orientation was never observed in deposits prepared in the camera and when left in air, and was observed in all deposits prepared in the external evaporator then the orientation is either due to the fact that the depositor filament is quite close to the substrate surface in the external evaporator or more probably due to the depositions being carried out at higher residual air pressures (about 10^{-5} mm.) than for those deposits prepared and examined in the camera. (about 10^{-5} mm.)

An example of what was thought to be a directed disorientation about the normal to the (111) planes is shown in Figures 6 and 7.

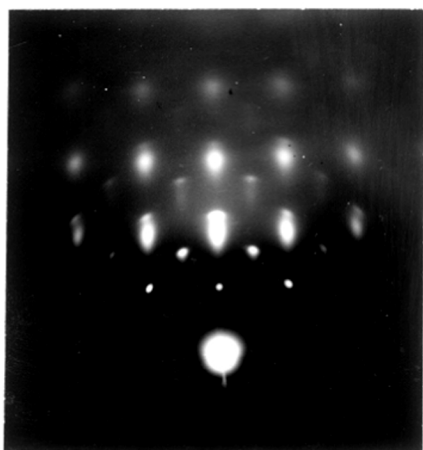


Fig. 8. 2130.

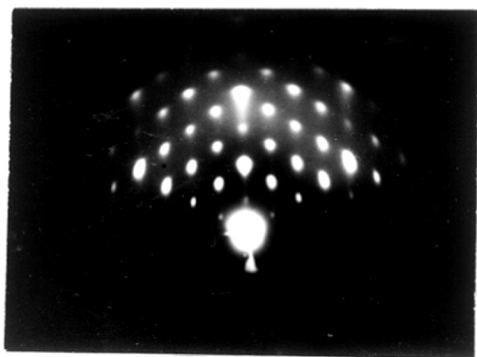


Fig. 9. 2131.

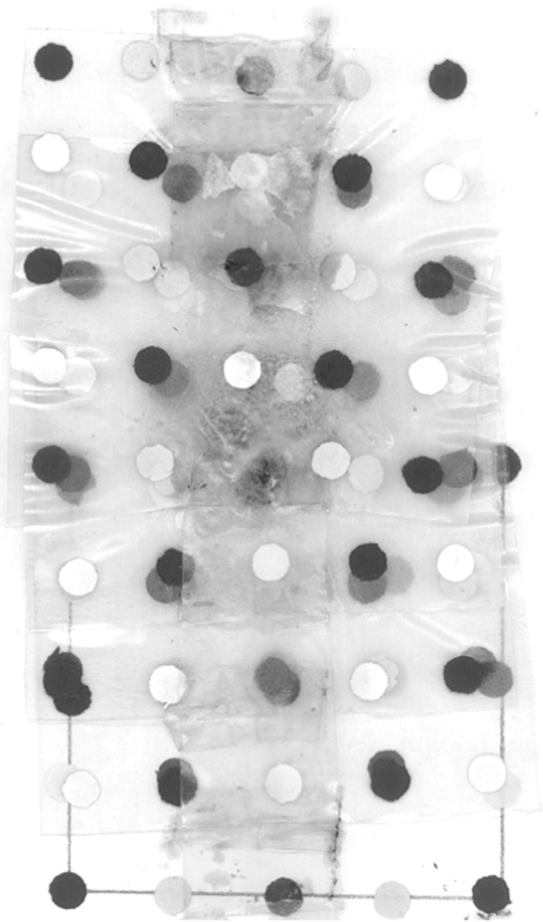
This is inferred by the observed arcing of the spot pattern in some azimuths and not in others. This directed disorientation was always observed when the NaF deposit was both thin and prepared at both a low substrate temperature, about 95°C and low rates of deposition otherwise a thicker deposit, greater than about 100 Angstroms, would tend to mask the effect.

Deposits prepared on (001) cleavage, (110) and (111) faces, all yielded deposit crystals having more or less smooth faces parallel to the mean substrate surface, but these faces were especially smooth in the cases of deposits prepared on (110) and (111) faces.

In the relative experiments where some rocksalt projected out and through the deposit crystals as a result of recrystallisation, or when the deposit crystals were thin enough (about 100 Angstroms) so that both NaCl as well as NaF were observed to be prominent in diffraction patterns, then the interatomic distance of the NaF could be calculated accurately by rocksalt comparison. It was found to be 2.81 Angstroms relative to Na-Cl = 2.81 Angstroms in all these cases. This value is in excellent agreement with X-ray data and indicates that effectively no solid-solution was formed.

It is important to note that even when accurate lattice constants are observed, although these indicate that effectively no solid-solution was formed, an undetectable amount may be present.

Fig. 10.



● = Na ION

○ = F ION

● = Cl ION

NaF-NaCl Superlattice.

Referring back to Table III, it is mentioned that in approximately one third of the total of the deposits prepared in the external evaporator a superlattice of NaF - NaCl was observed, this never being obtained for deposits prepared in the camera. The superlattice patterns are shown in Figures 8 and 9 and were observed to be the same over the whole of the substrate surface; also, the same patterns were unchanged after a deposit was left in the atmosphere for about 6 hours and replaced in the camera for re-examination.

As these two plates show, a centred-square pattern is observed for the beam in the (100) azimuth instead of the normal square pattern without the centering point, and a half-sized centred $\sqrt{2}$ rectangle instead of the full-sized one for the beam in the (110) azimuth. From this it is concluded that the NaF - NaCl superlattice was formed, and had a face-centred cubic unit cell of dimensions 9.24 Angstroms relative to that of rocksalt (5.63 Angstroms), this superlattice unit cell is twice as large as that of the ordinary NaF unit cell. No solid solution of NaF and NaCl appears to have been observed previously nor would any be expected in view of the difference in misfit between the F and the Cl ions.

A possible unit cell corresponding to the observed extinctions and spot intensities is shown in Figure 10, and the structure

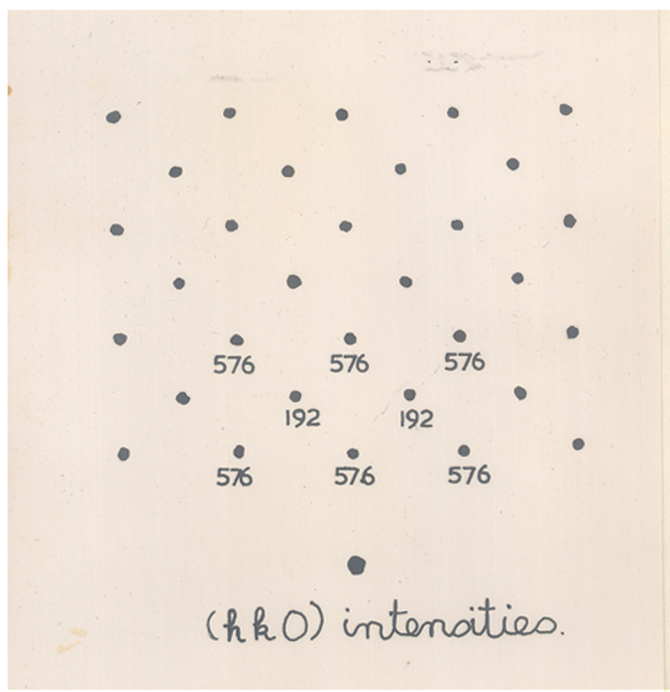


Fig. 11.

amplitude for the $hk0$ or $kh0$ diffractions corresponding to this is:-

$$S = \left\{ \begin{aligned} & (2Na + Cl + F) \cos \frac{\pi}{4} (3h + 3k) \cdot \cos \frac{\pi}{4} (h - k) \\ & + 2(Na + F) \cos \frac{\pi}{2} (h + k) \\ & + 2(Na + Cl) \cos \frac{\pi}{4} (h + k) \end{aligned} \right\} \cdot 4 \cos \frac{\pi h}{2} \cdot \cos \frac{\pi k}{2}$$

Assuming that these scattering factors Na , Cl and F are approximately proportional to their atomic numbers, i. e. 11, 17 and 9 respectively, then

$$S \approx \left\{ \begin{aligned} & 6 \cdot \cos \frac{3\pi}{4} (h + k) \cdot \cos \frac{\pi}{4} (h - k) + 5 \cdot \cos \frac{\pi}{2} (h + k) \\ & + 7 \cdot \cos \frac{\pi}{4} (h + k) \end{aligned} \right\} \cdot 32 \cos \frac{\pi h}{2} \cdot \cos \frac{\pi k}{2}$$

Figure 11 shows the calculated intensities for the diffractions in Figure 8. This is in agreement with the observed intensities, and so the unit cell illustrated in Figure 10 fits in with the data. The same pattern as Figure 8 would be observed for the beam along the a or b cube edges. The unit cell in Figure 10 is not truly cubic as a close examination will show. With the beam along the $[110]$ or the $[\bar{1}10]$ directions, a centred $\sqrt{2}$ rectangle similar to that observed from NaF would be obtained but with the beam along for example, a $[101]$ direction, a half-sized centred $\sqrt{2}$ rectangle would be obtained such as was actually observed in Figure 9. There is probably a statistical variation of the arrangement of the F and

the Cl ions corresponding to regions of such a superlattice orientated in all possible ways such that the cube axes are parallel to those of the rocksalt substrate.

What causes this superlattice is not entirely clear, and presumably, since it was only observed in deposits prepared in the external evaporator and not in any prepared inside the camera, and moreover, was stable when left in air for about 6 hours, then it is due to either lower residual air pressures during deposition or to an almost instantaneous effect of the moisture in the air whilst transferring to the camera for examination.

Several attempts were made to reproduce the superlattice by means other than deposition of NaF on rocksalt in vacuo. Firstly, molecular proportions of NaF and NaCl were taken, and then dissolved in distilled water. A little of this solution was placed on top of a freshly prepared collodion film and some graphite dust was powdered underneath the film, thus crystallising in the vacuum of the camera. The ring patterns observed showed mainly NaCl rings with a few NaF rings showing up faintly. Changing the concentration of the solution, by making it both stronger and weaker, or even boiling before using made practically no difference and again both NaCl and NaF rings were observed, and always in random polycrystalline formation.

Secondly, molecular proportions of the two alkali halides were

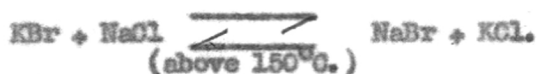
taken, mixed together thoroughly, and then melted in a porcelain crucible by the heat of two bunsen burners. This process took about five minutes continuous heating before the melt was assumed to be completely combined; it was then left to cool. A piece of the solid melt was broken off and ground in alternating directions on graded emery paper down to 0000 paper. The specimen was not etched in water as this would tend to upset the structure of a face which did not contain a regular density of atoms over its face, instead, it was gently brushed with a dry grease free camel hair paint brush to remove excess particles due to grinding from off this face. A reflection diffraction pattern was then taken and it was observed again that a random polycrystalline set of rings were in evidence indicating NaCl mainly and NaF faintly. A piece of this solid melt was broken off, ground to a fine powder and a little placed on top of a collodion film with some graphite powder on the underside of the film. This again indicated sharp intense NaCl rings and faint NaF rings.

Therefore it has been shown that the superlattice is only reproducible by chance, and then only in the case of deposits prepared in the external evaporator.

2. KBr deposits on rocksalt and NaBr deposits on sylvine (cleavage faces).

It was noted that when a KBr deposit prepared on rocksalt was heated above approximately 150° Centigrade or when deposited at substrate temperatures above this temperature, then a chemical reaction took place between the substrate and the deposit materials. The same thing was observed for the deposits of NaBr prepared on sylvine cleavage faces, and therefore, on this basis, it was decided that the two sets of experiments be taken together and compared where possible.

The reversible chemical reaction :-



is only slightly endothermic and therefore, the only factor which would influence the reaction to move in a definite direction, i. e. left to right, would be the excess of one or other of the halides involved. It is obvious that the halide in excess is that of the substrate, rocksalt or sylvine, according to the experiment, and therefore, for example, when KBr was deposited onto rocksalt cleavage (001) faces, NaBr and KCl were to be expected to be the prominent halides observed in the diffraction patterns; such was the case. However, even if a particular is observed to be the most prominent in the diffraction pattern this ^{need} ~~must~~ not be necessarily the product

of a chemical reaction but may be well due to the fact that for thin deposits, the projections from the substrate surface pierce the deposit layer and give rise to a diffraction pattern which corresponds to the substrate crystal and not its recrystallised form.

All deposits, both of KBr on rocksalt (001) cleavage faces and NaBr on sylvine (001) cleavage faces, were prepared and were examined in the high vacuum of the diffraction camera. Deposits prepared below a substrate temperature of 90° Centigrade were random polycrystalline, and those prepared in the substrate temperature range of 90° Centigrade to 250° Centigrade gave either one or more halides but always in parallel growth to the substrate. Deposits prepared above 250° Centigrade substrate temperature begin to become disorientated from the mean epitaxial growth; this being determined by the spots in the diffraction patterns beginning to arc from their mean. About 300° Centigrade, the disorientation is complete and the diffraction patterns usually consisted of four ring patterns corresponding to the four halides NaBr, KBr, NaCl and ~~NaI~~ KCl respectively.

Table IV shows the halides which were observed to be most prominent in diffraction patterns and their respective substrate temperatures, and then the treatment undergone and the new observance.

TABLE IV.

<u>No. of deposits.</u>	<u>Substrate temp.</u>	<u>Observation.</u>	<u>Treatment.</u>	<u>Observation.</u>
KBr deposits on rocksalt cleavage faces.				
2	90° C. - 160° C.	KBr	Htg to c. 180° C.	NaBr, KBr.
3	90° C. - 160° C.	KBr	Lvg. in air 20h.	All four.
NaBr deposits on sylvine cleavage faces.				
3	90° C. - 140° C.	NaBr	Htg.	KBr, NaBr & NaCl.
3	90° C. - 140° C.	NaBr	Lvg in air 20h.	All four.
1	170° C. - 230° C.	KBr, KCl.	Do..	Do..
1	280° C.	All four halides disorientated.		

There is a close similarity between these experiments and those of Fashley's (1952) when he found that AgCl deposits prepared from the vapour onto KBr cleavage faces reacted with the substrate at room temperature to form all four halides AgCl, KBr, AgBr and KCl as well as metallic silver.

As table IV shows, there were more experiments of NaBr on sylvine than of KBr deposits on rocksalt, this is because the reaction always took place at 150° Centigrade for the latter set of experiments but for deposits of NaBr on sylvine, the reaction took place at temperatures varying between 140° C. and 160° C., the reason for this was not known but could be due to the slightly

endothermic nature of the reaction. This means that a set of experiments on the exothermic reaction :-



would give a more consistent set of results than attempting to determine the reaction temperature of an endothermic reaction :-



It is known, that when KBr reacts with its rocksalt substrate, heat is given out, and that is why the transition temperature is more marked than in the case of deposits of NaBr prepared on sylvine cleavage faces, because as the temperature slowly rises to about 150° Centigrade the reaction can only take place by absorbing heat from the sylvine substrate, and so the temperature may drop a little although it was still being heated.

The mechanism of the reaction is very complex, as thermal effects, and therefore both the mobility and migration of the ions over the substrate's surface would have to be considered. There is a progressive interchange of all the four ions Na, K, Br and Cl above 150° Centigrade, both over the substrate surface and at right angles to this direction, i.e. into the deposit according to the deposit thickness.

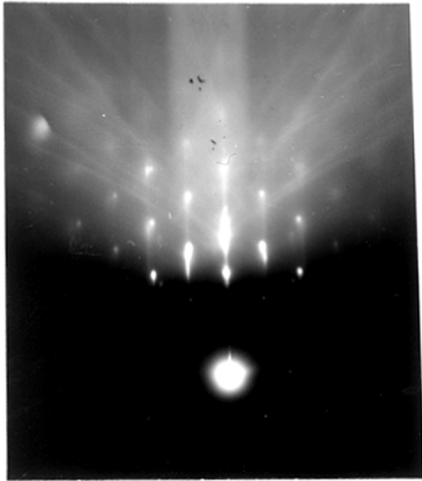


Fig. 12. 2573.

Table IV shows that there were several cases in which all the four halides:- NaBr, KBr, NaCl and KCl were observed to be prominent in diffraction patterns, a typical one of these is shown in Figure 12.

The interatomic distances were calculated from this plate by comparison with that of rocksalt (Na - Cl = 2.82 Angstroms) and were found to be 2.96, 3.11, and 3.26 Angstroms for NaBr, KCl, and KBr respectively. These three values are in excellent agreement with X-ray data and therefore indicate that effectively no solid solutions were formed.

KBr deposits prepared on rocksalt at substrate temperatures of 90° Centigrade to 140° Centigrade showed the KBr to be growing parallel to the substrate, but heating above 150° Centigrade causes the chemical reaction to take place and the rocksalt acts as though it were in excess and NaBr and KCl were observed most prominent in diffraction patterns. The same thing holds for NaBr deposits on sylvine when NaCl and KBr were observed to be the most prominent in the diffraction patterns. The same relation between structure and temperature was observed when a deposit was heated above its substrate deposit temperature. For example, when an initially random room temperature deposit was slowly heated, it then grew in parallel growth, then reacted according to the above data, and finally disorientated when the substrate temperature reached about 250°C..

3. NaCl deposits on rocksalt (001) cleavage, (110) and (111) faces
and KCl deposits on sylvine (001) cleavage faces.

These two sets of experiments were undertaken separately, but since the results were observed to be identical in both case, and this was of course expected, it is proposed that they be considered together. Rocksalt and sylvine (001) cleavage faces yield the same type of diffraction pattern as each other, and moreover, examination of these faces by the Vickers Projection Microscope indicated that topographical nature of the surfaces was identical as regards smooth portions of the surface and parts composed of step formation which give the surface the appearance of being grained.

All deposits were prepared and examined in the higher vacuum of the camera without exposure to air, and examination of the thickness and aggregation state of deposits was carried out using a Vickers Projection Microscope with magnifications varying between 200 times and 600 times. It was found easier to examine thin deposits, about 700 Angstroms thick, by methods of phase contrast transmission, this giving more contrast and definition. Deposits thicker than 1000 Angstroms were examined by reflection, and the definition increased by lowering the intensity of the light. It is important to note that although specimens were transferred from the camera to the microscope as quickly as possible, the atmosphere had

had ample time to effect the deposit so that the growth observed was not necessarily that which was observed in the camera. If the air had had an effect, then it must have been fairly rapid as no further change was observed when the specimen was left in the microscope for a few hours.

NaCl deposits on rocksalt (001) cleavage, (110) and (111) faces prepared at substrate temperatures below 90° Centigrade grew in random polycrystalline formation, as did KCl deposits prepared at the same temperatures on sylvine cleavage faces. However at substrate temperatures between 90° Centigrade and 220° Centigrade, both deposits of NaCl on rocksalt (001) cleavage faces, (110) and (111) faces, and KCl on sylvine (001) cleavages grew in continued growth through the substrate structure. The term "continued growth" has to be used because although the growth is parallel the term "epitaxial" does not apply as the substrate and deposit crystals are not different materials and thus not corresponding to the definition of epitaxy.

All deposits prepared at substrate temperatures above 220° Centigrade were observed to have become disorientated, as was determined by the spread of the diffraction patterns in arcs from the mean. A similar relationship between structure and temperature was observed for a deposit heated at or above its substrate deposit temperature. For example, consider an initially random deposit

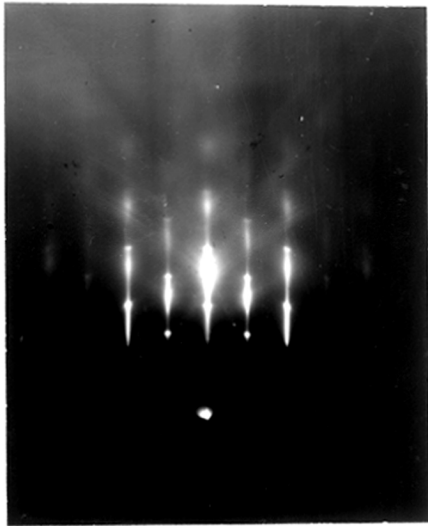


Fig. 13.

2632.

of NaCl prepared on a rocksalt (001) cleavage face when heated slowly up to about 300° Centigrade would be observed to grow in continued growth of the substrate's surface when the temperature reached about 90° Centigrade, and when the temperature reached about 195° Centigrade the deposit crystals were observed to twin on (111) planes in 5 experiments out of 9. Heating above 220° Centigrade causes the deposit crystals to become disorientated and at about 300° Centigrade the disorientation is complete and the deposit is in random growth again.

An example of this twinning is shown in Figure 13, it probably occurs in all cases but usually the deposit was thick enough to hide the effect; twinning of the rocksalt (or sylvine) substrate was never observed when it alone was heated to or above 195° Centigrade and therefore the twinning is due to a temperature effect on the deposit crystals, and not due to an epitaxial misfit. A possible explanation is that the electric furnace used for heating the substrate crystals may have caused uneven heating of the substrate surface, which is composed of steps; this would give rise to strains at the surface which were mechanical in nature but had exactly the same effect as that of an epitaxial misfit.

Figure 14 shows a typical pattern observed of a NaCl deposit



Fig. 14.

2705.



Fig. 15.

V.P.M. 249.

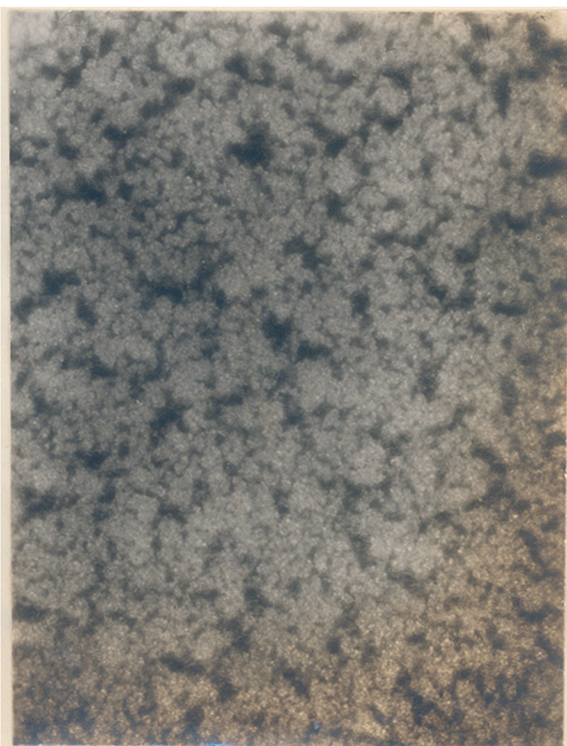


Fig. 16.

V.P.M. 251.

on a smooth rocksalt face. Deposits on all rocksalt (001) cleavage faces, (110) and (111) faces, and on sylvine (001) cleavages showed such typical beautiful refractive effects, especially deposits of NaCl prepared on rocksalt (110) and (111) faces.

Micrographs taken on the Vickers Projection Microscope showed that the higher the substrate temperature, the higher the state of aggregation of the deposit crystals into large crystal blocks. Figures 15 and 16 show micrographs taken of deposits prepared at room temperature and at a substrate temperature of 100° Centigrade respectively. The darker patches are where the aggregations of deposit crystals are present, both these deposits are about 2000 Angstroms thick.

Breathing on the deposit inside the microscope caused the dark patches to become visibly lighter which seemed to indicate that the deposit crystals had fused with the substrate surface to form a part of the main crystal block.

4. LiF deposits on rocksalt (001) cleavage faces.

LiF growing with its lattice axes parallel to those of rocksalt has a misfit of approximately -29 percent. (Li-F = 2.00 Angstroms, Na-Cl = 2.81 Angstroms.) Therefore LiF possesses the property in common with TlBr (Tl-Br = 1.99 Angstroms in its rocksalt type structure) that :-

$$\sqrt{2} \cdot a (\text{LiF or } \cancel{\text{NaCl}} \text{ TlBr}) = a (\text{NaCl})$$

This is why the preferred orientation of $\{001\}$ LiF parallel to (001) NaCl, $\langle 110 \rangle$ LiF parallel to $[100]$ NaCl was observed as well as the normal two degree orientation of $\{001\}$ LiF parallel to (001) NaCl, $\langle 100 \rangle$ LiF parallel to $[100]$ NaCl. Both these preferred second type of two degree orientations, for LiF and TlBr were observed only in specific temperature ranges. The orientation of $\langle 110 \rangle$ LiF is preferred parallel to $[100]$ NaCl as the misfit in this position is approximately zero.

At substrate temperatures below 105° Centigrade, the LiF grew in random polycrystalline form, and at substrate temperatures between 105° Centigrade and 230° Centigrade the growth was observed to be parallel to the rocksalt substrate. Deposits prepared at substrate temperatures above 230° Centigrade were observed to grow with both $\langle 100 \rangle$ and $\langle 110 \rangle$ LiF parallel to $[100]$ NaCl; in both cases

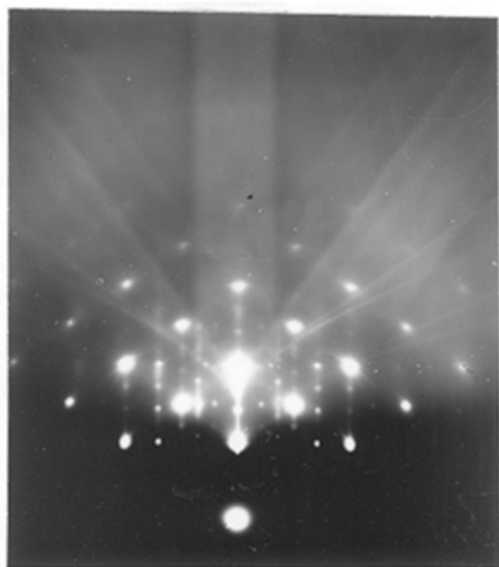


Fig. 17.

2770

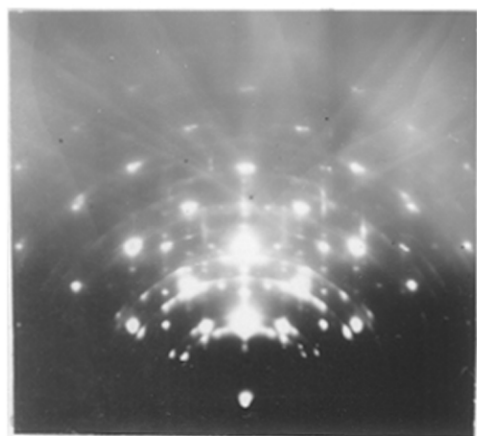


Fig. 18.

2779.

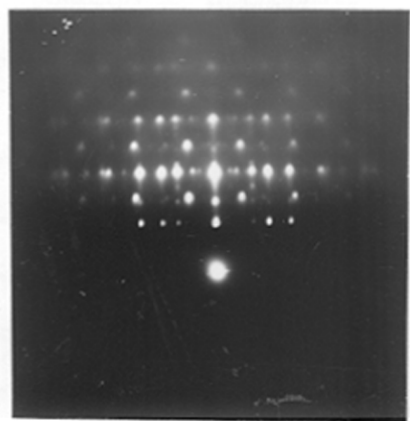


Fig. 19.

2818.

the $\{001\}$ LiF was parallel to (001) NaCl as Figure 17 shows. Deposits prepared at substrate temperatures higher than 260° Centigrade were observed to become disorientated; this being determined by arcing of the mean diffraction pattern and spreading from the mean spot pattern. At 320° Centigrade, the disorientation is complete, and the deposit crystals were observed to be in random polycrystalline formation again. Exactly the same relation between structure and temperature was observed when a deposit was heated at or above its substrate deposit temperature. For example, an initially random room temperature deposit when heated slowly to about 350° Centigrade would be first observed to grow with its lattice axes parallel to those of the rocksalt substrate and then when the temperature had reached 230° Centigrade, the deposit would be observed to adopt its second type of two degree orientation also; this being $\{001\}$ LiF parallel to (001) NaCl and (110) LiF parallel to $[100]$ NaCl.

Figure 17 gives an excellent opportunity of measuring the interatomic distance of LiF by comparison with that of rocksalt. (Na-Cl = 2.81 Angstroms). From this it was found that Li-F = 2.00 Angstroms, which is in excellent agreement with X-ray data and thus not indicative of the formation of solid solution, however, a little solid solution may have been present, but patterns of two sets of spots, one in direct arithmetical relation to the other tend to

be complicated and overlap and coincide with each other; this causes confusion in determining which diffraction spots are caused by the LiF and which are caused by the rocksalt substrate

An example of the development of smooth deposit crystal faces parallel to the substrate surface is shown in Figure 18, where we have revealed the two types of two degree orientation of the LiF, secondary scattering of the LiF primary diffractions, this pattern also shows recrystallisation of the rocksalt substrate, the disorientation of the LiF deposit crystals from their mean positions and finally the mosaic nature of the rocksalt interface which appears to give the whole pattern a rotation of approximately 3° about the central spot. Figure 17 also shows secondary scattering in the LiF pattern, this is a property common to all diffraction patterns where the 200, 220, 020 etc. diffractions are very intense, but of course it may only be noticed when these intense diffractions give rise to another diffraction pattern which is not coincident with the main one.

5. TlBr deposits on rocksalt (001) cleavage faces and on glass.

Schulz concluded that TlBr grew on rocksalt in an abnormal rocksalt type structure instead of its normal caesium chloride type structure. (1950) (1950). He also concluded that the axial lengths of the TlBr in the rocksalt and in the caesium chloride type structures differed by $\cdot 15$ Angstroms. The experiments carried out not only showed the similarity with deposits of LiF prepared on rocksalt (001) cleavage faces but also how difficult it was to reconcile Schulz's statements with the experiments described below.

At substrate temperatures below 100° Centigrade, the TlBr grew in random polycrystalline formation on its rocksalt substrate. At substrate temperatures in the range 100° Centigrade to 120° Centigrade, the TlBr was observed to grow in a mixture of both its rocksalt type and caesium chloride type structures and moreover in two type of two degree orientations (cf. III 4) of $\{001\}$ TlBr parallel to (001) NaCl, $\langle 100 \rangle$ TlBr parallel to $[100]$ NaCl; $\{001\}$ TlBr parallel to (001) NaCl, $\langle 110 \rangle$ TlBr parallel to $[100]$ NaCl. Figure 19 illustrates this complicated phenomenon and also shows the rocksalt substrate projections giving rise to a further diffraction pattern almost coincident with the main one.

At substrate temperatures in the range 120° Centigrade to 230°

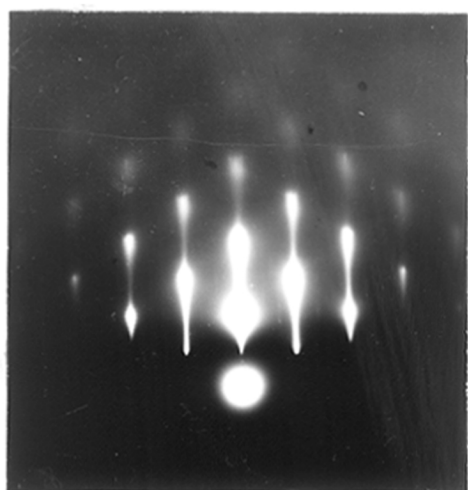


Fig. 20.

2809.

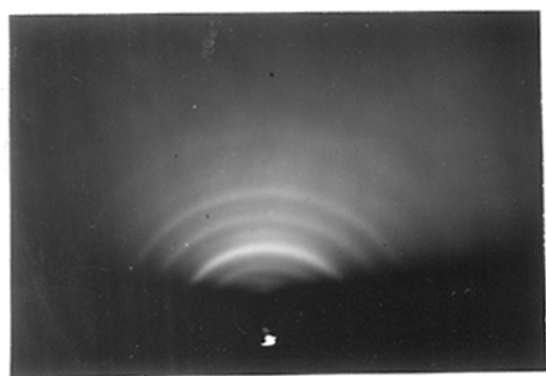


Fig. 21.

21125

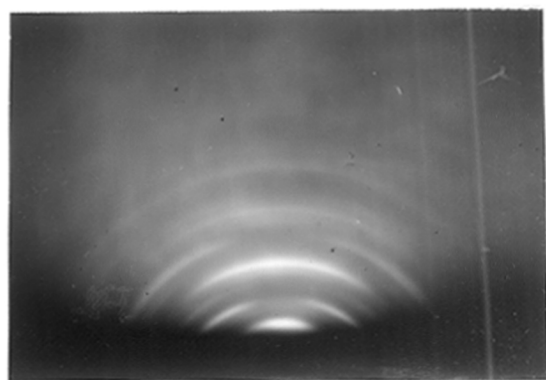


Fig. 22.

21127.

Centigrade, the TlBr adopts its rocksalt type structure only. Figure 20 shows TlBr in its rocksalt type structure and also the rocksalt substrate projections showing through and thus giving rise to a second diffraction pattern affording an excellent opportunity for measuring the interatomic distance of TlBr in its rocksalt type structure by comparison measurement.

Figure 19, which also shows secondary scattering as for similar deposits of LiF on rocksalt (001) cleavages, shows that TlBr in both rocksalt and caesium chloride type structures have exactly the same interatomic distances and by comparison with that of rocksalt, Tl - Br was found to 1.98 Angstroms, this was confirmed by Figure 20, and the result is in excellent agreement with X-ray data and thus not indicative of the formation of solid solution.

Figures 21 and 22 show deposits of TlBr on glass at room temperature and at 150° Centigrade respectively, these indicate both rocksalt and caesium chloride type structures in random polycrystalline formation with orientation in (110) planes in deposits prepared above 100° Centigrade glass substrate temperature.

6. NaCl deposits on glass.

Schulz (1949) concluded that NaCl deposits prepared on amorphous substrates were (110) orientated for deposits thicker than 100 Angstroms, and cube face (100) orientated for deposits thinner than 100 Angstroms. It was found difficult to reconcile these statements with the experimental results described in the section below.

All deposits were prepared and examined in the higher vacuum of the diffraction camera without exposure to air, the microscope slides used as substrates afforded opportunity of examination of normal and oblique incidence of the deposit atoms' path at the same time. However, there was no difference between these two types of deposition except that no orientations were visible and all obliquely deposited atoms were observed to form large crystal blocks in random polycrystalline formation. The only difficulty was loading the substrates, which were about 8 centimetres long into the specimen port, and then again, all such substrates had to be heated up very slowly before deposition to avoid breaking the glass.

Deposits prepared at glass substrate temperatures below 100° Centigrade showed random polycrystalline formation of the deposit

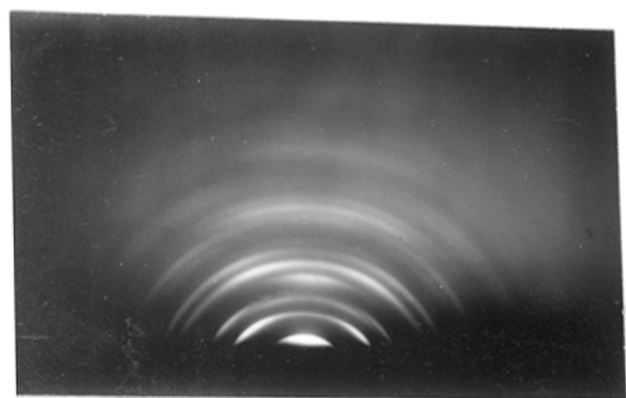


Fig. 23.

2766.

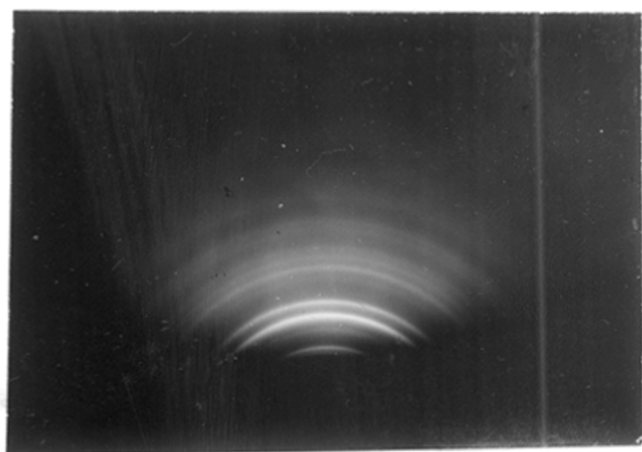


Fig. 24.

2767.

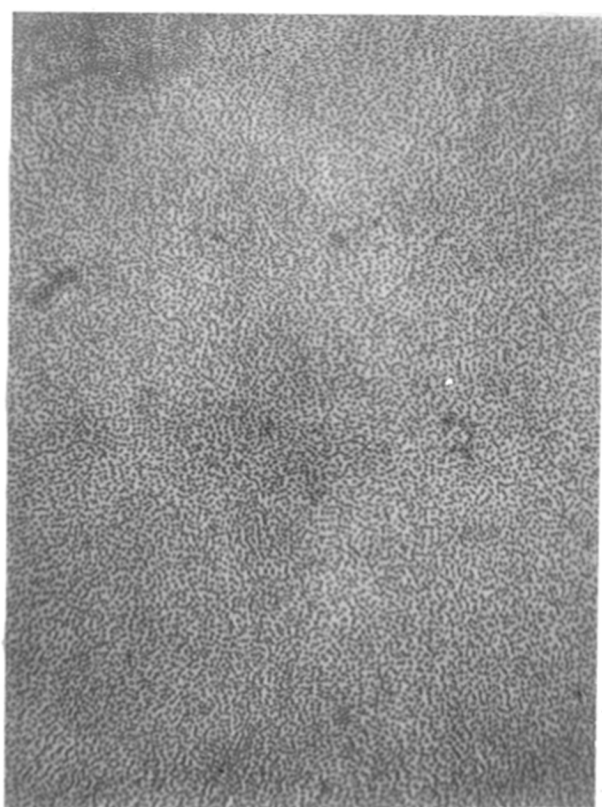


Fig. 25.

V.P.M. 314.

crystals; those prepared at substrate temperatures higher than 100° Centigrade showed cube face (100) orientation for normal incidence of the deposit atoms' path (see Figure 23), and no orientation at all for oblique incidence of the deposit atoms' path. (see Figure 24).

Both these diffraction patterns were taken off the same specimen, and a micrograph of the same specimen, Figure 25, showed the deposit crystals to be aggregated into large blocks, and also the deposit thickness to be about 1000 Angstroms, and thus in disagreement with the conclusions made by Schulz in 1949.

Breathing on the specimen whilst in the microscope caused the crystals to aggregate into larger blocks and leave quite large spaces between themselves, and an examination after this treatment in the camera gave negative results, and only a faint random polycrystalline deposit was visible.

IV. SUMMARY AND DISCUSSION.

Epitaxial misfit and mechanism of epitaxial crystal growth in ionic crystals.

Parallel growth was observed between the deposit and the substrate for all deposits prepared within suitable specific temperature ranges. As concluded in I3, this is due to the first two incident deposit atoms being endowed with sufficient energy so that they may take up positions of minimum potential energy relative to the combined field of themselves and that atomically smooth part of the substrate's interface. These two atoms then determine the final orientation of the crystals ~~for~~ which will grow from this "nuclear bud". In some cases, the degree of misfit between parallel lattice rows of the substrate and deposit was large enough to effect in addition the second type of two degree orientation of $\{001\}$ Deposit parallel to (001) NaCl; $\langle 110 \rangle$ deposit parallel to $[100]$ NaCl. This was observed in the cases of deposits prepared of LiF and TlBr onto rocksalt (001) cleavage faces.

In the present studies, the degrees of misfits between parallel lattice rows of the substrate and the deposit varied from 0 percent up to 30 percent as Table V shows. Throughout these experiments, it was noted that such misfits were alleviated according to their

degree of misfit, i. e. varying from (110) orientation and twinning for the case of deposits of NaF prepared on rocksalt (001) cleavage faces, (110) and (111) faces, to the aforementioned second type of two degree orientation in the case of deposits of LiF and TlBr prepared onto rocksalt (001) cleavage faces.

TABLE V.

Deposition.	Misfit between ^l lattice rows.	Orientation observed.	Remarks.*
NaF on NaCl.	-17.9 percent.	(100)	A.
KBr on NaCl	+16.7 percent	(100)	B.
NaBr on KCl	- 5.4 percent	(100)	C.
LiF on NaCl	-28.8 percent	(100) + (110)	D.
TlBr on NaCl	-29.5 percent.	(100) + (110)	E.

*. (100) = $\langle 100 \rangle$ deposit parallel to $[100]$ NaCl; $\{001\}$ Deposit parallel to (001) NaCl.

A. Twinning in (111) planes observed in 1 in 10 deposits.

B. Chemical reaction above 150° Centigrade, Misfit of NaBr on NaCl is 5.5 percent.

C. Chemical reaction as above. Misfit of KBr on KCl = 4.6 percent.

D. $\sqrt{2} \cdot a(\overset{\text{LiF}}{\text{TlBr}}) = a(\text{NaCl})$.

E. $\sqrt{2} \cdot a(\text{TlBr}) = a(\text{NaCl})$.

Deposits having misfits of the type $\sqrt{2} - 1$, $\sqrt{3} - 1$ etc. always have a preferred second type of orientation to the substrate crystal. LiF and TlBr are examples of two such alkali halides having a particular one of these properties.

The best method of considering the mechanism of epitaxial overgrowth of one alkali halide on another or of any ionic deposit crystals prepared on an ionic substrate is to consider the problem in terms of two mechanical models, one representing the deposit atoms and the other representing the substrate atoms. Both these will be in the form of close packed spheres each one representing a different ion and all packed in the form of the structure, i.e. simple cubic, face-centred cubic etc..

The mobility of an incident deposit ion over an atomically smooth portion of the substrate surface depends on the factors mentioned in I.3.(1), the rate of deposition, the temperature of the substrate, the position on which it first lands and the angle subtended by the substrate's surface and the incident atoms' path.

For example, let us consider a lone deposit anion landing on a general position of an atomically smooth portion of the substrate's surface. The tendency will be, if the above four factors are favourable, for this anion to take up its position over

a cation belonging to the substrate's interface, this being a position of minimum potential energy. Therefore, the partnerion, i. e. the deposit cation which would follow after the anion, will come under the influence of the combined field of the deposit anion and the surrounding ions at that part of the substrate surface and can therefore move up to a circle, radius minimum distance of approach from its partner anion, so if it too has enough mobility, it will move into the nearest potential trough to the deposit anion. By the same argument, if the next deposit anion and cation do exactly the same thing, then the growth would be orientated and thus epitaxial. If, of course, these first two atoms stick in the position on which they first land, then the growth is determined, and it is random.

It should be noted that this method of discussing epitaxial mechanism only applies to growth between ionic crystals and then only over atomically smooth locations of the substrate interface. It is simple to explain why twinning occurs by the same argument and using the same models. The degree of misfit is always the first thing to be taken into consideration when considering growth of crystals which is foreign to that of the normal parallel lattice row fitting.

Moisture and heating effects on ionic deposits on ionic substrates.

It has been observed that moisture, or more fully, the effect of atmospheric contact, and heating, are the two most important factors affecting the type of growth that ionic deposit crystals will take up on such substrates as rocksalt, sylvine etc.. It was noted that all NaF deposits prepared on rocksalt (001) cleavage faces in the external evaporator were (110) orientated, whereas those deposits prepared in the higher vacuum of the camera were not. This is almost certainly due to the fact that the deposit was prepared at a higher residual air pressure and the effect took place while the deposition was being carried out. The fact that the NaF-NaCl lattice was only observed for deposits prepared in the external evaporator also supports the fact that deposits prepared at pressures of the order of 10^{-5} millimetres pressure are liable to atmospheric effects.

Both (110) orientation and superlattice effects of NaF deposits prepared on rocksalt (001) cleavage faces were stable when the deposit was left in air for about 6 hours, and then placed back in the camera for re-examination. This infers that the effect was caused by air during deposition, and is finally backed up by the fact that when the camera suddenly developed a temporary leak after

a deposit of NaF was prepared the deposit was observed to have become disorientated from the mean, this being determined by the arcing of the diffraction spot pattern.

This effect seemed to be general for any deposit left in air for a considerable time (about 24 hours), and the moisture seemed to get rid of such things as twinning effects and cause such subsidences of the deposit crystals that the substrate ~~pro~~jections showed through the deposit and all smooth refractive effects of the deposit layer disappeared and usually two sharp spot patterns were observed, one corresponding to the substrate projections, and the other to the rough deposit crystals. This afforded excellent opportunity for measuring the lattice constants of deposits by comparison with that of rocksalt.

Breathing on a fresh deposit appeared to have the same effect as leaving it in air for 24 hours, but the deposit crystals become disorientated immediately instead of taking a whole day.

Of all the four conditions forwarded for governing oriented overgrowths in I.3, the temperature of the substrate surface is always the most important. Deposit crystals may only grow parallel to the substrate crystal within suitable specific constant temperature ranges. Effects such as twinning, directed disorientation, specific orientations and disorientations may only be observed at or within

suitable substrate temperatures. In addition certain deposits, such as LiF and TlBr prepared on rocksalt (001) cleavage faces, will only adopt their preferred orientation of 001 LiF or TlBr parallel to (001) NaCl, 100 LiF or TlBr parallel to 110 NaCl, within their suitable substrate temperature ranges.

In all experiments where possible, the deposit was heated up slowly to temperatures higher than the substrate temperature maintained during deposition, and the change in structure of the deposit crystals was observed. Usually heating to temperatures of the order of 300° Centigrade had exactly the same effect as leaving the same deposit in air for 24 hours, and the deposit crystals were observed to have become disorientated. In addition all refractive effects disappeared and the deposit crystals appeared to have "sunk" a little so that projections of the rocksalt or sylvine substrate gave rise to a second diffraction pattern and thus affording excellent opportunity for measuring the lattice dimension of the deposit by comparison with that of the rocksalt or sylvine substrate.

Exactly the same relation between structure and temperature was observed for all deposits heated at or above their substrate deposit temperatures. For example, a deposit prepared at X° Centigrade when heated up to Y° Centigrade (Y greater than X) would give the same type of deposit structure as a deposit prepared at

at a substrate temperature of Y° Centigrade.

Heating a deposit until it becomes disorientated is proof that the mobility of the deposit ions must also be in a certain range for oriented overgrowth to occur, because the growth is random if they either have too much or not enough mobility to lie in the potential troughs of the substrate interface.

Lattice Constants.

In several cases of deposits prepared in vacuum of ionic materials on rocksalt or sylvine, the deposit layer was thin enough (about 200 Angstroms) for the substrate diffraction pattern to be in evidence. Heating of a thicker deposit caused such subsidences that the substrate projections became in evidence, this being indicated by the sharp spots of the second diffraction pattern corresponding to the substrate material. Whatever the reason of the substrate pattern being in evidence, excellent opportunity was afforded of measuring the lattice constants of the various deposited halides by comparison with the lattice constants of rocksalt and sylvine. (These being taken as 5.63 Angstroms, and 6.28 Angstroms respectively.)

In this way no graphite comparisons were neither made nor were necessary. A great deal of consistency with X-ray data was observed in all calculated values of lattice constants of NaF , KBr ,

KCl, NaBr, LiF and TlBr. This indicates that effectively no solid solution between any deposit halide and its substrate were formed. A little formation of solid solution would have no noticeable effect on such measurements as they are subject to errors up to about 5 percent. It was very strange that there was never any indication of the formation of solid solution for deposits of NaF prepared on rocksalt cleavage, (110) and (111) faces, as this would explain the formation of the NaF - NaCl superlattice more easily.

Observations on changes in diffraction patterns during deposition and heating.

Simultaneous deposition and examination all carried out in the electron diffraction camera is a relatively new aspect in the field of electron diffraction. It was decided that all deposits be prepared in the higher vacuum of the camera after certain complications were observed of deposits of NaF prepared on rocksalt (001) cleavage faces. All the alkali halides and the thallium halides are very soluble in water and therefore it is recommended that all such deposits of halides be carried out at as low residual air pressures as possible.

An example that can be used to represent all cases may be taken as a deposit of NaCl prepared on a rocksalt (001) cleavage

face at a substrate temperature of 100° Centigrade and then being slowly heated up to 190° Centigrade.

The substrate pattern does not change when it is heated up to 100° Centigrade, this is a property common to all substrates no matter what temperature they are heated up to prior to deposition. The pattern corresponding to the substrate crystal is one composed of very sharp Kikuchi bands and sharp streaky spots in the zero order Laue zone; this indicates a very smooth crystal but with a few projections on it giving rise to the observed spots in the diffraction pattern. In nearly all deposits prepared, a plate of the substrate's diffraction pattern was taken to indicate the type of surface on which deposition was taking place.

As soon as the depositor filament was switched on, a film was temporarily drawn over the diffraction pattern, it lasted for about 2 seconds for slow rates of deposition and was almost instantaneous in its appearance and disappearance for faster and rapid rates of deposition. This "film" is presumably due to the ions of the deposit sliding about over the substrate's surface before becoming stable or an effect due to the depositor filament causing an unstable behaviour of the deposit ions. However, as the effect was only temporary and seemed to have no other effect on the crystal

in its final growth, it was ignored although it must be a property common to all deposits such as were prepared in the present studies. When the film disappears, a diffraction spot pattern was again observed, but this time it corresponds to the deposit crystals. No Kikuchi bands were observed and the spots were elongated into thick intense lines perpendicular to the shadow edge; this indicates that the deposit crystals are in the form of large crystal blocks.

Heating up slowly causes these lines to become less and less intense until the spots appear as single spots only and Kikuchi bands are observed, but this time they correspond to the deposit crystals. This infers that the larger crystal blocks have joined together and become much smoother; usually for deposits other than NaCl prepared on rocksalt, the deposit subsides a little so that the projections of the substrate crystal are observed as a second diffraction pattern.

Further heating causes the deposit crystals to become disorientated from the mean, this was indicated by the arcing of the spot pattern from the main positions. Heating up all deposits to about 300° Centigrade completes this disorientation, and the deposit was observed to be random polycrystalline.

NaF-NaCl Superlattice and directed disorientation of NaF deposits prepared on rock salt (001) cleavage faces, (110) and (111) faces.

The NaF-NaCl superlattice unit cell was the most important discovery made in the present studies. The superlattice unit cell was 9.24 Angstroms, which is exactly twice the unit cell dimensions of NaF (4.62 Angstroms). A possible configuration of the ions of Na, F and Cl inside this superlattice was suggested which gave values of the structure amplitude corresponding with the observed intensities.

The structure amplitude for the $hk0$ and $kh0$ diffractions corresponding to this suggested unit cell is:-

$$S = \left\{ \begin{aligned} & (2Na + Cl + F) \cdot \cos \frac{\pi}{4} (3h + 3k) \cdot \cos \frac{\pi}{4} (h - k) \\ & + 2(Na + F) \cdot \cos \frac{\pi}{2} (h + k) \\ & + 2(Na + Cl) \cdot \cos \pi (h + k) \end{aligned} \right\} \cdot 4 \cdot \cos \frac{\pi}{2} h \cdot \cos \frac{\pi}{2} k$$

The superlattice was presumably due to the effect of deposition carried out at higher pressures of the external evaporator or perhaps may be due to an instantaneous effect of the moisture in the air whilst transferring to the camera for examination.

Attempts were made to reproduce the superlattice by both preparing a solution and a melt of NaF and NaCl used together in

molecular proportions but these were unsuccessful and only produced diffraction patterns corresponding to mainly NaCl with a little faint NaF both in random polycrystalline formation.

The superlattice was only observed in deposits prepared in the external evaporator at substrate deposit temperatures varying between 150° Centigrade and 200° Centigrade but deposits of NaF prepared within these temperatures only gave the superlattice by causes other than those within control.

Examples of what were concluded to be directed disorientation caused by a lamellar slip about the normal to the (111) planes were observed of deposits of NaF prepared on all faces of rocksalt at substrate temperatures about 95° Centigrade and very low rates of deposition. It was only observed in very thin deposits about 100 Angstroms thick as the effect is confined to the atomic layers near to the interface and would therefore be hidden by thicker deposits.

Directed disorientation was observed by arcing of the diffraction spots in some azimuths and not in others, and the beam azimuth in which the spots are observed to arc determine the planes about which the lamellar rotational slip had occurred. (or more fully about the normal to these planes)

KBr deposits on rocksalt (001) cleavage faces, and NaBr deposits on sylvine (001) cleavage faces.

These two sets of experiments were undertaken together as the chemical reactions:-



occurs above substrate temperatures of 150° Centigrade or when a deposit prepared below this temperature is heated to or above this temperature. In some cases, all four halides were observed to be equally prominent in diffraction patterns, this not only proves the above chemical reaction took place but affords excellent opportunity for measuring the interatomic distances of three of the halides by relative comparison to the fourth halide.

The mechanism of the reaction is very complex as both the mobility and the migration of all the four ions Na, K, Br and Cl over and into the whole surface have to be considered.

It was also concluded by the halide observed to be the most prominent in diffraction patterns that as far as the above chemical reaction is concerned the substrate always reacted as being in excess and usually caused the two alkali halides on the other side of the reaction to become prominent providing the temperature was raised higher than about 190° Centigrade.

NaCl deposits(twinned in (111) planes) prepared on rocksalt cleavages.

Twinning of NaCl deposits prepared on rocksalt cleavage faces (and KCl prepared on sylvine cleavages) was one of the most important things discovered in the present studies. NaCl deposits on rocksalt and KCl deposits on sylvine do not actually come under the definition of epitaxial crystal growth but may be considered equally with all other deposits. So the twinning of NaCl is not due to an epitaxial misfit or any of the usual causes.

NaCl deposits prepared at, or above 195° Centigrade substrate temperature, or deposits heated to, or above this temperature, were observed to twin on (111) planes. This twinning remained when the specimen cooled down and when the deposit was heated up until the deposit crystals become disorientated. It is important to note that it was due to a temperature effect on the deposit as the substrate when heated alone to, or above 195° Centigrade showed no sign of twinning at all.

A suggested cause of this twinning is that since the rocksalt substrate was composed of step-like formations, then the electric furnace may have caused uneven heating at the interface and thus give rise to mechanical strains which were favourable to twinning effects.

TlBr abnormal structures on rocksalt cleavage faces and on glass.

Experimental results proved how difficult it was to reconcile statements made by Schulz (1950). TlBr is known to possess a caesium chloride type structure, but whether it was due to the method of preparing this halide or to some experimental errors, TlBr was never observed to possess a caesium chloride type structure by itself. In the case of deposits prepared on rocksalt (001) cleavage faces above a substrate temperature of 125° Centigrade, TlBr was observed to possess a rocksalt type structure. The same relation was observed between structure and temperature for an initially random room temperature deposit heated up to, or above this temperature.

In all other cases, both of deposits prepared on glass at any temperature and on rocksalt below a substrate temperature of 125° Centigrade, the TlBr was observed to possess both its normal caesium chloride type structure and its abnormal rocksalt type structure. A preferred orientation was taken up, viz. LiF deposits prepared on rocksalt cleavage faces, and moreover secondary scattering was also observed.

Values of lattice constants of the TlBr in both these type structures was observed to be the same and in agreement with X-ray data and infers that effectively no solid solutions were formed.

NaCl deposits prepared on glass.

It was again found difficult to reconcile Schulz's (1949) statement that NaCl deposits on amorphous substrates were (100) orientated for deposits thicker than 100 Angstroms, and were (110) orientated for deposits thinner than 100 Angstroms.

A deposit of NaCl prepared on glass at 100° Centigrade showed cube face (100) orientation, and a micrograph of the same specimen showed that the deposit was at least 1000 Angstroms thick in places.

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