ON THE STRUCTURE OF TREATED SURFACES OF ROCK SALT

(COMPARATIVE SURFACE EXAMINATION BY ELECTRON DIFFRACTION AND ELECTRON MICROSCOPE)

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(From German)

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1.   INTRODUCTION

It is known that a ground or polished surface of rock salt is more strongly hygroscopic than a cleavage surface of rock salt which, as experience shows, seldom becomes filmed over in open air.   Since crystals of rock salt have a practical importance on account of their infra-red properties and have to be ground and polished for the preparation of prism faces and the curved surfaces of lenses, it becomes necessary to treat these worked surfaces, i.e. to restore the hygroscopic resistance of a cleavage surface at least.   The firm of C.A. Steinheil Söhne employs two processes for treating rock salt, one by water and the other (more important) by heat.   To study the change in surface structure brought about by the treatment, the surfaces were examined before and afterwards by means of electron diffraction and the electron microscope and, most important, a comparison was made between the crystallisation state and roughness[*]. This demonstrated very clearly the efficacy and mutual complementing of the two methods, in the solution of surface problems.

2.   TREATMENT PROCESSES

Various cleavages of rock salt were taken as starting surfaces: cleavage planes (100), (110) and (111) and the (210) plane, i.e. planes cut at $26° 34'$ to a cube edge and finally faces of rock salt ground at $10°$ to a cube edge.   These were polished with chromium oxide on silk soaked in alcohol until they were of outstanding optical brightness.   When stored in the air they became dull and opaque in the majority of cases.

(a)   Water treatment of the surfaces — After being kept for about 15 minutes in air saturated with water vapour, when the surface dissolved, the polished surfaces were brought back into normal air.   The cube face which has been treated with water becomes to some extent smooth and transparent by this treatment, with a hygroscopic resistance similar to that of a cleavage face. On the other hand other surfaces, such as (110), (111) or (210), become dull as do also curved surfaces obtained by grinding.   Since water treatment gives reasonably good results with cleavage surfaces only, it is not practicable generally.

(b)   Heat treatment of the surfaces — The polished surface is kept for several hours in an ordinary furnace at a temperature of about $500°C$.   Quite independently of the orientation of the initial surfaces, that is to say even with a curved surface, a mirror-smooth, optically perfect surface is produced, which is no more hygroscopic than a cleavage face, thus showing that treatment by heat is practicable.

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[*]   Some of the findings reproduced here were reported in the Reichsberichten für Physik No. 5 (1945), p.159.

3. EXAMINATION OF THE SURFACE STRUCTURE

(a) EXAMINATION BY ELECTRON DIFFRACTION

The polished and treated surfaces were first studied by means of electron diffraction. A finely stopped-down electron beam, which had passed through a potential drop of about 40 KV ($\approx$ 0.6 Å), met the surfaces of rock salt under test at a grazing angle of some hundredths, the area of the surface was approximately 5 x 5 mm². The interference rays were photographed at a distance of about 30 cm from the crystal. To prevent complications, due to the insulating rock salt face becoming charged by the electron beam, and so distorting the diffraction pattern, the intensity of the electron beam was kept sufficiently low.

It would be superfluous to go into details about the diffraction apparatus since it is essentially the same as present day instruments: fast electrons generated in a hot cathode tube; electron beam from a hairpin cathode focussed by a biassed Wehnelt cylinder (C -50 volt), similarly to the cathode of the electron microscope[*]; stopping down of the beam by means of two fine stops (0.05 mm). The stop nearest the object can be pushed to one side, so that in the event of interruptions or cathode changing, the best concentration of beam intensity can be obtained, depending on the biassing and the position of the adjustable cathode. This proved to be a very efficient arrangement[**].

A noteworthy feature is the construction of the specimen holder. Figure 1a illustrates the construction. The object which is to be studied by means of grazing electron irradiation is fixed to the holder T. This can be rotated about its own axis (ball bearings), can be swivelled so as to vary the angle of incidence of the electron beam on the object, and can be modified in height. The height is regulated by means of the screw S_H, the spindle W being lowered by the vacuum-sealed control S, or raised by the spring F[†]. The space above the seal is filled with oil and closed by a cover D. The groove R contains apiezone wax for sealing the vacuum seal. The holder H is carried up and down on two pins Ft. When W rotates it also moves the metal disc M which is situated in the transverse slit L and this rotates the carrier T by means of a flexible steel wire D. This proved an efficient mechanism for obtaining a small swivelling movement of the carrier round the axle A, without causing the carrier to be brought back to its starting position. The rotation is effected by a second vacuum-sealed spindle, also attached to P but not shown in Figure 1a. By means of the plate P, which is vacuum-sealed to the tube K of the apparatus, with a rubber washer or apiezone wax, the specimen-carrier can be taken out complete. In order to study objects by radiation transmission, appropriate foil carriers are screwed on to T. As it is generally more desirable to move the foil in a direction perpendicular to the beam, instead of rotating it, a slide to carry the foil can be fixed on and this, working in conjunction with a disc attached eccentrically to T, converts the rotation of the spindle W into a moving of the slide. In addition to the two vacuum-sealed spindles already described, a Schott glass lead-in[ø] (SD in Figure 1b) is soldered on to P. This contains an insulated metal tube which can take, for example, the lead to a thermo-element.

Beneath the carrier T is a vaporization device, not utilized in this case, which it is possible to construct very simply with a vacuum seal and Schott glass lead-in: a steel tube R is led through the camera wall K by means of a vacuum seal S (D cover of the vacuum-seal, as in Figure 1a) and forms one lead Z_1 to the molybdenum strip M or tungsten wire, the other lead Z_2 being conducted through the middle of the steel tube through a lead-in of Schott glass, SD. The steel tube is kept at a low temperature from outside by a water cooling system (not shown).

The photographic plates required (6 x 6 cm Agfa electron plate) are stored - up to 12 in number - in vacuum and moved into and out of the path of the beam by means of an appropriate mechanism. The constructional details vary in the different diffraction cameras designed in the Institute, but further details will not be given here.

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[*]   Cf. for example B.M.v. Ardenne, Electronen-Übermikroskopie, Berlin 1940, p. 130.

[**]   Cf. H. Raether, Zschr. f. techn. Physik, 23, 266, 1942; and J. Beck, Physikal. Zschr. 40: 474, 1939; H. Geissmann loc. cit. 44, 268, 1943.

[†]   In Figure 1a there is shown only one spring F and one guide pin Ft[″]

[ø]   See F. Blumenstein, E u. M 59, 346, 1941.

The following is a brief explanation of the diffraction patterns: If a single-crystal surface is examined, e.g. a cleavage surface of rock salt, the result is what is known as a "single-crystal figure". This is characterized by the appearance of single interference spots, which form a cross lattice in certain directions, known as rational azimuths. From the disposition of the spots, whether, for example, they form a quadratic or rectangular pattern the crystal orientation can be determined. In addition to the diffraction spots, it is possible, with a good single crystal, to observe a system of intersecting "Kikuchi lines". Since these lines migrate with rotation of the crystal, their sharpness of definition is an indication of the quality of the crystal, i.e. whether the surface consists of one crystal or many small crystals. If, on the other hand, the photographic plate shows a system of concentric semi-circles, known as a powder diagram (only half the rings appear, the other half being covered by the crystal), it can be concluded that the surface of the test crystal is formed of a conglomeration of small crystals without any order. If there is a certain amount of order, i.e. mutual alignment, in the surface, there is not an even distribution of intensity in the rings, but it is concentrated in definite sectors ("fibrous structure" or "texture"). The electron beam irradiates the edges and points projecting from the surface and selects the crystal-lattice planes most susceptible of reflection. With high definition of the rings (width of ring equal in measurement to the diameter of the beam - which is mostly stopped down to 0.05 mm) the irradiated crystal projection in the given case amounts to at least 50 Å. Thus the surface is, electron-optically considered, very rough: as the roughness decreases the diffraction becomes less sharply defined because the height of the irradiated projection becomes less (reduced resolving capacity). It is also possible to make some statement about the roughness of the surface in the above case of a single crystal figure: when the electron beam enters a crystal it undergoes refraction. Owing to the smallness of the refractive index - its value for electrons of 40 KV is some 10^{-4} over one - this effect does not become noticeable until the limiting surface is formed from the reflecting lattice planes, as, for example in the cleavage surfaces of crystals. It is shown by the fact that with small angles the diffraction spots are transposed towards the primary beam (pure reflection figure)[*]. On the other hand, if the surface of the single crystal is not even but consists of steps, graduations, and blocks, which are irradiated, the interference points are not then transposed (pure transmission radiation figure). An evaluation of the types of diffraction patterns just described will be made later.

(b)   METHOD OF INVESTIGATING WITH THE ELECTRON MICROSCOPE

While an evaluation of the diffraction pattern chiefly yields information regarding the situation and size of the crystal, observation with the electron microscope is most likely to give the answer to the problem of the geometry of the boundary surface. There are two methods for obtaining this where the surface is massive: the reflection process and the replica process. With the reflection method[**] the same arrangement is used as in the reflection process for diffraction: the electron beam strikes the test surface at a grazing angle of about 4°. However, it is not the diffraction rays themselves which are observed, but a picture of the surface which is formed by means of an electronic lens. Due to the high degree of resolution, a large part of the surface, about 10^5 Å, appears in sharp definition at the same time. A white surface can then be noticed on the image, produced by the electrons scattered from the uppermost layers to a depth of about 10 Å. The points projecting from the surface, being permeable to electrons at the uppermost ends only, throw long shadows because of the grazing radiation and these give an indication of the roughness of the surface. The resolving power is sufficient to pick out projections to a height of about 125 Å. As opposed to this, the replica process[7] consists of the study of an impression of the surface by means of the electron microscope. For this purpose a thin metallic film (or plastic film) is applied to the surface under investigation and then separated from the crystal surface by suitable means. In the case of rock salt the crystal is put into water and the film comes off in a short time. This film containing an impression of the surface is examined in the transmission-type microscope, showing contrasts which correspond to the roughness. In order to accentuate these contrasts the

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*   Cf. the discussion in W. Kranert, K.H. Leise and H. Raether, Zschr. f. Phys., 122, 248, 1944.

**   B.v. Borries, Zschr. f. Phys., 116, 370, 1940.

7   H. Mahl, Naturwiss. 30, 207, 1942.

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surface is not located at right angles to the direction of the evaporating metal when the replica is being made, but at an angle generally of about 45°. Given the angle of vaporization, the height of the projection can be calculated from the length of the shadows; the diffraction method in general gives little information in this respect because, owing to their grazing incidence, the electrons only touch the highest points of the surface. The resolving power of the replica method can be estimated from the photographs to be about 100 $\overset{o}{A}$* .

In the present case of the investigation of rock salt the replica method is obviously the best because it is necessary to guard against charging, which would result from the high radiation intensity required in the reflection process. (Unless the metallic replica is studied by reflection: see Section (c)). In every case the material used for the replicas was aluminium which is easily vapourized and it was deposited at an angle of not more than 30° to the surface. Observation and photographic recording was carried out in the magnetic Siemens-electron microscope by RUSKA and v. BORRES in the electron-microscopy laboratory of Siemens and Halske A.G. Some of the photographs, shown in Figures 2c, 5b, 8b, were kindly made for me by Dr. H. MAHL in the electrostatic AEG electron microscope by MAHL in the AEG Research Institute** .

(c)   EXAMINATION OF THE REPLICA BY ELECTRON DIFFRACTION

This " diffraction-replica method" is specially important when the smoothness of an insulating surface which gives a picture without contrasts has to be determined with the electron microscope (impression method), that is to say it shows an electron-microscopically smooth surface. In such cases it is necessary, therefore, to make use of diffraction to determine the surface roughness. If it is particularly desired to find out whether the surface has the same degree of smoothness as a crystal lattice plane, this can be done by noticing the displacement of the reflections towards smaller angles as a result of refraction (see above). With an insulator such as rock salt, however, the surface charging involves some degree of uncertainty with regard to the reality of this displacement and this can only be eliminated by all kinds of precautionary measures. In such cases, the possibility of confirmation by studying the replica by diffraction is very welcome. The idea is as follows: If a cleavage surface of rock salt, heated to about 200°C, is coated with a metal, in this case silver, the silver lattice grows on to the rock salt lattice and hence forms a silver layer similar to a single-crystal††. If, then, electrons are reflected at a grazing angle, from the underside of the replica, the reflection should show some displacement due to refraction, if the original surface had the smoothness of a lattice plane and the impression has not been distorted in the removal process. The difficult process of removing the foil without creasing it, turning it over, and fixing it on to the specimen holder without wrinkling was solved, after many preliminary trials, as follows^{ø}: The silver film, still adhering to the rock salt is cemented to a smooth metal support. The crystal of rock salt can then be separated by immersion in water. The edges of the separated foil are now bent round the support to prevent transmission of radiation and, at the same time, make it possible to conduct electricity away from the layer. The photographs reproduced in the results (Figures 13-16) show that this method yields good results, although a slight deformation of the replica during the separation process cannot be avoided.

4.   RESULTS

(a)   POLISHED SURFACES

As can be seen from Figures 2a, b; 5a; 8a; 10a, the diffraction patterns of polished rock salt surfaces are powder diagrams with well defined texture, i.e. the small diffracting crystals are not distributed irregularly but show a considerable alignment with respect to each other. Thus, if the crystal is rotated on itself, the beam direction changes and the fibrous structure changes, as shown in Figures 2a, b [(110 surface]. An exception to this is the cleavage face (100) which retains the

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*   Cf. the general discussion in H. Raether, Optik I, 69, 1946.

**   See also H. Mahl and H. Raether, Reichsberichte f. Physik, No. 5, 1945, p.166.

†† H. Lassen, Physikal. Zschr. 35, 172, 1934.

^{ø} These experiments were conducted by W. Kranert in the Physical Institute of Jena University and Figures 13-16 were obtained.

same fibrous structure (Figure 5a) for every beam azimuth, as has already been described by the author[*] . In contrast to the metals the sharpness of definition of the rings does not become less, even with fairly long intervals of operation, i.e. the crystal dimensions do not fall below a certain size, which is approximately 50 Å. Evaluation of the diagrams shows that the small surface crystals (apart from the (100) surface) have the same orientation as in the parent crystal. When a rock salt surface is polished then, the "polish dust" is removed and the parent crystal exposed. The surface is broken up during working into many small crystals which fluctuate, even with the best polishing, by angles up to 10° from the single crystal position and in the case of the (100) surface by about 25°. The small crystals into which the surface is broken up are probably small cubes, corresponding to the cleavability, as in (100). This supposition is confirmed by electron-microscopical observation of the replicas of the polished surfaces. Figures 2c and 8b show clearly a structure which points to the fact that crystals bordering on the (100) surface are torn out of the surface, thus creating a structural roughness, characteristic of the cut surface. At certain individual spots this is made evident by the fracture edges on the polished (100) faces (Figure 5b) and also by the indentations shaped like three-sided pyramids, i.e. cubes standing on one corner, in the polished (111) face (Figure 8b). The same impression is given by the roof structure of the polished (110) face (Figure 2c), indicating cube-crystals inclined at an angle of less than 45° to the surface, and by the broken edges of the polished (210) faces (Figure 10b).

The above-mentioned independence of the diffraction pattern for the polished (100) face with respect to the direction of radiation can now be understood, in that the cube-crystals - which in the other faces are inclined to the surface and so are held firmly from underneath during the process of working - can in this case, where the surface is the cleavage plane, be turned with regard to each other on the (100) lower side, either singly or as whole areas, thus giving the same texture in every azimuth. A pre-condition, in the case of the surface structures discussed here, is that the working process must be carried out by circular movements of the crystal on the silk support. If, instead of this, the crystal is rubbed back and forth in straight lines a one-sided tilt appears in the small crystals of the surface, especially in the (100) and (210) surfaces as can be seen clearly in the diffraction pattern. This matter is dealt with more fully in Reichsberichten für Physik No. 5 (1945), p.159.

The structure of the polished faces is very sensitive to damp. Touching with the fingers or breathing on them gives them an appearance very similar to water corroded surfaces. Thus, from Figure 5b, breathing produces a surface which is very similar to that shown in Figure 7.

If replicas of polished faces are studied by electron diffraction, by the method given above under (c) it is found that the diffraction patterns, as can be seen from Figure 13, reveal the same structure as was obtained with the original surface (Figure 2a); they also show the same relation between azimuth and texture. What is remarkable here is that at times small silver crystals grow on the many individual cubes of rock salt in the polished surface; consequently the under-side of the replica becomes a faithful reproduction of the original face, not only in its roughness, but also in its crystal structure.

(b)   WATER-TREATED FACES

The diffraction patterns (Figures 9a, b) are single-crystal patterns with poorly defined Kikuchi lines, the reflections of which - apart from the (100) face - originate in transmission radiation, since no displacement of diffraction can be noticed as the result of refraction. They exhibit the same cross lattices as the polished faces at various azimuths (cf. Figure 8a with 9a), but the diffraction patches have contracted until they are only round spots. The Kikuchi lines are less sharply defined than those observed on cleavage faces. The surface has therefore re-crystallised, there is a great reduction in the variation of the small crystals with respect to the polished face, although this does not equal, for example, the uniformity of a cleavage face. Electron-microscopic examination reveals considerable roughening of the water-treated faces; the boundaries of the roughness are formed by (100) surfaces, as shown by the roof structure of the (110) (Figures 3a, b) and (210) faces (Figure 12) and the pyramids on the (111) faces (Figures 9c, d). The process of solution at the surface therefore has the effect of perfecting the crystal;

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[*]   Zschr. f. Phys. 86, 96, 1933.

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but the surface is not formed by the crystal lattice planes parallel to it, but by (100) planes
which delimit an almost undisturbed single-crystal surface.   For this reason water-treated surfaces
are dull and opaque[*].   An exception to this is the (100) surface.   Its diffraction pattern
indicatee a shift of the reflections towards small angles owing to refraction which leads to the
conclusion that the surface is unusually even.   From the finding given above this is evident:
a (100) face which has been treated for a short time is reproduced in Figure 7.   When sufficient
treatment has been carried out the cube faces which are visible there become so extended that
refraction appears in the diffraction pattern, as in the case of a cleavage face, and the electron-
microscopic image losses all contrast, as in Figure 6b.   Another consequence is the optical
smoothness of a water-treated (100) face.

Study of electron-microscopic pictures (Figure 9c) shows that, apart from the (100) faces,
there are also octahedral faces which appear as boundaries.   Since the (100) face represents the
equilibrium face, by reason of the considerations of growth, the appearance of the (111) face
cannot be explained[**].   There is a specially noteworthy feature regarding the (210) surface:
as a consequence of the position of the cutting surface, cubes project at an angle of $26°$ to the
(210) face, and these bring about a stepped structure of the surface.   Owing to the asymmetry of
the roughness it is possible, when producing replicas to use various directions of vaporisation
(cf. Figure 11), which are shown in the photographs 12a, b, c.   In (a) (direction 1) a great deal
of metal (aluminium) has been deposited on the steep, short edges and hence the absorption of
electrons is heavy at that point and the edges are dark by comparison with the cube edges which
are at a gentler slope and have less deposit.   On the other hand, when direction 2 is used, very
little metal can be deposited on the edges, so that these have a bright appearance, giving a less
plastic effect to the picture (12b).   In this case the mechanical coherence of the replica is
often very poor, making the production of a replica difficult.   In Figure 12c the surface was
coated in direction 3, as can be observed from the dark edges and bright shadows.   The replica
shows that in direction 3 also, i.e. in the direction of the cube side, the face is stepped, even
though irregularly.   Diffraction photographs in this direction are therefore, as has also been
observed, at the same time transmission radiation photographs.   It is also worthy of note that
the bright and the black shadows are bounded by parallel lines and are not wedge-shaped
(angle $26°$).   The cubes rest on cube faces and the cut face is only an imaginary plane.   If the
under side of the replica is examined with electron diffraction (process c), the same type of
diffraction pattern will be found here, as for the original surface.   This is shown by a comparison
of the diffraction photographs (Figures 9b with 14).   Instead of examining the under side of the
replica by diffraction it is possible - since the danger of surface charging is removed, by the
use of the metal sheet - to study it in the reflecting electron microscope.   Observation of, for
instance, the under side of the replica of the (110) surface (Figure 3c) shows the same roof
structure as the transmission radiation photographs of the replica (cf. Figures 3c with Figure 3a)[†].

(c)   HEAT-TREATED SURFACES

   (α)   Examination with electron diffraction and the electron-microscope:

Diffraction patterns of heat-treated rock salt surfaces give single-crystal pictures
with sharply defined Kikuchi lines, and sometimes Kikuchi bands (Figures 4, 6a), so that,
for example, a heat-treated (100) surface cannot be distinguished from a cleavage surface
(Figure 6a).   Thus recrystallisation is better than that of a water-treated surface.

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[*]   The fact that the polished surfaces (excepting the (100) face) become dull when stored in
      the air is thus connected with the fact that this constitutes a "water treatment" for them.

[**]   H. Morgenstern, Zschr. f. Kristallographie, A 100, 221, 1938, when observing the growth
      of rock salt spheres in an aqueous solution, also noticed the formation of (111) boundaries.
      This reappears, however, not only in the macroscopic, but, from the above observations,
      also in the electron-microscopic region.   It is not possible, for reasons of stability,
      to have a surface boundary of a (111) lattice plane; it is more likely that Stranski's
      idea of an imperfect lattice plane applies. (see p. 9).

[†]   It must also be pointed out that no "irrational" reflections were found on the interference
      photographs of water-treated faces, as L. Brück and W. Cochrane had observed on layers
      deposited by evaporation and electrolytically, and which were explained by M. v. Laue by
      means of the crystal form factor.   It is clear that the limiting (100) faces in the
      present case are too extended to cause any noticeable development of points;   cf. also
      M. v. Laue, Materiewellen und ihre Interferenzen, Leipzig, 1944.

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It is an interesting question whether the heat treated (110), (111) and (210) faces, when compared with the corresponding water-treated surfaces, merely have less roughness or whether they are bounded by atomically smooth faces, i.e. crystal lattice planes. Observation with the electron microscope of all replicas, including the under side (Figure 6c) shows a picture lacking in contrast (Figure 6b). In view of what has been said above, however, owing to the low resolving power, the height of the largest irregularities can still be as much as 100 Å, so that observations made with the electron microscope cannot help to solve this question. The diffraction patterns must also be studied before a conclusion can be drawn; in particular it must be decided whether the reflections are displaced towards smaller grazing angles in consequence of refraction. Evaluation showed that in a large number of the photographs the diffraction patches were displaced in the direction of the primary spot. There is the complication that charging of the insulating rock salt faces may lead to distortion of the diffraction pattern and transposition of the reflection and this may give the misleading impression of a refraction effect. It was, however, possible to prove* that distortion of the diffraction pattern plays no part and that the displacement of reflection which is observed is attributable to refraction effect. Table 1 gives as an example a series of measurements:

TABLE 1. DISTANCES (a) OF THE (600) AND (400) REFLECTIONS FROM THE PRIMARY SPOT

$a_{(600)}$:	18.4 mm	$a_{(400)}$:	9.5 mm
	18.0		10.4
	18.2		10.0
	18.8		9.8
	18.0		10.5
Mean:	18.3 mm		10.0 mm
a_0:	21.0 mm		14.0 mm
V:	10.5 volts		11.5 volts

a_0 is the distance obtained from the horizontal distance of the reflections and is unaffected by the internal potential. The internal potential V is calculated, from the equation

$$V = \frac{150\,n^2}{4\,d^2} \left[1 - \left(\frac{a}{a_0} \right)^2 \right]$$

from the difference in the values a and a_0**. Similar results are obtained with heat treated (110), (111) and (210) surfaces. The fact that the displacement could not be measured decisively in every case was obviously due to the inadequate smoothing of projections, caused by insufficient preparation or excessively rough starting faces. In some cases even the electron-microscopical replicas of heat-treated faces showed irregularities at various points, which conforms with what has just been said.

    Comment on the temperature-dependence of the surface smoothness: Since the results of heat treatment are very dependent upon the temperature employed, Herr W. KRANERT of the Jena Physical Institute, made several series of tests to study the relation between the surface structure of the rock salt faces and the temperature of the heat treatment, using electron diffraction and the optical microscope. The temperature of the rock salt crystals, which were heated in an electrically heated furnace, was measured by means of a thermo-element. When heat treated for a period of 3 hours at 200°C, there was scarcely any change in the diffraction pattern of the initial polished surface, while at 400°C, apart from the fibrous structure, a single-crystal diagram was observed. In the recrystallisation of the rock salt surface, there is not the usual transition of the fibrous structure, through gradual contraction of the segments in the diffraction rings, to a single crystal diagram, which in this case develops first at a few points of the parent crystal and finally reaches the surface. At 450° poorly defined Kikuchi lines are obtained and these reach their maximum attainable sharpness at 500°C, after the same period of heat treatment,

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*   Cf. Reichsberichten für Physik No. 5 (1945), p.159.

**   H. Raether, Zschr. f. Phys. 78, 532, 1932.

viz. three hours. These results are almost independent of which crystal planes are involved.

When the temperature exceeded 500°C various forms of roughening of the planes appeared. The cause was mostly atmospheric moisture which, with falling temperature, for example fluctuation in the heating of the furnace, gives rise to water-etching; this was apparent even with the optical microscope, from the characteristic surface structure. When this disturbing factor is eliminated, by previous heating of the furnace to dry it, and efficient ventilation during the process, it is still possible to employ even higher temperatures, as is shown in tests up to 700°C.

The recrystallisation process is correspondingly faster, although of course there are frequently surfaces which cannot be used: sometimes it seems that some residue from the polishing materials remains on the side faces, causing a green coating $(Cr_2O_3?)$, sometimes roughening appears, probably as the result of stray inclusions. In any case the character of the roughening is different from that described above. Hence, the most favourable temperature for smoothing lies between 450° - 500°C.

(β) Application of the diffraction replica process to the study of heat-treated faces:

As a check on the smoothing effect of the heat treatment, the under sides of replicas of heat-treated surfaces were examined with electron diffraction (process [C]). Since the evenness of the cleavage face is known the replica of this surface was studied first and Figure 15 was obtained. Here it is not possible to recognize either the Kikuchi lines or the reflections in the form obtained from the surfaces themselves (cf. e.g. Figure 6a). The strong unilateral lengthening of the non-displaced reflections towards the smaller angles, already discovered by electron diffraction of electrolytically polished metallic surfaces and then recognized as the consequence of a slightly undulating surface[*], appears in this case also and points to the partial operation of refraction as a result of a specially even surface. In the present case, however, the explanation of lengthened reflection by an undulating surface is less obvious, because the lattice planes of the metallic crystal (silver) grow on to the lattice planes of the rock salt, so that the boundaries of the surface lie parallel to the reflecting lattice planes. It is more probable that the vapour-deposited layer is built up, not of one coherent single-crystal, but of many well-aligned single-crystal grains, so that the electron beam irradiates a large number of single crystals which get tilted with respect to each other during the removal process, as indicated by the lack of Kikuchi lines. Thus, the underside of the replica would look somewhat like Figure 17, which shows the tilting in an exaggerated manner. The explanation of the form of the reflection is then somewhat as follows: The main component of the intensity originates in transmission radiation and is therefore not displaced (beam path 1). A smaller part of the electron beam penetrates the smooth, former contact surface of the rock salt and is refracted. However, the crystal faces are on the whole too small to permit the penetrating beam to pass in and out at the same face, consequently the normal reflection with refraction (true reflection) will be weak in intensity. More often the beam path will be (2) which leads to partially-displaced diffraction patterns. If the crystals become slightly tilted, a continuous and unilateral reflection-broadening will take place, allowance being made for a certain reflection width (excitation error). A tilt of about ± 1° is sufficient to explain the form of reflection observed and at the same time leads to such broadening of the Kikuchi lines that they disappear in the background. The removal of the replica, even when performed with special care, brings about some deformation even with the thick layers used in this case, and of course inevitably in the more usual, thinner layers; this is not noticeable with electron-microscopic investigation but only becomes apparent when the present diffraction method is used, which is very sensitive due to the effect of refraction[**].

Actually it is not necessary to know the origin of the diffraction patterns in Figure 15 before drawing a conclusion about the smoothness of treated surfaces, all that is needed is a comparison of the diffraction patterns of the replicas of heat-treated surfaces with those of the cleavage face. Figure 16 reproduces such photographs of the replicas of heat treated (110) and (111) faces. The character of the diffraction patterns is the same as in the case of cleavage faces and differs essentially from those of water-

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[*] Cf. the discussion in W. Kranert, K.H. Leise and H. Raether Zschr. f. Phys., 122, 248, 1944.

[**] From the fact that the reflections are not noticeably broadened in the direction perpendicular to the line joining the primary spot and the reflection it can be deduced, on the other hand, that the tilting does not exceed the value of 2-3°.

treated and polished faces.   Since the treatment of the metallic layers was exactly the
same in all cases and hence also the effect of any possible disturbing factors, and since
also the findings were confirmed by many series of tests, the result, that the heat treated
surfaces have the smoothness of a cleavage plane, can be regarded as confirmed.   If, in the
same way, the water-treated (100) faces are studied it is found, in contrast to the (110)
and (111) faces, that the diffraction pattern is similar to that of the heat-treated faces,
an indication of the unusual smoothing qualities of the treatment.   This result agrees with
the direct investigation of water-treated (100) rock salt faces and can be explained by the
fact that the water-treatment causes the (100) face to grow.

The photographs reproduced above illustrate typical diffraction patterns.   Some
deviations appear in them, e.g. the diffraction patterns obtained from replicas of water-
treated or heat-treated faces gave powder diagrams with fibrous structure, or the replicas of
polished surfaces showed not fibrous structure but single crystal reflections with the indication
of striated prolongation.   These deviations however, served to prove that the disturbing
factor could be attributed to the temperature of the base when vapour deposition was carried
out being either too low, or, for polished surfaces, too high.   In the first case the
alignment of the silver crystals was not complete and in the second there was recrystallisation
of the rock salt base.

5.   DISCUSSION OF THE RESULTS

(a)   RESULTS IN THE CASE OF POLISHED SURFACES

The results obtained with rock salt show that mechanical treatment of the surface
leaves a relatively ordered crystal mixture, instead of breaking up the structure completely,
as with metallic surfaces.   This differing type of behaviour of insulators appears even more
clearly when other substances are used.   If a harder substance than rock salt is polished,
e.g. the cleavage face of lithium fluoride, calcium fluoride, or calcite, there is less
breaking up of the surface as a result of the working process, i.e. the diffraction pattern
has a closer resemblance to a single crystal than in the case of rock salt.   If softer
substances are polished, e.g. potassium bromide, the texture of the Debye-Scherrer diagram is
less marked than with rock salt[*].   This confirms the earlier findings of the author which
showed that mechanical working of insulators does not appear to give rise to a layer of
finest crystalline structure, as is the case with a metallic surface under the same conditions,
but with the insulators, i.e. substances of very low plastic deformability, the hardness of
the crystal is the decisive factor in the structure of the worked surface and the character
of the appropriate diffraction pattern[**].

(b)   RESULTS IN THE CASE OF TREATED SURFACES

The results which have just been described should be compared with the observations
of KOSSEL[+] and STRANSKI[++] on the growth and dissolution of crystals of rock salt.   According
to these the development of the (100) face on water-treated rock salt faces is to be understood
as follows: If a rock salt face is surrounded by an only slightly supersaturated solution,
growth will occur at those points where the maximum amount of energy is released for the
attachment of a structural unit.   On the basis of the above-quoted observations - and if a
cube face itself is not the starting point - this leads to the formation of steps with (100)
boundaries, the larger growing at the expense of the smaller, which brings increasing
coarseness of the projections.   In the case of water treatment these pre-conditions exist:
if the solution resulting from the surface treatment should evaporate, it becomes supersaturated
and growth of the (100) boundary projections sets in.   In this way the typical surface
structures on the water-treated (110), (111) and (210) faces are created.   Since the drying
of the moist surfaces, and hence the growth of crystals, takes place relatively quickly this
is probably the origin of the lesser uniformity of water-treated surfaces, which can be seen
from the lack of definition of the Kikuchi lines.

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[*]   The findings about insulators will be reported by Herr K.H. Leise in the
         Zschr. f. Phys.

[**]   Cf. for example B.W. Kranert and H. Raether, Ann. d. Phys. 43, 520, 1943.

[+]   W. Kossel, Nachr. Göttinger Gesellsch. p.135, 1927: Leipziger Vortrāge p.1, 1928.

[++]   J.N. Stranski, Zschr. f. physikal. Chemie, 136, 259, 1928; op.cit. (B) 17, 127, 1932;
         also J.N. Stranski and R. Kaischew, Zschr. f. physikal. Chemie (B) 26, 100, 1934.

It is a different state of affairs with the heat treatment of polished surfaces because here there is disintegration of the structural units through evaporation. In this process the first of the structural units to vaporize from the surface will be those which, by comparison with all the others have the highest degree of separability, that is, on the whole, those situated at the points and the projections. This leads to a reduction in the height of the projection, i.e. a smoothing of the surface. For this the temperature must be adequate and this is obviously the case from 450° to 500°C. It is only on a cube face, however, that this levelling can lead to the appearance of a perfect lattice plane as boundary; in every other case it is at the most an "imperfect, uniform" lattice plane which arises as the boundary of optimal smoothnees. While a perfect (100) lattice plane, i.e. one in which no structural unit is missing, is possible and stable, as a boundary, the (111) and (110) lattice planes, e.g., are not stable as perfect boundaries. In the case of the (111) lattice plane the surface is just composed of similar ions which are a hindrance to the stability of the surface on account of their mutual repulsion and it is the same for the (110) surface for which Figure 18a illustrates an imperfect, uniform lattice plane in cross section. The imperfection shows as a lack of ions (white squares) between the projections and the uniformity in the equal height of the projections. As a result of the repellant forces of the ions which form the perfect lattice plane (b), this configuration is not stable; one white ion will evaporate spontaneously (1), then a second (2) and a third (3), until the stable condition (Figure 18a) is reached once more. (These considerations illustrate plainly the difference between the surface of a crystal and that of a fluid. While the latter, through surface tension, becomes covered with a film of maximum smoothness, the former becomes rough, from reasons of energy, in order to assume a stable form). Even though, according to these considerations, it is at the best an imperfect lattice plane which can form the limiting surface, nevertheless it is still smooth enough for the electron beam to bring about refraction of the electron waves. It is plain that the occasional lack of an ion signifies an unnoticeable roughening of the surface by comparison with a perfect lattice plane, since apparently the external layer of ions, particularly as it is only half occupied, is attracted by the one which lies below and is of the opposite charge[*].

This pronounced levelling, which occurs in rock salt faces of any cut, in conjunction with the recrystallisation of the structure, is, in all probability, the cause of the reduced attacking capacities of the water vapour. The points and sides of the small crystals of the surface of polished faces, for example, provide, on the other hand, a large number of points at which the process of solution may begin and are the cause of the hygroscopic properties of these faces. The present work, which was finished at the end of 1944, was produced partly at the Physical Institute of Jena University and partly in the KWI Institute for Physics, Berlin-Dahlem. My thanks are due to Professor H. KULENKAMPFF for making the resources of the Institute available and to Professor W. HEISENBERG for resources, accommodation for working and for hospitality in his Institute. I am specially grateful to Dr. W. ROLLWAGEN and Dr. A. HAMMER, of the firm of Steinheil Söhne, Munich, for their continued and varied support of my experiments. Dr. B.v. BORRIES and Dr. E. RUSKA very kindly gave me hospitality in their laboratory and helped me with the electron-microscope work. I am indebted to Professor J.N. STRANSKI for stimulating discussions.

SUMMARY

The present work is the result of a study of the practical problem of why it is possible by simple methods to counteract the effect of grinding and polishing on surfaces of rock salt, i.e. to reduce the sensitivity to moisture thus imparted to them and give them at least the resistance to moisture possessed by a cleavage face. The Firm of Steinheil Söhne, Munich, employed two processes in order to solve this problem: water-treatment and heat-treatment of the initially polished surfaces. With water treatment, apart from the (100) face, the surfaces became dull whereas with heat treatment, even with curved surfaces such as those of lenses, an optically perfect surface develops which resembles a cleavage face as regards hygroscopic properties. There was therefore a great attraction in the task of applying the sensitive surface testing processes of electron diffraction and electron-microscopical observation to the problem of the effect of these methods of treatment.

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[*]   Since only the normal component of the impulse, owing to the internal potential at the vacuum-crystal boundary layer, pursues an unstable course, the decisive factor in the above consideration is the true height of the roughness and not the effective height of the projections which will be much reduced as a result of the glazing incidence.

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The first starting faces investigated were (100), (110), (111) and (210) and it was found that the small crystals in the surface, which, due to cleavability according to (100), are small cubes, still have a certain alignment with respect to each other, reminiscent of the parent crystal. A greater lack of order is shown in the (100) face in that here the cubes appearing on the cleavage face as a result of the working process may be turned by any amount from the normal of the surface, a consequence of the smooth (100) base. Next a study was made of the modifications in this disturbed single-crystal structure as a result of the water and heat treatments. Both processes cause the surface to recrystallise and become a single crystal, less perfect in the first case than in the second, and recognizable by the sharpness of the Kikuchi lines in the diffraction pattern. Replicas of the surfaces, studied by the electron microscope, showed that the dull, water-treated face is composed of (100) bounded crystal elements and these form characteristic surface structures according to the cutting face. The KOSSEL-STRANSKI requirement is not always fulfilled, however, viz. that the (100) face should grow at the expense of the others. The development of the octahedral plane could be observed most clearly in the (111) faces (blunted corners of pyramid points). In contrast to this, electron microscopical observation of the replicas of heat treated surfaces produced pictures lacking in contrasts and consequently indicating "electron-microscopically smooth" faces. It appears, from discussion, that the resolving power of the electron microscope is not adequate to resolve irregularities less than about 10^2 Å. The only prospect of success in this case is to make use of the electron diffraction method which, in the appearance of refraction of the electron waves when the reflection method is applied, constitutes a very sensitive means of examining the smoothness of the surface. It has been shown that heat treatment, independently of the index of the cut surface, is capable, in the most favourable instances, of producing surfaces having a smoothness comparable with cleavage faces. (It must be assumed, however, that from reasons of stability, the lattice planes are not perfect). The explanation can be seen in the fact that the points and sides of rough polished faces are predisposed to vapourize at these high temperatures ($\sim 500°C$) on account of the lesser bond energy of the exposed atoms, and so the surface becomes levelled out. The same effect is obtained in faces of other alkali halides, such as for example, sodium fluoride, lithium fluoride, and potassium fluoride. The recrystallisation, in conjunction with the disappearance of the roughnesses restores to the face the hygroscopic resistance of a cleavage face. The effects of heat treatment on the smoothness of the surface were studied not only by electron diffraction of the surface itself, but also of a metallic replica. After careful removal, the diffraction pattern of the replica of a heat-treated surface shows that the metallic film is of the same degree of roughness as if it had been removed from a cleavage face. The same process of replica diffraction patterns used on water-treated and polished specimens also, confirms the findings of investigations of rock salt faces themselves. Thus the combination of electron diffraction and the electron microscope method for the purpose of studying surfaces has yielded a complete answer to the problem set out at the beginning of this work concerning the structure of treated rock salt faces.
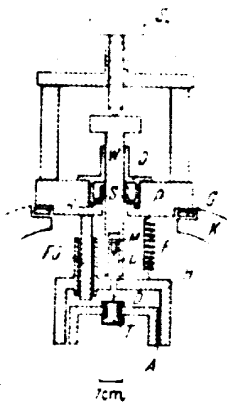
E. L.

1cm.

Fig.1a: Construction of the specimen holder used for the preparation of electron diffraction photographs

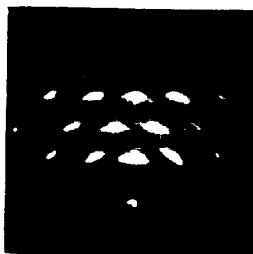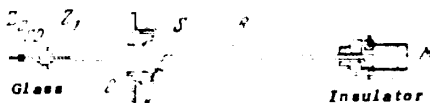Fig.1b: Apparatus for vapour-depositing metallic films inside the electron diffraction camera

Glass

Insulator

Fig. 2a

Fig. 2b

Fig. 2c

Fig. 3b

Figs. 2, 3 and 4: (110) rock salt face.   Fig. 2a, b polished (110) face, (a) and (b) electron diffraction photographs: (a) radiation perpendicular to cube side (see arrow in (c)); (b) radiation azimuth turned about $35°$ to (a), here the distance of the horizontal diffraction spot corresponds to d_{211}, while in (a) it is d_{100}.   The dependence of the fibrous structure on the direction of radiation shows that the small crystals after polishing are orientated approximately as in the parent crystal.
(c) electron microscopic photograph of a replica of the same face; in it can be seen the upper surfaces of the cubes left standing (cubes standing on one edge).
Fig. 3. Water-treated (110) face, (a) and (b) replica photographs which clearly show the cubes standing at less than $45°$.

Fig. 3c   1 μ   0.5 cm   Fig. 4
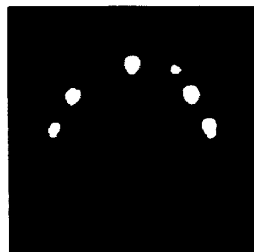
Fig. 5a   Fig. 5b   1 μ   0.6 cm
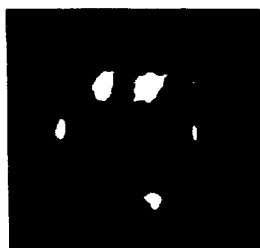
Fig. 6a   Fig. 6b   0.37 cm

Fig. 3c: Electron-microscopic reflection photograph of the contact
face of the replica of a water-treated (110) face; it shows the
same character as (a) and (b).
Fig. 4: Heat-treated (110) face.   Diffraction photograph:
direction of radiation as Fig. 2a.   The corresponding replica
lacks contrast, as Fig. 6b.
Figs. 5, 6, 7: (100) rock salt face.   Fig. 5: polished cleavage face.
(a) Diffraction photograph (b) corresponding replica.   Fig. 6: Heat-
treated cleavage face.   (a) Diffraction photograph, radiation
along the cube edge.   (b) corresponding replica ('electron-
microscopically smooth' face).

Fig. 8a

Fig. 8b   1 μ = 0,3 cm

Fig. 9a

Fig. 9c   1 μ   0,77 cm

Abb. 9b

Fig. 9d   1 μ = 0,77 cm
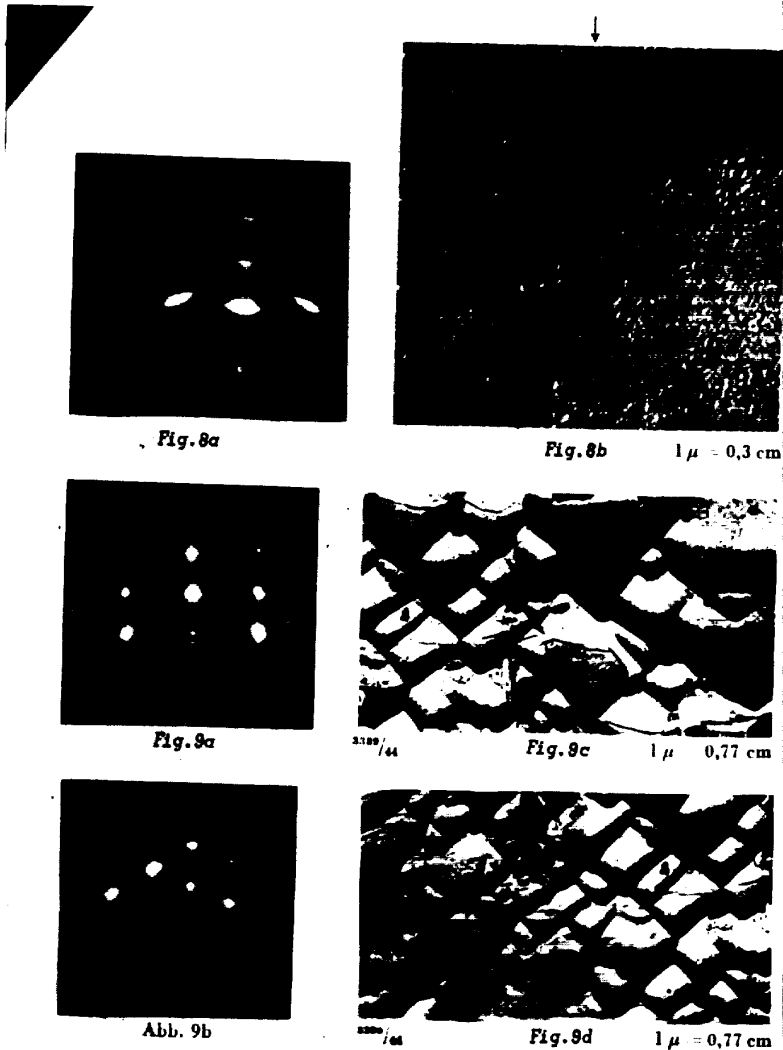
Figs. 8, 9: (111) rock salt face.   Fig. 8: polished surface
(a) Diffraction photograph, direction of radiation along the height
of the equilateral triangle forming the octahedral face of a cube,
see arrow in the corresponding replica.   Fig. 9: water-treated
surface - (a) and (b) diffraction photographs.   (a) direction of
radiation as in Fig. 8a (see arrow in (c)). (b) direction of
radiation turned 30° to (a).   (c) and (d) replica photographs,
in (c) the blunted corners are a striking feature.
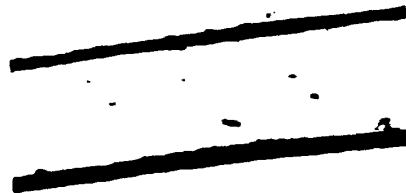
3414,'44 $1 \mu = 0.5$ cm

Fig.6c: Electron microscopic reflection photograph of the contact face of the replica of a cleavage face. Two steps, left standing during the cleavage, can be seen.

3393',44 $1 \mu = 0.7$ cm

Fig.7: Water-treated cleavage face. Replica photograph. The photograph was taken from a surface which had been treated for a short time; it is a preliminary stage to the incompletely smoothed plane, which, when adequate treatment has been given, gives a picture lacking in contrast. The rounded-off corners of the cube should be noticed.

Fig.10a

Fig.10b 1 μ 0.35 cm

Fig.12a 1 μ 0.72 c

Fig.12b 1 μ 0.6 cm

Abb.12c 1 μ 0.35 cm

Fig.12d 1 μ 0.72 cm
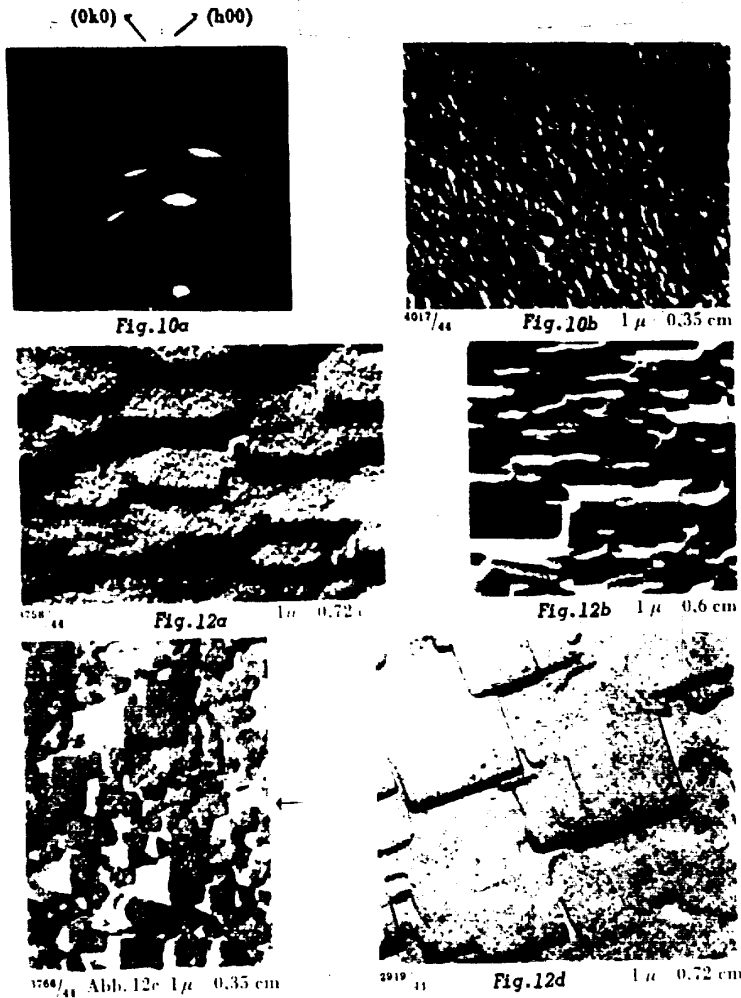
Figs.10 and 12: (210) rock salt face.
Fig.10: Polished face (a) diffraction photograph, direction of
radiation 3 (see Fig.11), the arrows mark the cube normals. The
diffraction pattern is a cross lattice, as arises in the case of
a (100) face in the (100) azimuth, inclined at about 26° to the
surface and, owing to crystal tilting, rotated a little about the
primary spot. Rotation of the crystal through 180° causes
reflection of the diffraction pattern about the dotted line.
(b) corresponding replica. The roughness due to the breaking
out of cube-bounded small crystals can be detected.
Fig.12: water-treated face. (a), (b), and (c) correspond to
the directions of vapour-depositing 1, 2 and 3 in Fig.11. The
surface of the rock salt is in the same position with respect
to the observer in (a), (b) and (c). The arrows show the
direction of vapour-depositing. (d) Replica of a water-treated
surface which was cut at an angle of 10° to the edge of a (100)
face: direction of vapour depositing 1.
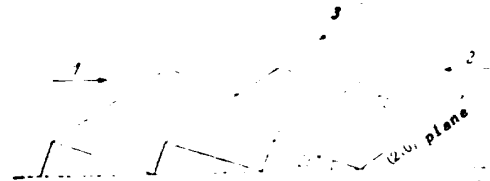
Fig.11: Schematic representation of a water-treated (210)
face. The arrows indicate the various possible directions
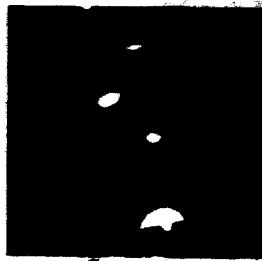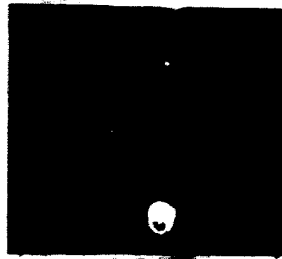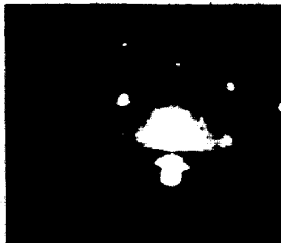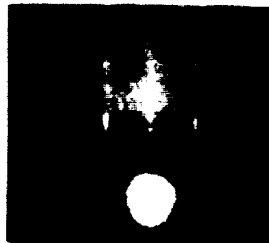for vapour depositing. cf. Fig. 12a,b,c
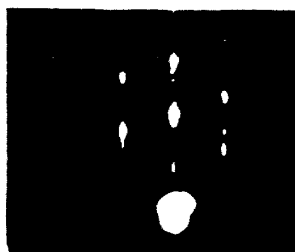
Fig.13a

Fig.13b

Fig.14

Fig.15

Fig.16a

Fig.16b

Figs.13-16: Diffraction patterns of the contact surfaces of silver replica of variously treated rock salt surfaces.
Fig.13: Polished faces (a) (110) surface, (b) (111) surface.
The diffraction patterns of the original surface are shown in Figs. 2a and 6a (other azimuth).
Fig.14: Inter-treated (111) face.   Original surface Fig.9b.
Fig.15: Heat-treated cleavage surface.   The original face gives an interference figure as in Fig.6a (another azimuth).
Fig.16(a) heat-treated (110) surface, the original surface is shown in Fig.4.
Fig.16(b) heat-treated (111) surface.   The silver replica (not the rock salt face) shows twin formation, recognizable by the fact that the diffraction pattern, which in this azimuth is normally asymmetrical about the middle line, cf. Figs.13b and 14, becomes symmetrical here as a result of the reflections which also appear.
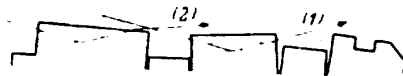

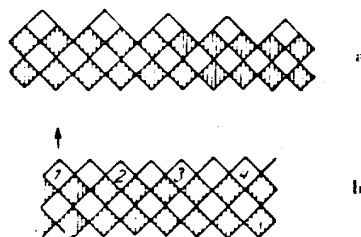Fig.17: Schematic construction of the contact surface of the replica of a cleavage face

Fig.18: Representation of an imperfect, uniform (a) and a perfect (b) (110) face.   The white and shaded squares stand for ions of different polarity