

## Growth of Alkali Halide Crystals from the Vapor Phase and from Solution onto Substrates of Mica

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Thin films of eleven alkali halides were formed by evaporation in a vacuum on mica substrates and were studied by means of electron diffraction. It was found that the crystals of all substances had a [111] direction normal to the substrate. In addition, there was an angular orientation about this direction which depended on the lattice constant,  $a_0$ , in the following way: (1) When  $a_0$  was larger than 5.32 Å. ( $a_0$  for KF) the angular orientation of the hexagonal net of atoms in the deposit at the interface matched exactly the orientation of the network of potassium atoms in the cleavage face of mica. (2) For LiCl ( $a_0 = 5.14$  Å.) the angular orientation was random, but the [111] fiber structure was well defined. (3) NaF ( $a_0 = 4.62$  Å.) had a [111] fiber structure but was mixed with a component of crystals having random orientation. (4) For LiF ( $a_0 = 4.02$  Å.) the hexagonal network at the interface was turned  $30^\circ$  in respect to the potassium network of the substrate. Almost identical results were obtained when the crystals were grown from solution. Substances which closely matched the interatomic spacing of the substrate gave support to a monolayer hypothesis of crystal growth from the vapor, whereas substances for which the mismatch exceeded about 10% began growth according to an oriented-nucleus hypothesis.

### Introduction

In the past, cleavage surfaces of mica have often been used as the substrate material on which to form oriented overgrowths (van der Merwe, 1949). Royer (1928) has given a complete account of experiments in which the overgrowth was formed by crystallization from solution. Observations with alkali halides indicated that orientation ceased when atomic mismatch at the interface exceeded 12%. Overgrowths on mica have also been formed from the vapor phase (Rudiger, 1937) and from the melt (West, 1945).

In this paper experiments will be described in which oriented overgrowths of alkali halides were formed from the vapor phase and then studied *in situ* using the reflection type of electron diffraction. (A preliminary report has already been published (Schulz, 1950).) Information was obtained on orientation, mechanism of crystal growth, and the effect of contaminations. In an earlier paper the results of growth on amorphous substrates were presented, the techniques developed at that time being continued in the present work (Schulz, 1949).

### Experimental equipment and procedure

The electron-diffraction equipment, built in the machine shops of the University of Chicago, has a vertical axis and possesses several special features which are necessary for the experiments. The plate chamber accommodates thirteen lantern-slide plates on which about thirty exposures can be taken without reloading. Four electric heaters of 1 mil molybdenum,  $\frac{1}{4}$  in. wide and about 1 in. long, were bent to form shallow V-shaped troughs to contain the alkali halides. They

could be moved to the axis of the instrument during evaporation and then moved back out of the path of the diffracted electrons. The radiation of the vapor in an upward direction was about three times that from a point source. Thicknesses of deposits given in this paper are accurate to about 20%.

The mica substrates,  $1\frac{1}{2} \times \frac{1}{4}$  in., were the two freshly cleaved surfaces of a lamina. The mechanical support provided all the required motions, including rotation of the samples in their own plane. Two separate samples could be inserted at one time. They were secured to the supports with double-sided Scotch tape which covered a small part of the area of one of the two cleavage faces of each sample. Adjustable shadowing barriers could be so placed that only a small part of a substrate would receive a given evaporation.

Usually an experiment was done at least once by observing the diffraction patterns on the fluorescent screen before photographs were taken. With two double-sided substrates and four sources it was possible to perform many variations in a given experiment without interruptions to replace substrates or charges. Four windows permitted observation of the fluorescent screen, the sources, and the sample holder at all times. Films were formed by both direct and indirect deposition (Schulz, 1949). The more important of the operating conditions were: (1) a residual gas pressure of  $10^{-5}$  mm. of Hg or lower; (2) an accelerating voltage of usually 50 kV. but continuously variable from 10 to 70 kV.; (3) a beam cross-section of 20 mils at the sample and 5 mils at the photographic plate; and (4) the substrates at room temperature.

### Experimental results

Electron-diffraction patterns from the mica (muscovite) substrates alone are shown in Fig. 1. Fig. 1 (*a*) is from a particular angular position which will arbitrarily be called the  $0^\circ$  position. If the mica is turned  $30^\circ$  in its own plane (to a  $30^\circ$  position) the diffraction pattern changes to that of Fig. 1 (*b*). Fig. 1 (*c*) and (*d*) show the corresponding angular positions of the potassium-atom network in the cleavage surface relative to the incident beam. Fig. 2 shows the general characteristics of diffraction patterns given by alkali halide films formed by deposition from the vapor onto mica cleavage surfaces. (The very prominent 'extra points' are due to multiple scattering (Thirsk & Whitmore, 1940).)

An analysis of patterns such as those of Fig. 2 shows that for all deposits a [111] direction is normal to the substrate. The angular orientation about this direction depends on the atomic matching at the interface. Fig. 4 shows the atomic positions in the substrate (Jackson & West, 1930; Bragg, 1937, chap. 14). It is evident that there are two hexagonal nets. The scale of Fig. 5 shows the interatomic distances in the (111) plane of the deposited materials, together with the mica distances. On the right side of the figure are given the experimental results for growth from the vapor phase, and on the left side growth from solution. Considering now only the right side, when  $a_0$  is larger than that for KF, the atomic network of the deposit at the interface matches the angular orientation of the larger network of Fig. 4. This, in general, does not mean an atomic matching over an extended area, but rather a matching of directions of corresponding rows of atoms in the substrate and the deposit. For LiCl, with a mismatch of 30%, a [111] fiber structure results. The mismatch is even larger for NaF, and, although a [111] fiber structure is observed, there is considerable dilution with crystals having random orientation. LiF, with the smallest  $a_0$ , is unique in orienting in respect to the smaller hexagonal network of Fig. 4.

### Multiple angular orientations

Since alkali-halide crystals grown from the vapor or from solution tend to be bounded by cube faces, it is convenient to represent the octahedral corners of a [111] orientation by triangles (Fig. 6). Fig. 6 (*a*) illustrates a 'double-positioned' type of angular orientation observed for substances with  $a_0 > 5.32$  Å. when grown from the vapor. Salts for which the mismatch is less than about 4% when grown from solution show the 'single-positioned' orientation given in Fig. 6 (*b*). Crystals of LiF (Fig. 6 (*c*)) are rotated  $30^\circ$  and have single positioning across cleavage steps in growth both from solution and from the vapor. Friedel (1926, chap. 17) has shown that the single positioning of Fig. 6 (*b*) indicates that mica possesses a glide plane.

In Fig. 6 (*d*) the solid lines connect the centers of atoms forming the first atomic layer of a deposit. If the second layer in all crystals occupies exclusively either

the  $x$  positions only, or the  $y$  positions only, there will be single positioning. The discriminating force which decides between the  $x$  and  $y$  positions is very weak for substances which orient in respect to the potassium-atom network. The results for RbI (Fig. 6 (*a*) and (*b*)) show that the force is more effective in crystal growth from solution. For LiF, on the other hand, the force is relatively strong, being effective in growth from both the vapor and solution. Discriminating forces arise from underlying atomic layers at greater distances than those of nearest neighbors; consequently the single-positioned orientation involves more than two-dimensional matching at the interface of the substrate and the deposit.

### Crystal growth from solution

The experimental procedure was as follows: A layer of about 50 Å. of the salt was deposited from the vapor on a mica substrate which was then removed from the vacuum system and exposed to moist air. During exposure sufficient moisture condensed on the deposit to dissolve it. When returned to the vacuum system of the the diffraction camera the water evaporated and the salt recrystallized. Using this procedure it was found that crystal growth from solution gave the results shown on the left of Fig. 5. They are almost identical with those obtained from the vapor phase.

With this new method it might be objected that perhaps all the original deposit formed from the vapor did not dissolve and therefore growth from solution began around undissolved crystals acting as nuclei. That such is not the case is shown by this result: When RbI was deposited from the vapor the diffraction pattern showed double positioning (as in Fig. 6 (*a*)). After exposure to moist air there was single positioning (as in Fig. 6 (*b*)). This indicates that solution was complete enough to remove the critical second layer. Furthermore, previous experiments have shown that the alkali atoms on the cleavage surface of mica are quickly removed by an aqueous solution (Hofman & Bilke, 1936). Accordingly, solution of the second atomic layer would indicate solution of the first as well. Usually laboratory air was humid enough to dissolve even LiF, but the experimental results were no different when a visible amount of water from the human breath was condensed on the samples. These observations indicate that the small crystals in a thin deposit grown from the vapor are probably more soluble than the bulk material.

### Mechanism of film growth from the vapor

Recent experiments by Tolansky show that the area of a single cleavage plane of mica can be several square centimeters (Tolansky, 1948). During cleavage it is reasonable to assume that approximately one-half the potassium atoms in the cleavage plane go with each of the separated parts (Scheibe, 1939). Thus on a large scale the substrates are crossed by widely separated

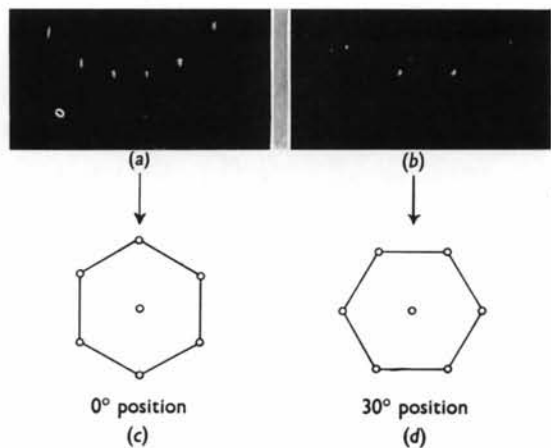


Fig. 1. Diffraction patterns from mica substrates in (a) 0° position, (b) 30° position. (c) and (d) Corresponding positions of potassium-atom network in cleavage surface.

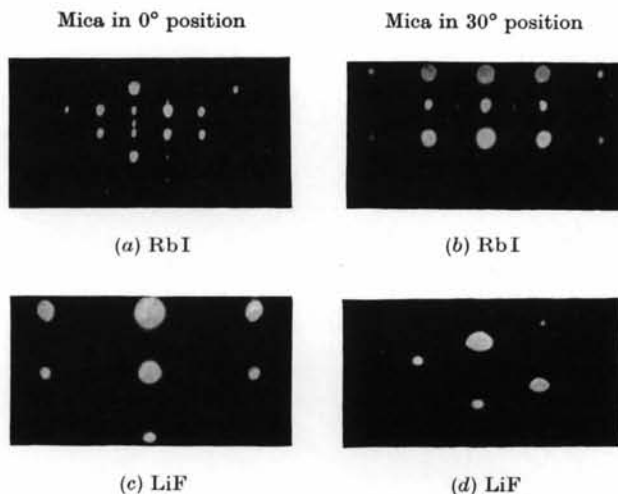


Fig. 2. Typical patterns given by alkali halide films on mica in the positions indicated.

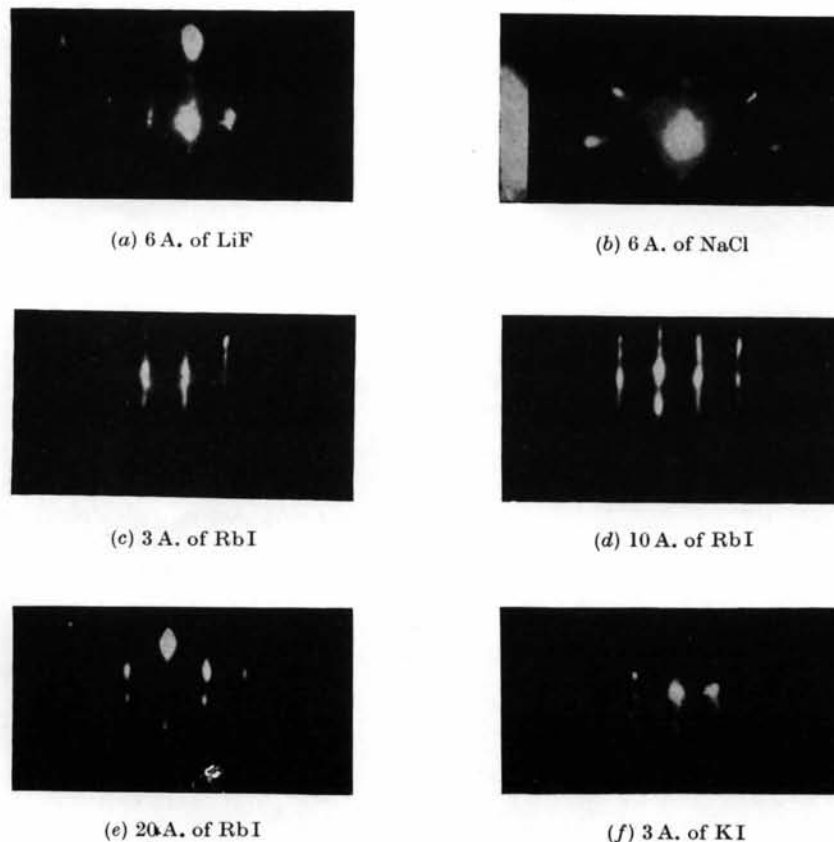


Fig. 3. (a) and (b) Patterns for very thin deposits, illustrating growth by the oriented-nucleus hypothesis. In (a) the mica is in the 0° position; in (b) in the 30° position. (For comparison see Fig. 1 for mica substrate patterns, and Fig. 2 for patterns given by thick deposits.) (c), (d) and (e) Patterns for RbI, showing the change with increased thickness for a monolayer.

cleavage steps, and on a small scale are made up of irregular regions of potassium atoms. On such substrates the experimental results suggested two distinct

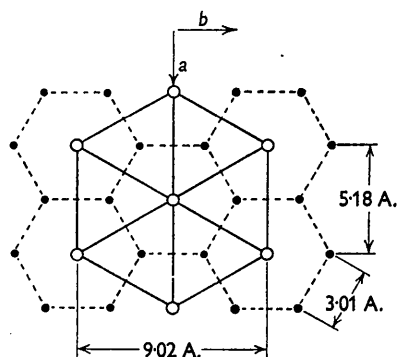


Fig. 4. Atomic positions in mica. The solid lines of the larger hexagon connect the potassium-atom sites in the cleavage plane. The broken lines connect points located at the centers of the triangles of the large network and represent in projection the silicon-atom positions.

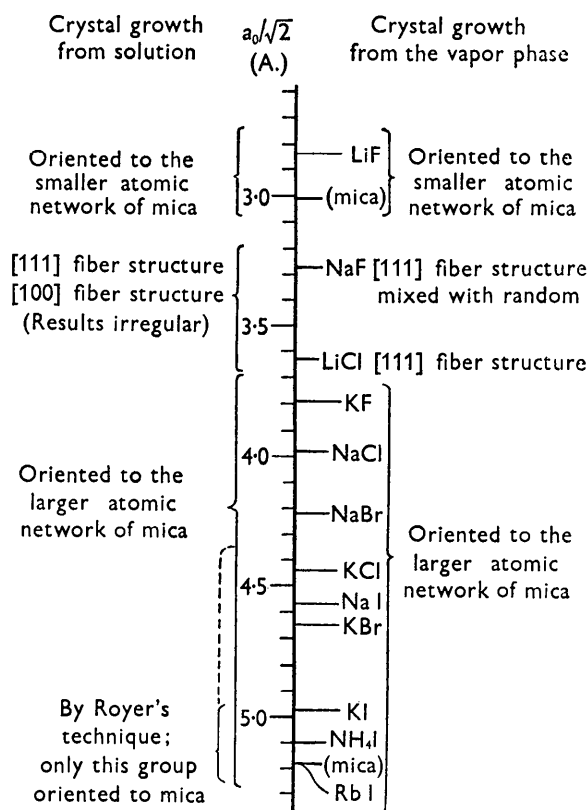


Fig. 5. Experimental results. The broken line indicates a region of uncertain results by Royer's technique.

types of growth from the vapor depending on the extent of mismatch:

(a) The 'oriented nucleus' hypothesis of Friedel (1926, chap. 17) was supported by substances with  $a_0 < 6.5$  Å. ( $a_0$  for KBr is 6.58 Å.). The technique employed was sufficiently sensitive to show diffraction patterns given by deposits having an average thickness

of only 3–4 Å. In Fig. 3 (a) and (b) are shown photographs taken of deposits 6 Å. thick. Since crystals which are only two to three atomic spacings on an edge are too small to give points of this sharpness, it is clear that the much larger crystals which must exist are formed by the migration and collection of the molecules at nucleation centers. This process leaves much of the substrate area uncovered, and consequently a well-defined substrate pattern appears in conjunction with that of the deposit.

Speculation on the details of the nucleation process suggests that the first molecules migrate until they strike an irregularity and then stop. This would tend to accentuate the irregularity, and molecules arriving subsequently would be even more likely to lodge at the growing aggregation center. Because the crystals are highly oriented from the beginning, it is almost required

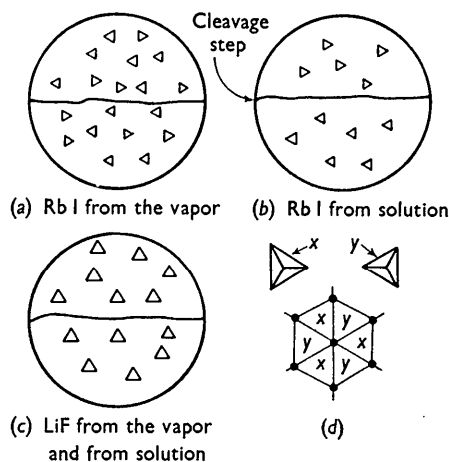


Fig. 6. Drawings illustrating single and double positioning. In all cases the mica is in the 0° position. (a) and (c) of this figure can be associated respectively with patterns (a) and (c) of Fig. 2.

by this explanation that the original irregularity be a part of the substrate and not a foreign body. Cleavage steps, however, are far too rare to provide the required irregularities (Tolansky, 1948). Conceivably the edges of areas containing potassium atoms could serve as irregularities. Most likely the orientation is already determined at the time of aggregation of as small a number as three or four molecules. A unit of that size would have such a small area in contact with the substrate that the matching would be very close. Having oriented a nucleus, the influence of the substrate would vanish; all further deposited material would grow onto the existing crystals.

(b) The behavior of substances with  $a_0 > 6.5$  Å. supported the 'monolayer hypothesis' (van der Merwe, 1949). An initial deposit of about 0.5 Å. produced considerable background such as do randomly spaced lines in a diffraction grating. Increasing the deposit to 1–2 Å. changed the pattern to a set of vertical streaks running through the diffraction spots of mica, as in Fig. 3 (c) for RbI. Further increases in the deposit

caused the streaks to break up gradually into discrete points, as in Fig. 3 (d) and (e). The comparable transition for KI involved a change from diffuse vertical bands matching the mica spacing to sharp streaks with a separation consistent with the  $a_0$  of the deposited substance. This sequence of changes with thickness can be understood as the tendency of the molecules of the first deposit to accommodate to the mica spacing. For close matching it is more likely that the first molecules will become anchored in a monolayer rather than grow into independent crystals. The experimental results showed that the binding to the substrate remained dominant for mismatching up to 10%.

#### Successive deposits of several different alkali halides

It was found that when films were composed of two or more successive deposits of different alkali halides the orientations of all deposits were the same as that of the first. Even details such as a preference for single or for double positioning were carried through several deposits. A special aspect of the propagation of orientation arose when the first deposit was too thin to cover the mica substrate. A 'contamination' deposit of KBr thicker than about 0.5 Å. was sufficient to cause subsequently deposited LiF to have the same angular orientation as the KBr. To the LiF the trace of KBr provided nucleation points on which it grew rather than to the substrate. Since KBr is spread out in a monolayer it is very effective as a contaminant.

When the sequence was reversed, LiF being deposited first, much more of a contamination was required. Only after the substrate area was approximately one-fourth covered with crystals of LiF, roughly 100 Å. on an edge, did the KBr of a second deposit change its angular orientation to that of the LiF. From these observations it was estimated that the range of migration of molecules of a deposit before they become bound is of the order of several hundred Ångström units.

#### Tests for the presence of contaminations on substrates

The results already described indicate that any accidental contamination of the substrate was too small to interfere noticeably with orientation. To determine more definitely the possible presence of minute contaminations additional experiments were performed: (1) By a suitable arrangement it was possible to cleave crystals within the vacuum of the diffraction equipment. The results obtained were no different from these substrates than from those cleaved in air and then inserted in the equipment. (2) The voltage was reduced to 20 kV. without appreciably changing the substrate patterns. The greatly reduced penetrating power of the electron beam would have enhanced the effect of any contamination. (3) Known thicknesses of  $MgF_2$  were deposited on a mica substrate previous to the addition of an alkali halide. (Earlier experiments had shown that  $MgF_2$  in thin layers is amorphous and non-porous (Schulz, 1948).) It was found that a 10 Å. deposit

completely cut off the substrate diffraction pattern for angles of incidence  $< 5^\circ$ ; a 2 Å. barrier was sufficient to cut off all orienting forces from the substrate; and an average thickness of 0.5 Å. was sufficient to upset decidedly the orientation of deposits. These results show that the contamination was effectively less than about 0.1 Å. of  $MgF_2$ . Substrates could be kept in the vacuum system several days before a contamination, probably pump oil, caused a slightly increased background scattering. Since experiments were performed within a few hours after the substrates were inserted, this source of contamination was of no consequence.

#### Conclusions concerning overgrowths of alkali halides on mica

(1) Close atomic matching at the interface is not required for an oriented overgrowth. The previous idea of a limiting mismatch, 5 or 10%, was a result of the method used. These figures have significance only when the conditions of the experiment are stated.

(2) The angular orientation about the [111] normal to the substrate depends on the lattice constant of the deposit.

(3) The new method of studying crystal growth from solution gave results on orientation essentially the same as those for growth from the vapor phase.

(4) Deposits for which the atomic mismatch is larger than 10% begin growth according to an oriented-nucleus hypothesis, while deposits for which the mismatch is smaller than 10% grow according to a monolayer hypothesis.

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