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Growth of Alkali Halides from the Vapor on Single-Crystal Substrates of Alkali Halides

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Alkali halides of the sodium chloride type structure (LiF, NaF, LiCl, KF, NaCl, NaBr, KCl, KBr, KI and RbI) were deposited from the vapor phase by evaporation in a vacuum on to cleavage surfaces of LiF, NaCl, KCl and KBr. It was found by electron diffraction that the crystals of the initial deposit were oriented with their crystallographic axes parallel to those of the substrate for all deposit–substrate combinations. Through the examination of deposits which had an average thickness of only a few atomic layers, the mechanism of crystallization of the initial deposit was determined.

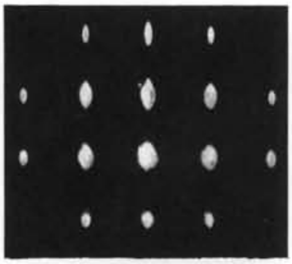
Introduction

In earlier publications a description was given of the growth of alkali halide crystals from the vapor phase on amorphous materials (Schulz, 1949) and on mica cleavage surfaces (Schulz, 1951*a*). The results of an extension of the experimental methods to a study of oriented overgrowths of alkali halides on single crystals having the sodium chloride type structure are presented in this paper (Schulz, 1950*a*). The substrates were prepared by cleaving large single crystals obtained from a commercial source (Harshaw Chemical Co., Cleveland, Ohio) into smaller pieces having a useful face about $\frac{1}{4}$ in. on an edge.

Experimental observations

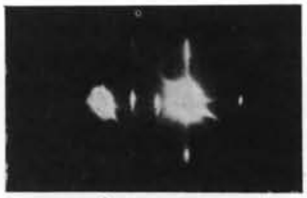
All deposits in the thickness range 10–100 Å gave patterns similar to that of Fig. 1. When the atomic mismatch at the interface exceeded 20 % (see Table 1) crystal growth began at widely separated nuclei according to the oriented nucleus hypothesis (Schulz, 1951*a*). The sequence of changes with increasing deposit is shown schematically in Fig. 3, and two of the associated diffraction patterns are given in Fig. 2. When the atomic mismatch was less than 20 % (see Table 2) an initial deposit of a few Ångström units did not migrate to form independent crystals, as in Fig. 3 (*a*), but remained dispersed over the substrate. With thicknesses above about 10 Å, however, independent crystals did appear. The binding to the substrate which produced the even covering is therefore effective only for a few atomic layers. For greater thicknesses mutual attraction of the atoms in the deposit brings about the formation of independent crystals. (See Frank & Merwe (1949) concerning misfitting monolayers.) When the deposit was of the same material as the substrate (NaCl on NaCl for example), deposits under 10 Å produced no detectable change in the substrate pattern, but with increasing thickness independent crystals appeared.

These results, together with earlier ones (Schulz, 1949, 1951 *a*), suggest that crystal growth from the vapor may begin by the formation of units made up of several molecules and that these units in turn combine to form crystals. The vapor which strikes the substrate is made up of diatomic molecules in which the atomic separation

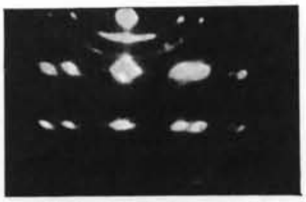


30 Å of NaCl on KBr

Fig. 1. A representative diffraction pattern for deposits between 10 and 100 Å. in average thickness. This photograph, taken with the electron beam approximately parallel to a [100] direction in the substrate, indicates that the crystals of the deposit are oriented with their axes parallel to those of the substrate. During the exposure the substrate was rotated about an axis normal to the electron beam and in the surface of the substrate.



(*a*) 2 Å of KCl on LiF



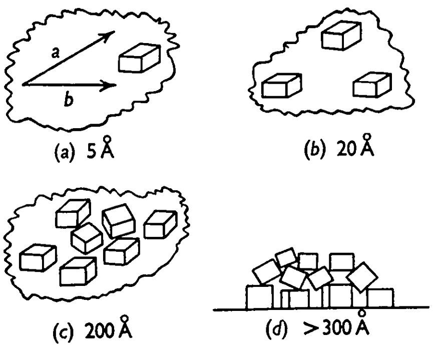
(*b*) 200 Å of KBr on LiF

Fig. 2. Pattern (*a*) is to be associated with Fig. 3 (*a*). (It was obtained by repeated scattering of electrons (Schulz, 1950*b*).) Pattern (*b*) is for a state intermediate between Fig. 3 (*c*) and (*d*).

is 10% smaller than in the corresponding crystals (Maxwell, Hendricks & Mosley, 1937). Because the mutual attraction between the molecules is much stronger than their attraction to the substrate (Lennard-Jones & Dent, 1928) (or to any large crystal) intermediate units would tend to form. Within such a unit the atomic separation would increase somewhat over that in the vapor, and thus the necessity of a full increase of 10% in one step would be avoided.

The structure of the substrate surface

Several of the relevant results of an extended study of cleavage surfaces are shown in Fig. 4 (experimental details will be given elsewhere). The mechanical action of cleavage formed many step edges which radiated from the corner at which the cleavage tool was inserted. In the *y–y* direction of Fig. 4 (*a*) no discontinuities could be detected, but the contour along a line *x–x* was irregular as shown in Fig. 4 (*b*). Optical measurements on silver-coated surfaces showed that the step height *h* was usually in the range of 500 Å down to 30 Å, the latter being the limit of sensitivity. The separation *D* of the steps was about 5000 times as great as the associated heights. Whereas the direction of the edges shown in Fig. 4 (*a*) were determined by the mechanical action of cleavage, electron microscopy revealed that between the steps of Fig. 4 (*b*) there were steps still smaller than 30 Å which tended to follow [100] directions. If the ratio of *D*/*h* is maintained in this region, steps of a single atomic layer would be approximately 1000 Å apart. This distance is of the same order of magnitude as the migration range of the initial deposits of those combinations listed in Table 1.



(*a*) 5 Å (*b*) 20 Å

(*c*) 200 Å (*d*) >300 Å

Fig. 3. Schematic representation of growth by the oriented nucleus mechanism. The numbers are the average thickness of the deposit. In (*a*) two of the substrate axes are indicated by *a* and *b*. Complete orientation is shown in (*a*) and (*b*); [100] fiber structure in (*c*); and a transition to random structure in (*d*).

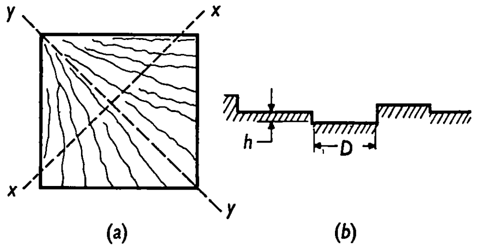


Fig. 4. Drawings showing the nature of the cleavage surface. In (*a*) is shown the direction of the cleavage steps, while (*b*) gives the contour along a line *x–x*.

There was no experimental evidence from which to determine whether or not step edges acted as nucleation centers. If such edges have suitable crystallographic directions, they could exert orienting influences and reduce the importance of atomic matching at the interface (Thomson & Cochrane, 1939; Thomson, 1949). There were no features of the diffraction patterns which could be attributed to cleavage-step edges.

Table 1. *Combinations for which the atomic mismatch exceeds* 20%

Growth was by the oriented nucleus mechanism. (The numbers following each deposit entry indicate the number of trials.)

Substrate	Deposit
LiF	LiCl 1; KF 1; NaCl 5; NaBr 1; KCl 1; KBr 2; CsCl* 2; RbI 2; CsBr* 2; CsI* 2
NaCl	LiF 3; KI 1; RbI 1
KCl	LiF 2; NaF 1
KBr	LiF 2; LiCl 1; KF 1

* Abnormal NaCl-type structure (Schulz, 1951*b*).

Table 2. *Combinations for which the atomic mismatch is less than* 20%

The initial deposit produced a uniform covering of the substrate. (The numbers following each deposit entry indicate the number of trials.)

Substrate	Deposit
LiF	NaF 2
NaCl	LiCl 1; KF 1; NaBr 1; KCl 1; KBr 3
KCl	NaCl 1; NaBr 1; KBr 3; RbI 2
KBr	NaCl 3; NaBr 1; KCl 1; RbI 2

Growth from solution

Previous experiments have shown that on mica substrates crystals grown from solution had essentially the same orientation as those grown from the vapor (Schulz, 1951 *a*). A similar experiment with alkali halide substrates was begun by 'contaminating' a LiF surface with about 15 Å of MgF_2. This was sufficient to cut off the influence of the substrate and cause a subsequent deposit of NaCl from the vapor to have random orientation. When exposed to moist air the thin MgF_2 layer broke up, enabling the recrystallized NaCl to contact the LiF. After drying in the vacuum of the diffraction camera the NaCl crystals were found to be oriented. For substrates other than LiF the observations were complicated by the formation of mixed crystals.

Earlier results with alkali halides grown from solution suggested that for atomic mismatches of more than 12 % (Royer, 1928; Sloat & Menzies, 1931) orientation ceases. Results of this kind have significance only when the experimental conditions are considered.

A careful search was made for the possible effect of water vapor during growth from the vapor. Since most of the salts used are highly soluble, water vapor could lead to the formation of mixed crystals, but none was observed. LiCl and KF, which are very soluble as well as deliquescent, were selected as the most sensitive test materials. With a pressure below 10^{-5} mm. of Hg and a liquid-air trap near the substrate, even thin deposits were in all respects like deposits of relatively insoluble salts. They possessed the correct lattice constants and showed no alteration with time. Without the liquid-air trap, however, the diffraction patterns became obscured by background after about fifteen minutes. For deposits other than LiCl and KF there was no change with time, even without the liquid-air trap.

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The Crystal Structure of Sodium Nitrite

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The crystal structure of $NaNO_2$ has been re-examined by X-ray methods. The general features of the structure reported by Ziegler in 1931 are confirmed but significant changes in the shape of the nitrite ion are indicated. Fourier and least-squares refinement lead to these dimensions for the NO_2^- ion: $N\text{–}O = 1{\cdot}23$ Å, $\angle$ O–N–O = 116°. The significance of the structure is discussed briefly.

Twenty years ago Ziegler (1931) published a determination of the crystal structure of sodium nitrite, $NaNO_2$. His determination led to values for the N–O bond length and O–N–O bond angle of 1·13 Å and 132°, respectively, within rather wide limits of error. This value for the bond length is less than the sum of pure *double*-bond radii (Pauling, 1945, p. 164) and the bond angle value is greater than simple considerations indicate. In view of these puzzling results, and of the desirability of knowing the structure of simple ions with some precision, a careful redetermination of parameters by modern techniques appeared desirable.

Unit cell and space group

Ziegler's determination of the unit cell and space group was verified in the present work, incidental to the preparation of photographs for estimation of intensities. For convenience his results are quoted here (with interchange of *b* and *c* axes to conform to *Internationale Tabellen* (1935) usage).

Body-centered orthorhombic lattice, space group C_{2v}^{20}–*Imm*

$$a=3{\cdot}55,\quad b=5{\cdot}38,\quad c=5{\cdot}56\ \text{Å}$$

2 $NaNO_2$ per unit cell.

Relative structure factors

Photographs for intensity estimation were prepared with a rod-shaped crystal of approximately square cross-section, measuring 0·20 × 0·20 mm. The crystal was 0·84 mm. long in the direction of the *a* axis. It was grown by evaporation of an aqueous solution. Equatorial-, first- and second-layer equi-inclination Weissenberg photographs about the *a* axis were recorded with nickel-filtered Cu $K\alpha$ radiation. Since there were only three structure parameters to be evaluated, the 61 reflections recorded on these photographs were judged to be sufficient for a reasonably precise determination.

Intensities were estimated by the multiple-film technique (Robertson, 1943) with the help of a set of