munication (Dulmage & Lipscomb, 1951). These distances and bond orders are summarized in Fig. 6.

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References

Abrahams, S. C., Collin, R. L., Lipscomb, W. N. & Reed, T. B. (1950). *Rev. Sci. Instrum.* **21**, 396.

Bauer, S. H. & Pauling, L. (1936). *J. Amer. Chem. Soc.* **58**, 2403.

Clark, H. H. & Hoard, J. L. (1943). *J. Amer. Chem. Soc.* **65**, 2115.

Dulmage, W. J. & Lipscomb, W. N. (1951). *J. Amer. Chem. Soc.* **73**, 3539.

Hedberg, K. & Schomaker, V. (1951). *J. Amer. Chem. Soc.* **73**, 1482.

Hedberg, K., Jones, M. & Schomaker, V. Private communication.

Kasper, J. S., Lucht, C. M. & Harker, D. (1950). *Acta Cryst.* **4**, 436.

Pauling, L. & Weinbaum, S. (1934). *Z. Krystallogr.* **87**, 181.

Pitzer K. S. (1945). *J. Amer. Chem. Soc.* **67**, 1126.

Reed, T. B. & Lipscomb, W. N. To be published.

Schomaker, V., & Shaffer, P. A. (1947). *J. Amer. Chem. Soc.* **69**, 1555.

Shoemaker, D. P., Donohue, J., Schomaker, V. & Corey, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.

Zhdanov, G. S. & Sevast'yanov, N. G. (1941). *C. R. Acad. Sci. U.R.S.S.* **32**, 432.

Waser, J. (1951). *Rev. Sci. Instrum.* **22**, 563.

Acta Cryst. (1952). **5**, 264

Overgrowths of Alkali Halides on $CaCO_3$ and $NaNO_3$

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Crystals of ten alkali halides (NaCl, KCl, KBr, CsCl, CsBr, RbI, KI, NaF, LiF, and CsF) were grown from the vapor and from solution on cleavage surfaces of $CaCO_3$ and $NaNO_3$. The orientations observed (Schulz, 1951*a*) with the electron-diffraction techniques employed in previous experiments (Schulz, 1949, 1951*b*) are listed in Table 1 with certain details added in Figs. 1 and 2. From the vapor, growth was by the oriented nucleus mechanism (Schulz, 1951*b*) for all deposits. Usually a deposit of 10 Å average thickness was sufficient to show a well-defined pattern. With thicknesses above about 150 Å there was a transition to random orientation. The size of the crystals grown from the vapor was about 200 Å on an edge; from solution, about 3000 Å or larger.

The experimental results listed in Table 1 may be explained by considering the following general factors:

I. Low-index planes parallel to the substrate. NaCl-type deposits (except for LiF) were oriented with the (100), (110) and (111) planes parallel to the substrate. For CsCl-type materials only the (110) plane was parallel to the substrate, but possibly with a greater range of lattice constants other orientations would also appear.

II. Electrical neutrality at the interface. There was a tendency for a plane of mixed ions (both positive and negative) of the deposit to contact the substrate plane, also a mixed ion plane. For a NaCl-type deposit these are the (100) and (110) planes and for CsCl the (110) plane. Exceptions in growth from solution are RbI and KI on both substrate materials. In growth from the vapor there is the additional exception of CsF on $CaCO_3$.

III. Atomic matching along rows of like ions. In Fig. 2(*A*) are shown the atomic separations in the $CaCO_3$ substrates, 4·99 and 4·03 Å. A deposit grew in such a manner that one of these distances was matched as closely as possible. This result would be expected from the short range of the orienting forces. There was no orientation which exhibited a tendency to get the best overall match for both separations. Even for

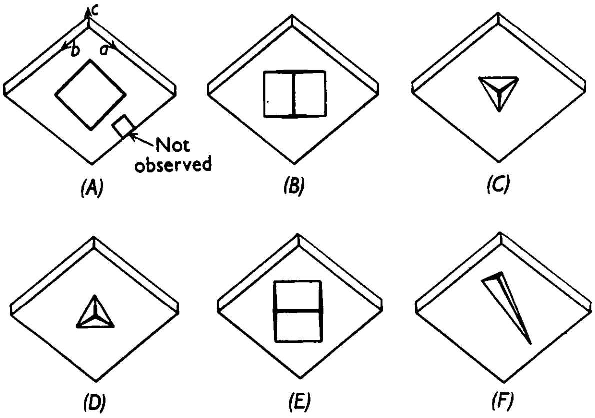

Fig. 1. Schematic representation of orientations. The faces of the substrates are bounded by cleavage surfaces while those of the deposits are (100) planes. The axes of the substrate are defined by the edges of the cleavage rhomb in the manner shown in (*A*).

Table 1. *Orientations observed*

The last column indicates where additional information is presented.

Deposit	Substrate	Method of deposition	Orientation	Figures
NaCl	$CaCO_3$	Vapor	$(100)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*A*)
KCl	or	or		
KBr	$NaNO_3$	solution	$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*B*)
CsCl	$CaCO_3$	Vapor	$(100)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*A*)
CsBr	or		$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*B*)
	$NaNO_3$		(NaCl type structure)	
CsCl	$CaCO_3$	Solution	$(110)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*B*)
CsBr	or			
	$NaNO_3$		$[100]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*C*)
RbI	$CaCO_3$	Vapor	$(100)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*A*)
KI	or			
	$NaNO_3$		$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*B*)
RbI	$CaCO_3$	Solution	$(111)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*C*)
	or			
	$NaNO_3$		$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*D*)
KI	$CaCO_3$	Solution	$(111)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*C*)
	or			and (*D*)
	$NaNO_3$		$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*D*)
NaF	$NaNO_3$	Vapor	$(100)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*A*)
		or		
		solution	$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*B*)
NaF	$CaCO_3$	Vapor	$(100)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*A*)
			$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	2(*B*)
NaF	$CaCO_3$	Solution	$(110)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	1(*E*)
KF			$[110]_{\mathrm{dep}} \perp [1\bar{1}0]_{\mathrm{sub}}$	2(*E*)
LiF	$CaCO_3$	Vapor	$(741)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	
	or	or		1(*F*)
	$NaNO_3$	solution	$[1\bar{2}1]_{\mathrm{dep}} \parallel [1\bar{1}0]_{\mathrm{sub}}$	
CsF	$CaCO_3$	Vapor	$(111)_{\mathrm{dep}} \parallel (100)_{\mathrm{sub}}$	2(*D*)
			$[110]_{\mathrm{dep}} \parallel [110]_{\mathrm{sub}}$	

LiF one aspect of the orientation can be understood as a consequence of good matching of the $[1\bar{1}0]$ direction of the substrate with the $[1\bar{2}1]$ direction of the deposit. No orientation was observed in respect to the 3·20 Å separation of unlike ions (see Fig. 1(*A*) and Fig. 2(*A*)) as had been reported earlier (Heintze, 1937).

Of these three generalizations only the third is always satisfied; the first and second are only tendencies. The third, however, even with the help of the first two, is not capable of predicting completely the orientation of a given salt, as can be illustrated with the case of RbI. The expected [100] orientation of Figs. 1(*A*) and 2(*B*) is observed in growth from the vapor, but from solution the unexpected [111] orientation of Figs. 1(*C*) and 2(*D*) is obtained. For completeness Fig. 2(*D*) also shows that the [110] orientation for RbI is excluded because certain ions of like sign are almost coincident, for example, at substrate ion *X*.

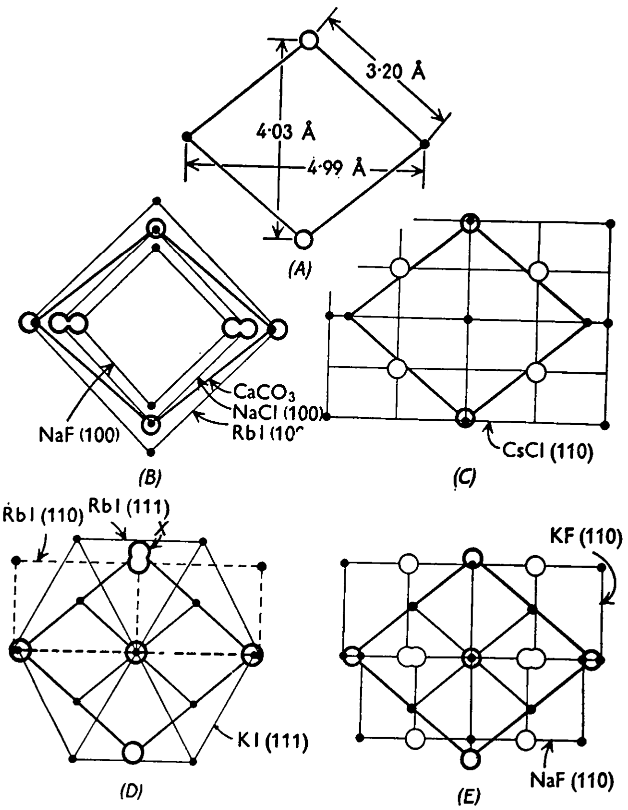

Fig. 2. Drawings showing the atomic positions at the interfaces. It has been assumed that the substrates have an oblique NaCl-type structure. In (*A*) are given the principal atomic separations for $CaCO_3$.

In addition to the three general factors just considered several other details are significant: (1) To account for the angular positions of (*C*), (*D*), and (*F*) of Fig. 1 it is necessary to consider next-nearest neighbors below the cleavage surface of the substrate. This would be especially difficult to carry out in detail for calcite-type substrates. (2) Growth from solution is occasionally of different orientation from that from the vapor (CsCl and CsBr even have different structures (Schulz, 1951*c*)). This suggests that the mechanism of growth is also different. (3) Divalent $CaCO_3$ gives practically the same results as monovalent $NaNO_3$. (4) LiF orients with a high-index plane parallel to the substrate. Because the contacting planes of both the substrate and deposit have onefold symmetry the LiF deposit is single positioned.

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References

Heintze, W. (1937). *Z. Krystallogr.* **97**, 241.
Schulz, L. G. (1949). *J. Chem. Phys.* **17**, 1153.
Schulz, L. G. (1951*a*). *Phys. Rev.* **82**, 314.
Schulz, L. G. (1951*b*). *Acta Cryst.* **4**, 483.
Schulz, L. G. (1951*c*). *Acta Cryst.* **4**, 487.