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Oriented Overgrowths of Alkali Halides on Silver Substrates

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CsCl, CsBr, LiF, NaCl, NaBr, KCl, RbBr and KI were deposited from the vapor phase and from solution on oriented silver films. Electron diffraction was then used to determine the orientation of the crystals in these alkali halide deposits. In growth from the vapor both NaCl- and CsCl-type salts oriented with planes containing only metal ions (or only non-metal ions) parallel to the plane of the substrate. The angular position tended to be consistent with best atomic matching at the interface. In growth from solution a greater variety of orientations occurred including those in which mixed-ion planes were parallel to the substrate. The interaction between the deposit and substrate was sufficiently strong to induce polymorphism of CsCl, CsBr and RbBr. Growth from solution often gave orientations different from those given in growth from the vapor.

Introduction

Johnson (1950) has recently shown by light-microscope methods that metal substrates exert strong orienting forces on ionic crystals grown from solution. In this paper are given the results of an electron diffraction study of oriented alkali halide crystals grown from the vapor and from solution on silver substrates.

Oriented silver films (Brück, 1936; Rudiger, 1937) were prepared by deposition from the vapor on substrates of NaCl and mica heated to about 230° C. These silver-covered substrates were then moved into an electron diffraction camera where the alkali halides were deposited from the vapor onto the silver which was kept at room temperature. Crystal growth from solution was brought about by exposing the deposited alkali halides to moist air which dissolved the deposit. The samples were then dried in the vacuum of the diffraction equipment and the orientation was redetermined. The details of the experimental procedures were the same as previously described (Schulz, 1949, 1951*a*). The crystal constants of all the salts used as deposits are listed in Table 1.

Table 1. *Crystal properties of the materials used*

Material	Crystal structure	Lattice constant (Å)	Atom separation (Å) (100) plane (see Fig. 1(*c*)–(*e*))	Atom separation (Å) (111) plane
Ag	f.c.c.	4·08	2·88; 4·08	2·88; (4·99)
CsCl	CsCl	4·11	4·11; 5·81	5·81
CsBr	CsCl	4·29	4·29; 6·07	6·07
RbBr*	CsCl	4·08	4·08; 5·77	5·77
LiF	NaCl	4·02	2·01; 2·84	2·84
NaCl	NaCl	5·63	2·82; 3·98	3·98
NaBr	NaCl	5·96	2·98; 4·21	4·21
KCl	NaCl	6·28	3·14; 4·44	4·44
RbBr	NaCl	6·85	3·42; 4·84	4·84
KI	NaCl	7·05	3·52; 4·98	4·98
CsCl†	NaCl	6·94	3·47; 4·91	4·91
CsBr†	NaCl	7·23	3·61; 5·11	5·11

* RbBr has the abnormal CsCl structure (Schulz, 1951*b*).

† CsCl and CsBr have the abnormal NaCl-type structure (Schulz, 1950).

Nature of the silver films

Extensive studies of the structure of silver films grown from the vapor on NaCl substrates have shown that thin films are twinned (Goche & Wilman, 1939). For thicker deposits, however, twinning becomes less evident and the diffraction patterns indicate the orientation shown schematically in Fig. 2(*a*). The silver deposits used in these experiments were approximately 1000 Å thick and gave patterns consistent with the description of the films as pseudo single crystals with pronounced mosaic character. On mica a [111] direction of the silver deposit was normal to the substrate with the angular position of the (111) plane (as shown in Fig. 1(*a*)) rotated 30° relative to the potassium atom network in the mica cleavage surface (Thirsk, 1950).

Electron microscopy has shown that the average size of the silver crystals is of the order of 500 Å and that their shape is rather irregular (Hass, 1942). Because of the resultant surface roughness it is not strictly correct to speak of atomic matching at any particular plane as interface; nevertheless, the idea of atomic matching of the deposits with the silver

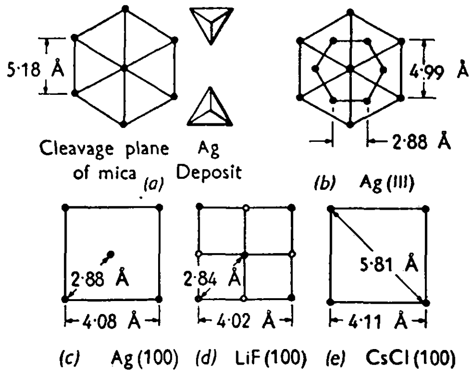

Fig. 1. (*a*), (*b*) Drawings used for describing the orientation of silver on mica. (*c*), (*d*), (*e*) Drawings indicating atom separations.

substrates proved to be helpful in directing the selection of the deposits as well as in explaining the results.

Experimental results

A summary of the orientations observed is given in Tables 2 and 3; the drawings of Figs. 2 and 3 show schematically some of the details. These orientations are for deposits of about 50 Å or less. With increasing thickness there is a change to random structure. Previous results are in agreement with those listed in the tables: NaCl and KCl on (Ag–NaCl) from solution by Johnson (1950); and NaCl on (Ag–NaCl) from the vapor by Brück (1936) who used substrates heated to 340° C. It was found that chlorides were no more active than other halides, a result which is contrary to Johnson's observations.

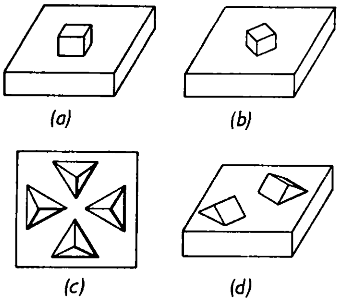

Fig. 2. Schematic representation of typical orientations. In all cases the bounding surfaces of the solid figures are (100) planes.

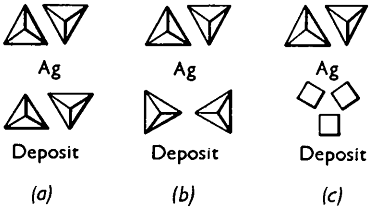

Fig. 3. Schematic representation of typical orientations of deposits made on (Ag–mica).

Table 2. *Orientations observed on substrates of silver on sodium chloride*

Deposit	Substrate (Ag on NaCl)	
	From the vapor	From solution
CsCl and CsBr	$(100)_{\mathrm{dep}} \| (100)_{\mathrm{sub}}$ $[100]_{\mathrm{dep}} \| [100]_{\mathrm{sub}}$ (See Fig. 2 (*a*))	Same orientation as from the vapor but the deposit grows into a smaller number of larger widely separated crystals
LiF	Completely random	LiF is not sufficiently soluble to be grown from solution
NaCl, NaBr and KCl	$(111)_{\mathrm{dep}} \| (100)_{\mathrm{sub}}$ $[110]_{\mathrm{dep}} \| [100]_{\mathrm{sub}}$ (See Fig. 2 (*c*)) Tendency toward [111] fiber structure	$(100)_{\mathrm{dep}} \| (100)_{\mathrm{sub}}$ $[110]_{\mathrm{dep}} \| [100]_{\mathrm{sub}}$ (See Fig. 2 (*b*))
RbBr	Same as for NaCl, NaBr and KCl	CsCl-type structure $(100)_{\mathrm{dep}} \| (100)_{\mathrm{sub}}$ $[100]_{\mathrm{dep}} \| [100]_{\mathrm{sub}}$ (See Fig. 2 (*a*))

Table 3. *Orientations observed on substrates of silver on mica*

Deposit	Substrate (Ag on mica)	
	From the vapor	From solution
CsCl and CsBr	[100] fiber structure, CsBr slightly diluted with random orientation	NaCl type structure. $(111)_{\mathrm{dep}} \| (111)_{\mathrm{sub}}$ $[110]_{\mathrm{dep}} \perp [110]_{\mathrm{sub}}$ (See Fig. 3 (*b*))
LiF	$(111)_{\mathrm{dep}} \| (111)_{\mathrm{sub}}$ $[110]_{\mathrm{dep}} \| [110]_{\mathrm{sub}}$ (See Fig. 3 (*a*))	LiF is not sufficiently soluble to be grown from solution
NaCl, NaBr, KCl and KI	$(111)_{\mathrm{dep}} \| (111)_{\mathrm{sub}}$ $[110]_{\mathrm{dep}} \perp [110]_{\mathrm{sub}}$ (See Fig. 3 (*b*)) Tendency to be slightly diluted with random orientation	$(111)_{\mathrm{dep}} \| (111)_{\mathrm{sub}}$ The angular position was predominantly that of Fig. 3 (*b*) but there was nearly always a trace of Fig. 3 (*a*) and (*c*)

Tables 2 and 3 show that in growth from the vapor those planes in a deposit which are parallel to the substrate contain ions of one kind only, all metal or all non-metal. For NaCl-type salts it is a (111) plane and for CsCl-type salts a (100) plane. In growth from solution, however, NaCl, NaBr and KCl on (Ag–NaCl) have a mixed-ion plane parallel to the substrate plane. The only deposit not exhibiting any orientation was that of LiF from the vapor on (Ag–NaCl). Because of the uncertainties of the present understanding of cohesion of even pure materials it is not possible at this time to offer a general explanation of the observed orientations. The significance of atom matching indicates that binding to metal substrates is not through electrical image forces.

An examination of certain of the experimental conditions

Auxiliary optical experiments (Schulz, 1951*c*) on silver films showed that in a period of one hour's exposure to laboratory air the contamination layer, oxide or otherwise, which formed was less than 1 Å in average thickness. When the sample was exposed to air at a relative humidity of 90% or more AgCl formed at the rate of about 5 Å per day. Below 70% the rate was reduced to one-tenth and in a desiccator was not detectable even over a period of a month. Because of this accelerated corrosion by moisture, silver films were not removed from the NaCl substrates by the usual solution methods (Brück, 1936). On silver films exposed to air for only a few minutes it will be assumed that the alkali halide deposits from the vapor actually 'contacted' the metal. Silver films exposed even to dry air for more than about 10 hr. began to lose their orienting power on crystals grown from the vapor, but in growth from solution oriented overgrowths were obtained on films several weeks old. The induced polymorphism (Schulz, 1951*b*) of RbBr (which depends on good atomic matching) indicates that also in growth from solution the deposit probably contacts the silver.

It might be objected that during the growth from solution the orientation was induced not by the silver but by the substrate for the silver (the mica or NaCl) acting through imperfections in the silver film. Against such objections are these cases: (1) NaCl on (Ag–NaCl). The orientation (Fig. 2(*b*)) is different from NaCl directly on NaCl (Fig. 2(*a*)). (2) CsCl and CsBr on (Ag–mica). The orienting forces were sufficiently strong to induce the abnormal structure. Directly on mica these salts have the normal structure and a [100] fiber orientation. (3) CsCl and CsBr on (Ag–NaCl). The orientation (Fig. 2(*a*)) is different from that of the direct deposit on NaCl which gives either the abnormal structure with the orientation of Fig. 2(*a*) or the normal structure with the orientation in Fig. 2(*d*). These examples indicate that the silver films are the effective orienting agents.

Conclusion

In addition to showing the actual orientation in a large number of particular cases (Tables 2 and 3) the experiments lead to the following more general conclusions: (1) Although an oriented silver substrate may have a very irregular microscopic geometric surface, it can, nevertheless, induce a definite orientation in a deposit. This indicates that the orienting influence of the substrate is propagated to the deposit across any crystallographic plane as interface. As a consequence it is rather artificial (even if convenient) to speak of matching onto the particular crystallographic plane which happens to be parallel to the macroscopic substrate surface. (2) Factors determining the orientation of a deposit would include (*a*) the relation of its lattice constants to those of the substrate, (*b*) the method of its growth (vapor or solution) and (*c*) electrical conditions at the interface. These results are of importance in the study of corrosion since a typical case is that of an ionic layer forming over a metal substrate (Cabrera & Mott, 1948–49).

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X-ray Studies of the Terpenes. I. Crystallographic Data for α-*l*-Menthol

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The α form of *l*-menthol has been found to be trigonal with space group $C3_1$, $a = 21{\cdot}60 \pm 6$, $c = 6{\cdot}11 \pm 1$ Å and with three molecules in the asymmetric unit. Previous powder work is thus shown to have been interpreted wrongly and is here corrected.

1. Introduction

Menthol has played a prominent part in the development of the study of optical activity in organic materials and, therefore, its chemical constitution and the relations between its isomers have received considerable attention (for a summary see Simonsen, 1947, vol. 1, p. 230). As a result, the number of possible molecular models has been reduced, but an investigation of the stereochemistry, especially at the three asymmetric carbon atoms, is desirable.

Comparatively little, however, has been recorded

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