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Polymorphism of Cesium and Thallium Halides

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Six salts (CsCl, CsBr, CsI, TlCl, TlBr and TlI) which normally have the CsCl-type crystal structure were found to have the NaCl-type structure when grown from the vapor phase on appropriate single-crystal substrates. The lattice constants of the new structures were measured by electron-diffraction methods to an accuracy of ± 0·02 A.

Introduction

In previous papers a description was given of the structure and growth of thin films of alkali halides which have the NaCl-type structure (Schulz, 1948, 1949, 1950*a*, *b*). The films are prepared *in situ* by evaporation and deposition in a vacuum and are examined by electron diffraction. When the experiments were extended to include a study of alkali halides of the CsCl-type structure, it was found that the initial deposit on certain single-crystal substrates possessed an abnormal NaCl-type structure (Schulz, 1950*c*). Procedures were then devised for accurate measurements of the lattice constants of the abnormal structure. For the examination of very thin deposits a new method was developed which depends on repeated scattering of electrons, first by the substrate and then by the deposit (Schulz, 1950*d*). During the experiments several new types of preferred orientation were observed.

Experimental observations

The sequence of changes in the diffraction patterns for increasing thickness of the deposit for the case of CsCl on LiF substrates is shown in Fig. 1. Very thin deposits under 10 A. in thickness were examined by repeated scattering of electrons, and gave patterns such as (*a*). The thin deposit has migrated and grown into widely separated crystals 100–200 A. on an edge. These crystals have the abnormal NaCl-type structure and are oriented with their axes parallel to those of the substrate. With increasing thickness additional crystals are formed until most of the substrate is covered. The pattern for a 20 A. deposit given by single scattering of electrons is shown in (*b*).

New crystals that do not contact the substrate have the usual CsCl-type structure. Fig. 1 (*c*) shows the diffraction pattern given by a deposit containing two structures. The points are from the crystals of the initial deposit of the NaCl-type, while the arcs are from crystals of a later deposit which have a [100] fiber orientation and a CsCl-type structure. Deposits thicker than a few hundred ångströms show no trace of diffraction from crystals of the initial deposit and give patterns such as in (*d*). As has been shown earlier, evaporated films of the alkali halides are rather porous and are composed of relatively independent crystals which tend to be uniform in size and shape (Schulz, 1949).

A summary of most of the experimental results is given in Table 1. On one of the substrate materials, KBr, the initial deposit of all six salts possessed the abnormal NaCl structure. On substrates of NaCl the same was true with one exception: TlCl possessed the CsCl structure for even the thinnest deposits. This result for TlCl on NaCl is not surprising, since the atomic matching at the interface would tend to favor the CsCl structure. To obtain additional information on TlCl it was deposited on KI and KCl, and was found to have the NaCl structure. For positions on the table indicated by question marks the structure was neither NaCl nor CsCl, but the diffraction patterns were not suitable for complete structure determinations. The two general

Table 1. *The structure of the initial deposit for various deposit–substrate combinations*

	Substrate material			
Deposit	LiF	NaCl	KBr	Mica
CsCl	NaCl	NaCl	NaCl	NaCl
CsBr	NaCl	NaCl	NaCl	NaCl
CsI	NaCl	NaCl	NaCl	CsCl
TlCl	?	CsCl	NaCl	CsCl
TlBr	NaCl	NaCl	NaCl	?
TlI	NaCl	NaCl	NaCl	?

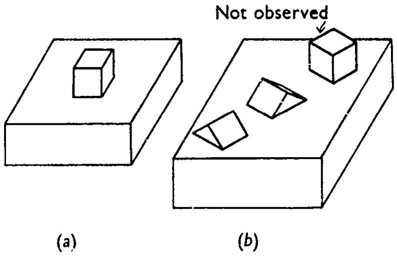
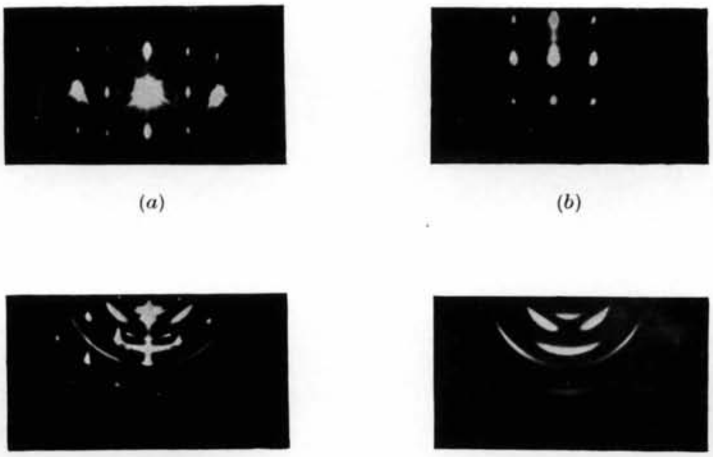


Fig. 2. Principal types of orientation observed on NaCl-type substrate. (*a*) NaCl-type deposit with axes of the deposit parallel to those of the substrate. (*b*) CsCl-type deposit with (110) plane of the deposit parallel to the (100) substrate plane with two equally likely angular positions. The orientation labelled 'Not observed' was the one reported by Royer (1928).



(*a*) (*b*)

(*c*) (*d*)

Fig. 1. Typical electron-diffraction patterns for various thicknesses of CsCl on LiF. (*a*) Pattern given by two exposures taken with the LiF substrate in two slightly different positions. The three largest spots are from the substrate, whereas the smaller ones are from the deposit (thickness = 2 A.). (*b*) Pattern from crystals of the deposit only (thickness = 20 A.); these crystals, like those of the deposit in (*a*), have the NaCl structure. (*c*) Pattern showing the presence of both the normal- and abnormal-type structures. Thickness of deposit = 100 A. (*d*) The [100] fiber pattern from normal-type crystals in the surface of a thick deposit (thickness = 500 A.).

types of orientation observed are given in Fig. 2. It should be noticed that for the case of CsCl-type deposits on NaCl-type substrates the orientation is different from that observed by Royer (1928).

In addition to mica and to NaCl-type substrates, single crystals of various other materials were used. The complete results will be given later, but the case of CsCl on calcite is of interest at this point. When grown from the vapor the NaCl structure was observed, but from solution the usual CsCl structure appeared. The orientations were different for each structure, but in each case were consistent with the best atomic matching at the interface. On amorphous substrates the deposits always had the normal CsCl structure both from the vapor and from solution.

Lattice-constant measurements

The most important property of the abnormal structure is the lattice constants, which were measured by the following two general methods:

(1) *Comparison with the substrate.* For thin deposits it was usually possible to obtain the substrate pattern superimposed on the pattern of the deposit. The lattice constant of the deposit could then be obtained without a knowledge of the electron acceleration voltage or the geometry of the diffraction camera. The procedure was especially accurate for patterns such as that in Fig. 1 (*a*) given by repeated scattering. On good photographs an accuracy of ± 0·01 A. was possible.

(2) *Comparison with the normal* CsCl *structure.* In photographs such as Fig. 1 (*c*) the CsCl-type pattern acted as an internal standard in the same manner as the substrate pattern did in the first method. The best accuracy was about ± 0·02 A.

For particular deposit–substrate combinations less general methods were employed, as, for example, the case of CsBr on mica. CsBr deposited from the vapor on a mica substrate has the NaCl structure. If a thin deposit is exposed to moist air, it recrystallizes into the CsCl structure with a [100] fiber orientation. If additional CsBr is then added from the vapor, the diffraction pattern shows spots due to both the CsCl and NaCl structures, together with the mica substrate pattern. Comparison of measurements on all three patterns gave very precise values for the lattice constant of abnormal CsBr.

In the second column of Table 2 are listed the experimentally determined lattice constants of all the new structures. Also included are the interatomic distances in the normal and abnormal structures and the difference in these distances. According to the most recent table of ionic radii the difference should be 0·08 A., whenever the binding is predominantly ionic (Zachariasen, 1950).

To ensure that there was no atomic mixing of the deposit and the substrate at the interface, validity tests were made in which the lattice parameters of the deposited material, as well as those of the substrate, were known. Measurements on several dozen combinations of alkali halides showed that the lattice constants of the deposit were always the standard values to within the accuracy of the experimental methods. (Details of these experiments are given in another paper.)

Discussion of the results

Calculations have shown that the crystal energies for the NaCl and CsCl structures are very nearly the same (Born & Mayer, 1932; Mayer, 1933; Huggins & Mayer, 1933; May, 1937); accordingly, it is not surprising that polymorphism should occur. Since the CsCl structure is the denser, an increase in pressure would be expected to produce a transition from the NaCl to the CsCl structure. Slater (1924), Bridgman (1935, 1937), and Jacobs (1938) have observed such transitions for potassium and rubidium salts, but Bridgman failed to find any change for sodium and lithium salts up to pressures of 50,000 kg. cm.$^{-2}$. An increase in temperature would be expected to produce a transition in the opposite direction, that is, from the CsCl to the NaCl structure. This has been observed by Wagner & Lippert (1936) for CsCl at about 50° C. below the melting temperature.

It is not convenient to describe the occurrence of polymorphism given in this paper as the result of unusual pressure or temperature conditions. It is more profitable to consider the mechanism by which the individual atoms unite to form crystal nuclei. The essential experimental condition appears to be growth from the vapor phase on a suitable single-crystal substrate. It is by no means necessary that there be good atomic matching at the interface, although matching is certainly a significant factor. The experimental results which have been given here are insufficient in themselves to give an explanation for the structure of the deposits. These data, however, in combination with those from many similar experiments, make possible a general description of crystal nucleation from the vapor. This general conclusion will be given later.

Table 2. *Lattice constants and interatomic distances*

Salt	a_0 (A.) NaCl-type	Interatomic distances (A.) NaCl-type	Interatomic distances (A.) CsCl-type	Differences in interatomic distances (A.)
CsCl	6·94	3·47	3·56	0·09
CsBr	7·23	3·62	3·72	0·10
CsI	7·66	3·83	3·95	0·12
TlCl	6·30	3·15	3·32	0·17
TlBr	6·58	3·29	3·44	0·15
TlI	6·94	3·47	3·64	0·17

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De l'Usage des Inégalités de Harker–Kasper*

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The various limits set by Harker–Kasper inequalities are compared. It is shown that the simple inequality

$$(U_H \pm U_{H'})^2 \leqslant (1 \pm U_{H+H'})\,(1 \pm U_{H-H'})$$

is the most powerful. A table is given for its systematic use.

Harker & Kasper (1948) ont les premiers attiré l'attention sur la possibilité d'établir des limites entre lesquelles doit se trouver le facteur de structure F_{hkl}. Ces limites étant fonctions des F^2_{hkl}, quantités fourniers par l'expérience, il est possible d'en déduire le signe de F_{hkl} (nous nous limiterons dans tout ce qui suit au seul cas des structures qui ont un centre de symétrie).

Les inégalités de Harker–Kasper, qui fixent ces limites, sont déduites, d'une manière purement formelle, de l'application de l'inégalité de Cauchy:

$$|\sum_i a_i b_i|^2 \leqslant \sum_i |a_i|^2 . \sum_i |b_i|^2.$$

Toutes les inégalités obtenues de cette manière peuvent être ramenées à deux types fondamentaux dont on peut dériver un grand nombre d'autres inégalités, en particulier en appliquant systématiquement les opérations de symétrie du réseau réciproque. Cette dérivation systématique a été mise en lumière par MacGillavry (1950).

Par ailleurs, Karle & Hauptman (1950) ont démontré que la condition nécessaire et suffisante pour que la densité électronique soit positive pouvait être mise sous la forme d'une certaine série d'inégalités; la *n*ème inégalité de la série fait intervenir des déterminants d'ordre *n*; c'est donc une relation entre les puissances d'ordre $\leqslant n$ des F_{hkl}. La 2ème inégalité relie les F_{hkl} et leurs carrés.

Goedkoop (1950), approfondissant et précisant la théorie mathématique qui est à leur base, a fait la synthèse de ces divers travaux.

Nous nous limiterons ici à l'examen de celles de ces inégalités qui sont d'un intérêt pratique pour la solution du problème des phases et nous tenterons d'en préciser les meilleures conditions d'utilisation. Nous ne considérons que les inégalités faisant intervenir les facteurs de structure et leurs carrés. Nous nous conformerons à la notation d'usage où l'indice H remplace l'indice triple *hkl* et où $U_H = F_{hkl}/Z\hat{f}$ ($\hat{f}$ facteur atomique 'unitaire').

Les deux types fondamentaux de Harker–Kasper sont:

$$\left.\begin{aligned}(U_H \pm U_{H'})^2 &\leqslant 2(1 \pm U_{H+H'}),\\ (U_H \pm U_{H'})^2 &\leqslant 2(1 \pm U_{H-H'}),\end{aligned}\right\} \quad (1)$$

$$(U_H \pm U_{H'})^2 \leqslant (1 \pm U_{H+H'})\,(1 \pm U_{H-H'}). \quad (2)$$

L'inégalité du 2ème ordre de Karle peut s'écrire:

$$||U_H . U_{H'}| - |U_{H\pm H'}|| \leqslant \sqrt{(1-U_H^2)}\,\sqrt{(1-U_{H'}^2)}. \quad (3)$$

(1) Les inégalités du type (1) sont moins strictes que l'inégalité (3). En effet de (1) on déduit:

$$||U_H . U_{H'}| - |U_{H\pm H'}|| \leqslant \tfrac{1}{2}(1-U_H^2) + \tfrac{1}{2}(1-U_{H'}^2). \quad (4)$$

Or $\sqrt{(1-U_H^2)}\,\sqrt{(1-U_H^2)} \leqslant \tfrac{1}{2}(1-U_H^2) + \tfrac{1}{2}(1-U_{H'}^2)$. (5)

Mais par addition des deux inégalités (1) on obtient un renseignement supplémentaire qui n'est pas inclus dans (3):

$$U_H . U_{H'} \leqslant \tfrac{1}{2}(U_{H+H'} + U_{H-H'}), \quad (6)$$

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