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ON THE STRUCTURE OF  
 $\text{SrCl}_2, 6\text{H}_2\text{O}$

BY

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## INTRODUCTION

This investigation was undertaken in order to study the function of the water of crystallisation in hydrates of metallic salts which do not form "Coordination compounds" in the chemical sense of the words.

### Trigonal hexahydrates of alkali earth halides.

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  is a member of an isomorphous group of salts comprising the members given in table 1.

Table 1.

#### Trigonal hexahydrates of alkali halides.

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{CaJ}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{SrJ}_2 \cdot 6\text{H}_2\text{O}$   
 $\text{BaJ}_2 \cdot 6\text{H}_2\text{O}$

The compounds  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  have been examined goniometrically by A. EPPLER<sup>1</sup> who proved their isomorphy. In the other cases the isomorphy has been established by Z. HERRMANN<sup>2</sup> who has shown that powder and rotation

<sup>1</sup> A. EPPLER: Z. f. Krist. **30** (1899) 149.

<sup>2</sup> Z. HERRMANN: Z. Anorg. Allg. Chem. **187** (1930) 231, *ibid.* **196** (1931) 79, *ibid.* **197** (1931) 212, *ibid.* **197** (1931) 339.

photographs of the compounds not investigated goniometrically are closely similar to photographs of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and may be indexed with a similar unit cell. Experiments by the author show that a supersaturated solution of one of the compounds, e. g.  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  may be brought to crystallisation by seeding with crystals of another compound e. g.  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ , but they do not readily form mixed crystals. It was for instance found that a solution containing equal amounts of  $\text{SrCl}_2$  and  $\text{CaCl}_2$  on slow evaporation deposited crystals of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  in which Ca could be found by very sensitive methods only, such as the method of S. P. L. SØRENSEN (precipitation of  $\text{Ca}^{++}$  as  $\text{CaNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ )<sup>1</sup>.

### The structure proposed by Z. Herrmann.

In the series of papers listed above, Z. HERRMANN describes a variety of X-ray diagrams of all the seven isomorphous compounds, deduces their unit cells, and in the final paper proposes a complete structure. The structure consists of equidistant alternating layers of  $\text{Sr} \cdot 6\text{H}_2\text{O}^{++}$  and of  $\text{Cl}^-$  ions. The  $\text{Cl}^-$  layers are perfectly plane and the  $\text{Sr} \cdot 6\text{H}_2\text{O}^{++}$  very nearly so. In the  $\text{Sr} \cdot 6\text{H}_2\text{O}^{++}$  plane the oxygen atoms form a practically flat regular hexagon around the strontium atom. The O—O distance between atoms belonging to different hexagons is very small, in some of the salts below 2 Å. The physical meaning of this low distance is that the waters of crystallisation form closely bound double molecules. The structure did not seem very probable to me. Moreover it has been criticized by the "Strukturbericht" and by C. HERRMANN in the Landolt-

<sup>1</sup> Described in S. P. L. SØRENSEN: Z. Anorg. Ch. 11 (1896) 307.

Börnstein Handbook. Z. HERRMANN does not in his paper give any comparison between calculated and observed intensities.

### Specimens.

The calcium chloride, strontium chloride, and bromide used in this investigation were good commercial products marked I or "Zur Analyse" and were used without further purification. In order to obtain suitable crystals, saturated solutions were brought to crystallisation over different  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  mixtures in vacuo.  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  developed prism faces and well developed rhombohedra, but  $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6 \text{H}_2\text{O}$  in general grew to extremely long six-sided prisms, often 10 cm. or more, and extending from one side of the crystallisation dish to the other. The prisms<sup>1</sup> were not terminated by basal or rhombohedral faces, but ended in curious craters—craters that sometimes appeared to be inverted step pyramids but of which a goniometric examination proved unsuccessful.

In a single case big crystals of  $\text{SrBr}_2 \cdot 6 \text{H}_2\text{O}$  were obtained which were short six-sided prisms with well developed rhombohedral faces. Unfortunately, this batch of crystals deliquesced before it was ascertained whether they were structurally or electrically different from the ordinary long prisms.

### X-ray technique.

Series of  $30^\circ$  oscillation photographs were taken with Fe radiation from a MÜLLER tube operated at 40 KV const. potential 10 MA current. The beam was filtered through a layer of  $\text{MnO}_2$ .

<sup>1</sup> as described by O. MÜGGE: C. Min. 1918, 105 for the similar crystals of  $\text{BaJ}_2 \cdot 6 \text{H}_2\text{O}$ .

Of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  complete sets of  $30^\circ$  oscillation photographs were taken with the crystal oscillating round the orthohexagonal A, B and C axes successively.

Of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  photographs were taken only with the crystal oscillating around the C-axis as it proved difficult to handle the deliquescent crystals of this compound. The photographs were obtained on a cold winter day when the temperature was only slightly above  $0^\circ\text{C}$  in the laboratory. Under these circumstances,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  decomposes only very slowly.

The crystals of the stable compounds  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  were adjusted goniometrically and dissolved down to cylindrical shape by the aid of a moist brush. In case of the wet and unstable crystal of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  which was rod-shaped, it was sufficient for taking c-axis photographs to adjust the crystal by means of a microscope.

The photographs were indexed after BERNAL'S<sup>1</sup> method. With very few exceptions every spot was registered four times or more. In order to get reflections of the same hkil from as many different places on the crystal as possible (to estimate and eliminate the influence of small irregularities in the crystal shape) the crystal was turned  $30^\circ$  between any two photographs instead of the usual  $15^\circ$ .

Spots were labelled in a scale comprising 7 strengths ranging from very weak to very strong. The difference between intensities estimated for the same hkil on different films seldom amounted to one class.

### Cell sizes.

As found by Z. HERRMANN, the unit cells of these compounds are hexagonal and very flat. The c-axis is about

<sup>1</sup> J. D. BERNAL: Proc. Roy. Soc. A **113** (1926) 117.

half the length of the a-axis. There is only one molecule in the unit cell.

The effect of isomorphous substitution is clearly shown on the cell dimensions (table 2).

Table 2.  
Lattice spacings from reflections at high angles.

Compound	a-axis	c-axis
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	7,860	[3,87]*
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	7,940	4,108
$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	8,205	4,146

\* Inaccurate. From layer-line measurements.

With the exception of the c-axis of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  which is obtained from layer-line measurements, the figures are from measurements of zero-layer-line spots at high glancing angles. They are measured on films where reflections from the same face or from different faces with the same value of  $\sin \theta$  occur on both sides of the film. The values of  $\theta$  were obtained by reference to shadows cast on the film at a very high angle by a brass desk which is part of the collimator system, in a similar way to the knife edges developed by BRADLEY and JAY<sup>1</sup> for powder cameras.

Values of a lattice constant obtained by measuring different reflections on the same film or the same reflection on different films were found to agree within a few parts in 10000, so the lattice dimensions given in table 2 should be correct to less than 1 part in 1000. The value of the c-axis found for  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  has been put into brackets as it is due to layer-line measurements and scarcely correct to more than 2 pCt.

<sup>1</sup> BRADLEY and JAY: Phys. Soc. Vol. 45 (1933) 507.

### Test for piezoelectricity.

The crystals were tested for piezoelectricity by a single crystal method. A crystal was clamped between a brass plate and a brass nib. The pressure on the crystal was varied between 100 and 400 g and the potential between nib and plate was registered by the aid of a LINDEMANN electrometer. The apparatus was tested on some ten substances known to be piezoelectric and on a few neutral substances. The results of these tests were always unambiguous, and crystals (e. g. cane sugar) described in the literature as weakly piezoelectric when tested gave deflections of the electrometer needle from one end of the scale to the other. A number of crystals of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  were tested in several directions. The result was in every case negative.  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  was not tested because of its deliquescence. The crystals failed to give etch figures, so from this source no information could be gathered about the crystal class of the substances.

### Crystal class, space group and possible atomic arrangement.

The crystal class of these hexahydrates has not been shown with certainty.

Z. HERRMANN<sup>1</sup> quotes EPPLER<sup>2</sup> as giving the crystal class as "hexagonal rhomboedrisch", meaning by this the  $C_{3i} - \bar{3}$  class. Yet EPPLER (loc. cit.) only measured the angle between rhombohedral and prism faces, calculated the axial ratio and assigned the crystal to one of the "rhombohedral" classes. I determined the crystal class and space group in the following way.

<sup>1</sup> Z. HERRMANN: Z. Anorg. Allg. Ch. **187** (1930) 234.

<sup>2</sup> EPPLER: Z. f. Krist. **30** (1899) 149.



The photographs with the A-axis as axis of oscillation are symmetrical with respect to the zero-layer-line. The photographs with the long orthohexagonal axis as axis of oscillation show no such symmetry.

Any two c-axis photographs the oscillation intervals of which are  $60^\circ$  apart are alike when one is rotated  $180^\circ$  in the plane of the photograph.

These symmetries are characteristic of the class  $D_{3d} - \bar{3}m$  but as the photograph symmetry always adds a center of symmetry to the symmetry element of a crystal the following classes become possible:

$$D_{3d} - \bar{3}m, \quad D_3 - 32, \quad C_{3v} - 3m.$$

That piezoelectricity has not been found makes  $D_{3d} - \bar{3}m$  most probable without definitely excluding  $D_3 - 32$  and  $C_{3v} - 3m$ .

Since no reflections are systematically absent the following space groups become possible:

$$D_{3d}^1 - C\bar{3}1m, \quad D_{3d}^3 - C\bar{3}m1, \quad D_3^1 - C312, \quad D_3^2 - C321, \\ C_{3v}^1 - C3m1 \quad \text{and} \quad C_{3v}^2 - C31m.$$

The presence of a plane of symmetry in the photographs perpendicular to the a-axis, requires the same element of symmetry or alternatively a digonal axis parallel to the a-axis in the space group. This condition rules out

$$D_{3d}^1 - C\bar{3}1m, \quad D_{3d}^1 - C312, \quad C_{3v}^2 - C31m \quad \text{and leaves} \\ D_{3d}^3 - C\bar{3}m1, \quad D_3^2 - C321, \quad C_{3v}^1 - C3m1.$$

1 Sr, 2 Cl and 6 O must now be placed in point positions of one of these space groups. The following one- and two-fold positions are found:

$$D_{3d}^3 - C\bar{3}m1: (a) 000, (b) 00\frac{1}{2}, (c) 00z \ 00\bar{z},$$

$$(d) \frac{1}{3}\frac{2}{3}z \ \frac{2}{3}\frac{1}{3}\bar{z}.$$

$$D_3^2 - C321: (a) 000, (b) 00\frac{1}{2}, (c) 00z, 00\bar{z},$$

$$(d) \frac{1}{3}\frac{2}{3}z \ \frac{2}{3}\frac{1}{3}\bar{z}.$$

$$C_{3v} - C3m1: (a) 00z, (b) \frac{1}{3}\frac{2}{3}z, (c) \frac{2}{3}\frac{1}{3}z.$$

Space considerations make it impossible to place Sr and 2 Cl on the z-axis, so whichever space group is the right one it is possible to fix the x and y coordinates of Sr and 2 Cl. They are:

$$1 \text{ Sr in } 00 \text{ and } 2 \text{ Cl in } \frac{1}{3}\frac{2}{3} \ \frac{2}{3}\frac{1}{3}.$$

With this as a starting point the hki0 intensities were considered (as described in detail later on) and it was shown that none of the possible positions for O in  $D_{3d}^3 - C\bar{3}m1$ ,  $C_{3v}^1 - C3m1$  are compatible with the intensities. In the final structure O atoms are placed in positions which are found only in  $D_3^2 - C321$ . This proves that the crystal class is  $D_3 - 32$ .

### Parameter determination.

The problem in hand is well suited for Fourier methods. There is a heavy atom at the origin and intensities from isomorphous compounds may be compared.

As no spectrometer measurements were available to place the observed photographic intensities on an absolute scale, the method of successive approximations was em-

ployed<sup>1</sup>. All computations were accomplished by the aid of the BEEVERS and LIPSON strips<sup>2</sup>.

The prism zone reflections  $hki0$  from  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  were first employed to give a projection on the base of the unit cell. The structure factor for the Cl-atoms at  $\frac{1}{3} \frac{2}{3}$  and  $\frac{2}{3} \frac{1}{3}$  in this series of reflections is +2 when  $h-k = 3n$ , -1 in all other cases. All the reflections  $h-k = 3n$  were of considerable strength. The order of magnitude of the corresponding  $F(hki0)$  is given by the maximum contributions from one Sr and two Cl's at the appropriate glancing angle. With this as a starting point a chart was drawn to enable one to read off an approximate  $F(hki0)$  for a reflection whose glancing angle and estimated spot intensity are known.

Such charts were widely used in this investigation. An example is given in fig. 1. It contains a family of 6 curves, one for each step in the scale of spot intensity. The ordinate  $F$  of a curve marked  $p$  at the abscissa  $\theta$  represents  $F(hkl)$  of a reflection registered on the film with the strength  $p$  at the glancing angle  $\theta$ .

The shape of the curves, their relative positions and the ordinate scale is determined by the cell size, number of molecules in the cell and the usual absorption, extinction, polarisation, LORENTZ and temperature factors, as well as by the size and shape of the specimen.

It was not attempted to calculate these influences. Instead it was assumed that they were roughly the same as in  $\text{ZnBrO}_3 \cdot 6\text{H}_2\text{O}$ <sup>3</sup>, a compound of similar type and of not much heavier elements.

A chart for  $\text{ZnBrO}_3 \cdot 6\text{H}_2\text{O}$  was constructed from Jü's

<sup>1</sup> See Jü and BEEVERS: Z. f. Krist. A **95** (1936) 426—34.

<sup>2</sup> LIPSON and BEEVERS: Proc. Phys. Soc. **48** (1936) 772.

<sup>3</sup> Jü and BEEVERS: loc. cit.

and BEEVER's data and one with curves of similar shape and giving  $F(hki0)$  values about the sum of  $f_{Ca}$  and  $2f_{Cl}$  for strong reflections was drawn. From this chart a set of preliminary values of  $F(hki0)$  were read off. The signs of

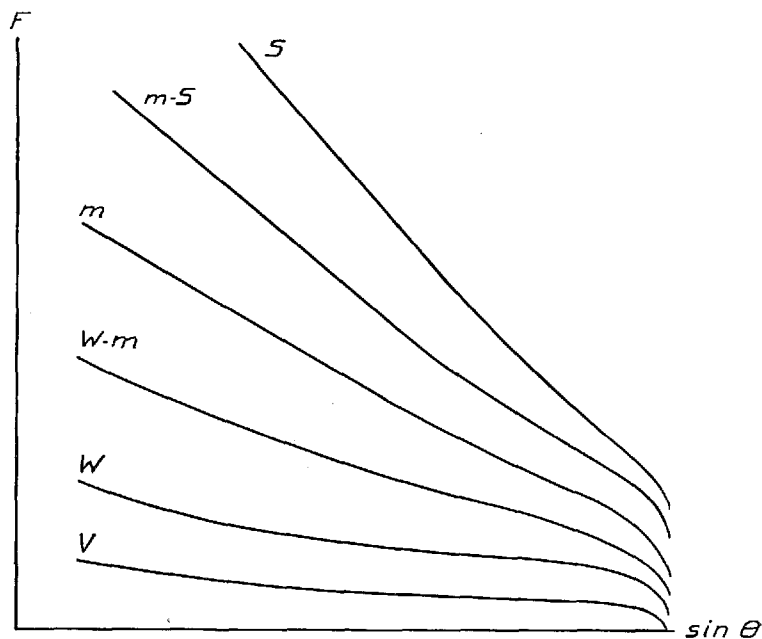


Fig. 1. Example of chart for converting spot intensity  $O$  into approximate "observed  $F$ ".

reflections with  $h-k = 3$  were  $+$ , and it was possible by comparing the  $CaCl_2 \cdot 6H_2O$  and  $SrCl_2 \cdot 6H_2O$  spot intensities to determine the signs of 5 more reflections unambiguously so that the signs and approximate  $F(hki0)$  values were known for 13 out of the registered 21 reflections. This list includes all reflections of higher intensity than weak.

Computation gave fig. 2 as a result.

Fig. 2 b shows the portion of the unit cell of which the density projection is shown in fig. 2 and the two following

figures. There is a concentration of matter around the Ca atom at the origin. The peaks marked *p* were taken to be the projection of the O-atoms. With the coordinates of these peaks:

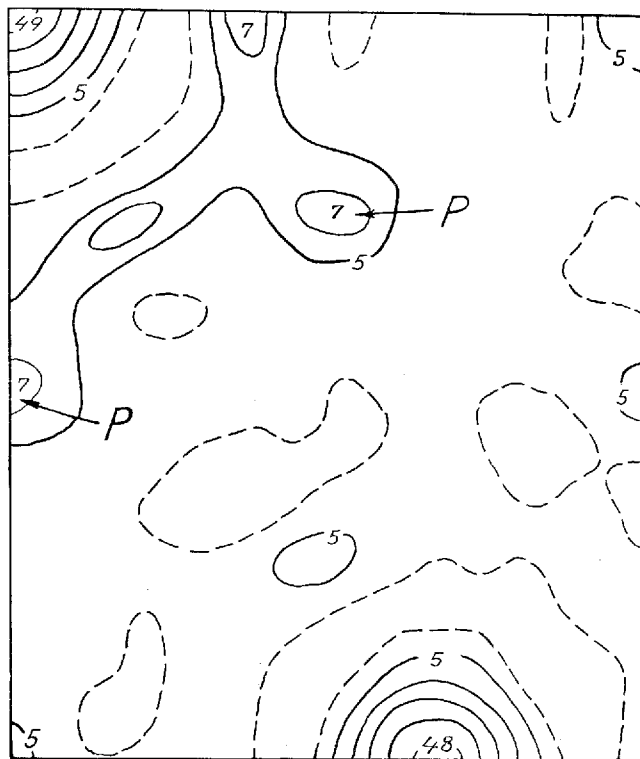


Fig. 2. Preliminary Fourier projection on a-b plane in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ .

0.25 etc. the O-contributions were calculated, *f* values from BRAGG and WEST<sup>1</sup>. These and all the following structure factor calculations were made with the hexagonal Structure Factor Fields by BRAGG, LIPSON and BEEVERS<sup>2</sup>, to whom

<sup>1</sup> BRAGG and WEST: *Z. f. Krist.* **69** (1928) 139.

<sup>2</sup> W. L. BRAGG: *Nature* **138** (1936) 362. BEEVERS and LIPSON: *Proc. Phys. Soc.* **50** (1938) 275.

the author is indebted for permission to use their tables in manuscript.

The calculated  $F_s$  agreed well with the observed intensities. The new values were plotted as in fig. 1, a new family of curves drawn and new values of  $F(hki0)$  were read off from the chart.

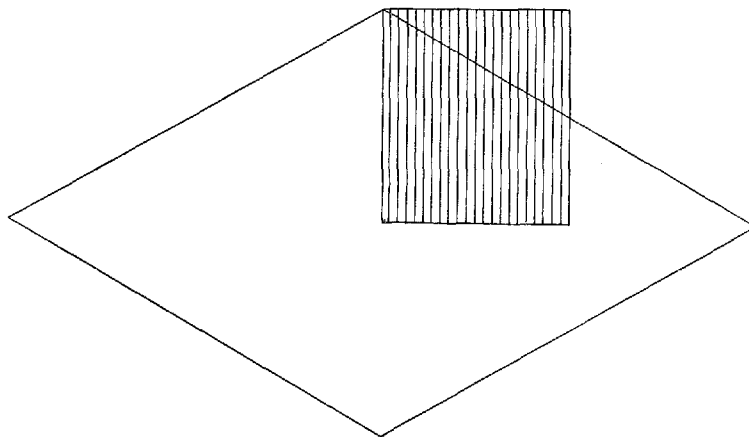


Fig. 2b. a-b plane in the hexagonal unit cell. The shaded area is the area of projection in a-b syntheses.

The signs of the eight reflections omitted in the first synthesis were now taken as the sign of the  $F$ 's calculated with O-contribution from an atom at 0.25. A new synthesis shown in fig. 4 was performed.

It is a marked improvement on fig. 3. The ring around the Ca atom is lower. The O peaks are clearer. Their coordinates are still 0.25 etc.

The agreement between calculated and "observed"  $F_s$  (from the second chart) is excellent.

In the same way fig. 4 was obtained from the  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  prism zone intensities. The O peak has shifted from 0.25 to 0.28<sub>4</sub> in accord with the larger radius of the  $\text{Sr}^{++}$  ion.

When comparing the oxygen parameters found with the atomic positions of the space group  $D_{3d}^3 - \bar{C}3m1$  it is seen that they correspond to one of the six-fold positions (g) and

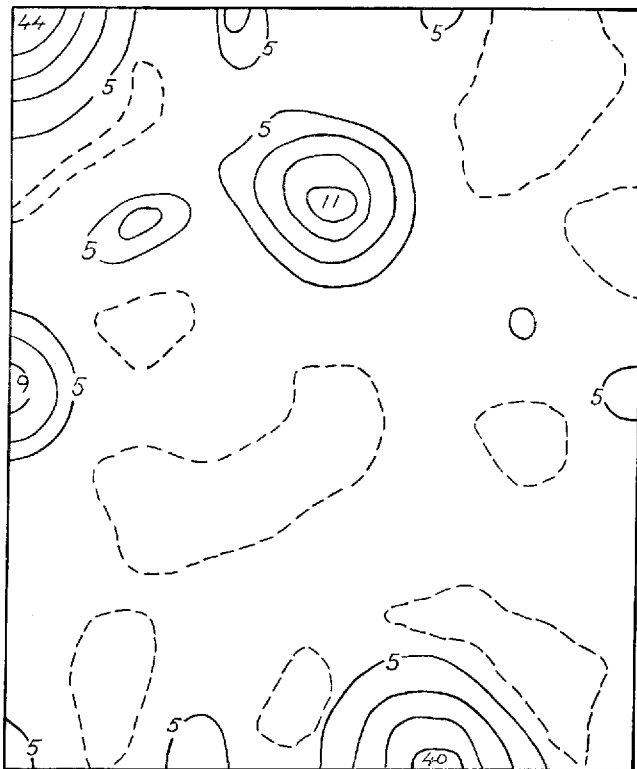


Fig. 3. Improved projection on a-b plane in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ .

(h) which are plane hexagons. They are both impossible with the parameters found, as they give O—O distances of 1,96 Å in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  and 2,23 in  $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$ . This rules out the space group  $D_{3d}^3 - \bar{C}3m1$ . A projection of  $C_{3v}^1 - C3m1$  on the x—y plane will have no center of symmetry at the origin. If the structure is framed upon  $C_{3v}^1 - C3m$  the “observed projection” will not be a true image of the

atomic arrangement. Still, when most of the scattering matter in the unit of projection is centrosymmetrical (as in this case Sr and 2Cl) it may be interpreted. The centro-

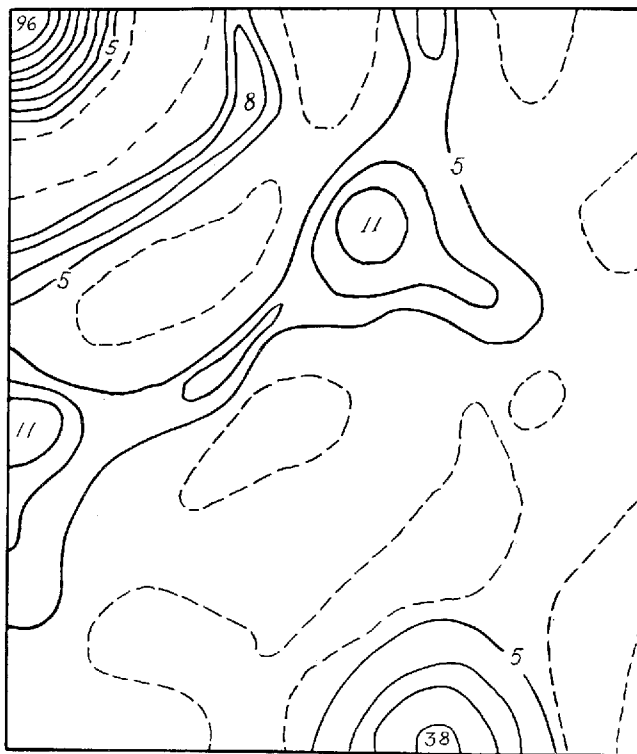


Fig. 4. Final projection on a-b plane in  $\text{SrCl}_2, 6 \text{H}_2\text{O}$ .

symmetrical peaks (Sr and 2Cl) will appear in their proper positions, and to a very good approximation instead of an acentric peak at  $xy$  there will appear in the projection two peaks at  $xy$  and  $\bar{x}\bar{y}$ . These peaks will be of half the height of the true peak.

Three-fold positions (d) for Oxygen are ruled out because they would produce peaks on the line  $xx$ , and in the projections the O peaks appear on the line  $xo$ .



The six-fold position (e) which is plane is excluded by space considerations. It would lead to too small O-O distances as would the plane six-fold positions of  $D_{3d}^3 - C\bar{3}m1$ . The remaining possibilities are the  $D_3^2 - C321$  or an arrangement not based on space group principles.

### Projection on $11\bar{2}0$ .

The same chart as before was used to give a set of preliminary F's. As for the signs of the F's it is + for all the stronger reflections because of the heavy Sr atom at the origin.

The reflections of doubtful sign were treated in the following way. A curve was drawn of  $A = f_{\text{Sr}} - (2f_{\text{Cl}} + 6f_0)$  as a function of  $\sin \theta$ . All reflections the preliminary F's of which were larger than A at the same value of  $\sin \theta$  were taken to be positive. Of the observed 49 reflections the sign of 12 could not be determined by this procedure, they include some reflections of low order up to medium strength but the remnant 37 reflections including all the strong ones were thought to be sufficient to determine the Cl parameters unambiguously even if the signs of a few were wrong. The Cl atom in fact gave rise to a clear peak at  $xz = \frac{1}{3} \cdot 42$ . Oxygen peaks could not be identified. A new synthesis was performed in which 47 reflections were included. The Cl parameter remained unchanged. The background showed no reasonable peaks.

It was conjectured that some of the intensities were wrong because the photographs were taken with a crystal with developed faces. A new set of photographs was taken. With F's from the new spot intensities a synthesis was performed in which only 35 F's were included in order not to introduce the Cl parameter obtained from a set of intensities a number of which were wrong.

The Cl atom remained at  $\frac{1}{3} \cdot 42$ . The background was somewhat reduced. In a new synthesis the remaining F's were included. It is given in fig. 5.

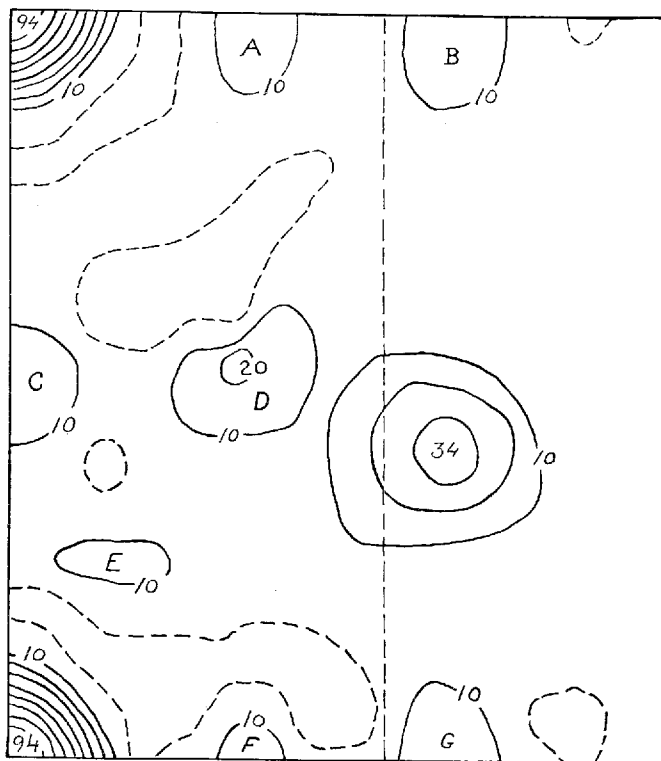


Fig. 5. Projection on  $11\bar{2}0$  plane in  $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$ . All preliminary F's included.

Fig. 6 shows a synthesis of the calculated F's from an arrangement of a Sr at the origin and 2 Cl atoms at  $\frac{1}{3} \cdot 42$  and  $\frac{2}{3} \cdot 58$ . It is remarkably similar to fig. 5.

A comparison of the two shows that most of the peaks in fig. 5 (of which most are rather small to represent atoms) are "ghosts". This applies to peaks marked A, E, F and to the left hand side of the big peak D.

The dotted line is drawn where the O atoms were expected to appear according to the C-axis projection. Other atoms should appear on the line connecting the Sr atoms.



Fig. 6. Projection on  $11\bar{2}0$  plane from calculated  $F$  values for an arrangement of  $\text{SrCl}_2$  with Sr at  $000$ , Cl at  $\frac{1}{2}, \frac{2}{3}, 0.42$  and  $\frac{2}{3}, \frac{1}{3}, 0.58$ .

There is a peak on the latter line at  $0, \cdot 50$ , but the corresponding peak at  $\cdot 28, \cdot 50$  is missing. There is a peak (right side of D) at the same  $Z$ , but nearer to the  $Z$ -axis. The coordinates are  $\cdot 24, \cdot 50$ .

Then there is another peak  $B+G$  at  $\cdot 33, \cdot 50$ . A corresponding peak at  $\cdot 00, \cdot 00$  is hidden behind the Sr peak.

Both of these "sets of peaks" might represent an amount

of scattering matter at six, or three points lying in a plane around the Z-axis.

These are the only possible atomic position for O and

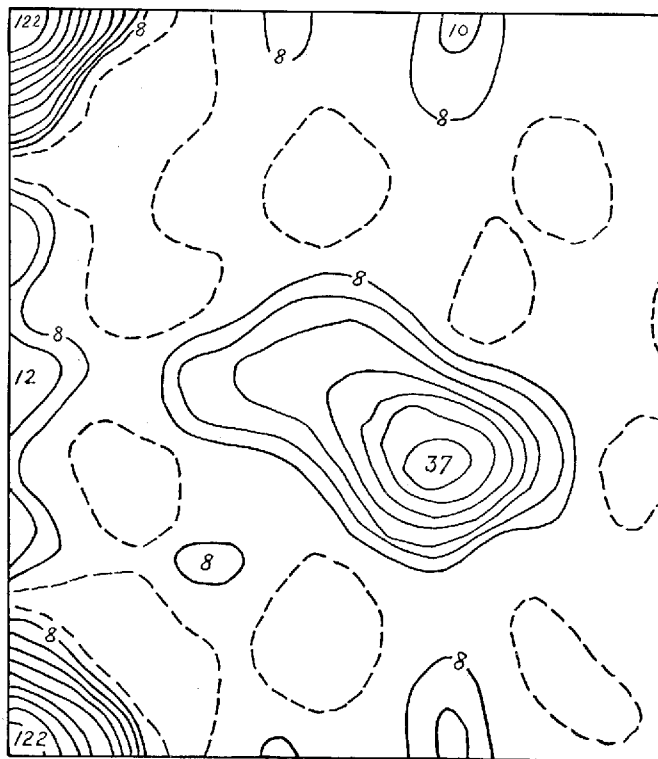


Fig. 7. Final projection on  $11\bar{2}0$  plane in  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ .

it is seen that an octahedral arrangement of O-atoms around Sr is impossible. If, however, we take the space group to be  $D_3^2 - C321$  we may put 3  $O_{(I)}$  atoms on (e)  $x00$  with  $x = \cdot 33$  and three  $O_{(II)}$  on (f)  $x0\frac{1}{2}$  with  $x = \cdot 24$ .

A comparison between "observed" F's and (not reproduced) F's calculated on this assumption showed a very good agreement, only the calculated F's were without

exception larger than the observed F's. The calculated F's were plotted as described above, a new family of curves was drawn and a new set of F's obtained from the chart. From



Fig. 8. Projection on  $11\bar{2}0$  plane in proposed arrangement of  $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$ .  
From calculated F values.

this new set of observed F's an improved observed projection was obtained, shown in fig. 7. For comparison is given a projection of the proposed atomic arrangement on  $11\bar{2}0$  computed from the calculated F values (fig. 8.) The "observed projection" is seen to contain the appropriate number of peaks and "ghosts" and to a certain extent the same areas of "negative density" as the "calculated projection".

The new arrangement is not incompatible with the observed projection on the a-b plane, as its projection does not differ very much from it.

### Discussion of the structure and the powder photograph intensities.

The arrangement having no center of symmetry should, however, make the crystal as a whole piezoelectric in conflict with the experimental evidence. An attempt was therefore made to explain the structure as an intimate twinning of cells like those described and their mirror images. Space considerations permitted such a structure but it need not be described in detail since the subsequent evidence shows it to be incorrect. Such a statistical twinning of "right" and "left" units would give the same  $A(hkl)$  values as the acentric structure and the  $B(hkl)$  parts of the "right" and the "left" parts of the crystal would cancel out, and a crystal built upon it would of course show no electrically or optically acentric properties.

It is in agreement with the observed intensities from the  $oh\bar{h}l$  zone, for in this zone there are no  $B$  parts of the structure factors, and in the  $hki0$  zone the  $B$  parts are all small compared with the  $A$  parts, as they needs must be since the projection of the arrangement on the plane  $0001$  is very nearly centrosymmetrical. Only in a very few of the general  $hkil$  reflections is  $B^2$  of the order of magnitude of  $A^2$  and only in one, i. e. the reflection  $11\bar{2}1$ , is  $B^2$  much larger than  $A^2$ . Here  $A$  is 2,6.  $B$  has the very large value of 28,4 corresponding to a line of medium strength at this part of the diagram. The line  $11\bar{2}1$  is registered on the powder photograph with medium strength, so the acentric

Table 3.  
Comparison between calculated and observed intensities.

hkil	$\sin^2 \theta$	calc. int.	obs. int.	hkil	$\sin^2 \theta$	calc. int.	obs. int.
$10\bar{1}0$	.0197	51.0	m-S	$23\bar{5}0$	.3749	.6	O
0001	.0553	.3	O	$30\bar{3}2$	.3988	7.8	m
$11\bar{2}0$	.0592	38.0	m-S, S	4150	.4143	7.5	m
$10\bar{1}1$	.0750	39.0	S	$23\bar{5}1$	.4302	8.1	m
$10\bar{1}\bar{1}$							
$20\bar{2}0$	.0789	1.2	O	2242	.4579	2.2	W
$11\bar{2}1$	.1145	14.6	m	$41\bar{5}1$	.4696	.4	O
$20\bar{2}1$							
$20\bar{2}\bar{1}$	.1342	29.0	S	$31\bar{4}2$	.4776	3.7	W-m
$21\bar{3}0$							
$30\bar{3}0$	.1381	3.8	V	$31\bar{4}2$	.4932	.7	O
$21\bar{3}1$	.1776	25.0	m-S	5050	.4932	.7	O
$21\bar{3}\bar{1}$	.1934	40.3	S	0003	.4977	.2	O
0002							
$30\bar{3}1$	.2212	6.1	W-m	$10\bar{1}3$	.5174	1.5	W
$30\bar{3}\bar{1}$							
$22\bar{4}0$	.2329	3.2	W	$10\bar{1}3$	.5327	2.7	W
$10\bar{1}2$	.2367	5.2	W	$40\bar{4}2$	.5368	2.4	W
$10\bar{1}\bar{2}$							
3140	.2409	6.7	W-m	$50\bar{5}1$	.5485	1.6	V
1122							
$22\bar{4}1$	.2564	2.7	W	$50\bar{5}\bar{1}$	.5524	0.4	O
$20\bar{2}2$	.2804	3.6	W	2460	.5524	0.4	O
$20\bar{2}\bar{2}$	.2920	.5	O	1123	.5569	1.7	O
$20\bar{2}2$	.3001	4.0	W, W-m	$20\bar{2}3$	.5766	2.0	V
$20\bar{2}\bar{2}$							
$31\bar{4}1$	.3117	9.8	m	$20\bar{2}\bar{3}$	.5880	1.2	V
$31\bar{4}\bar{1}$							
$40\bar{4}0$	.3156	1.5	O	$23\bar{5}2$	.5961	2.1	V
$21\bar{3}2$							
$21\bar{3}\bar{2}$	.3593	4.1	W, W-m	$23\bar{5}\bar{2}$	.6077	5.3	W-m
$40\bar{4}1$							
$40\bar{4}\bar{1}$	.3709	2.2	W	$24\bar{6}1$	.6077	5.3	W-m
$40\bar{4}\bar{1}$							
				$24\bar{6}\bar{1}$	.6116	.7	O
				5160			

C321 structure is correct. If the twinned structure had been right the line should have been absent because a structure factor of 2,6 is negligible here. As the final proof of the correctness of the proposed structure is given in table 3 a comparison between intensities on the powder photograph

and the calculated values for the structure up to as high values of  $hkil$  as the figure fields contain.

These intensities were not employed in the derivation of the structure, but they give the most direct test of its correctness.

### Description of the structure.

The structure arrived at is:

Space group:  $D_3^2 - C321$

1 Sr in (a) 000

2 Cl in (d)  $\frac{1}{3} \frac{2}{3} z$   $\frac{2}{3} \frac{1}{3} \bar{z}$  with  $z = .42$

3 O<sub>(I)</sub> in (e)  $x00$   $0x0$   $\bar{x}\bar{x}0$  with  $x = .33$

3 O<sub>(II)</sub> in (f)  $x0\frac{1}{2}$   $0x\frac{1}{2}$   $\bar{x}\bar{x}\frac{1}{2}$  with  $x = .24$

Fig. 9 depicts the structure projected on 0001.

Table 4.

Interatomic distances in  $SrCl_2 \cdot 6H_2O$ .

Sr—Sr (c-axis) . . . .	4.108 Å
Sr—Sr (a-axis) . . . .	7.940 „
Cl <sub>1</sub> —Cl <sub>1</sub> = Cl <sub>2</sub> —Cl <sub>2</sub>	4.108 „
Cl <sub>1</sub> —Cl <sub>2</sub> . . . . .	4.64 „
Sr—Cl <sub>1</sub> . . . . .	4.90 „
Sr—Cl <sub>2</sub> . . . . .	5.17 „
Sr—O <sub>1</sub> . . . . .	2.62 „
Sr—O <sub>2</sub> . . . . .	2.80 „
Cl—O <sub>1</sub> . . . . .	3.17 „
Cl—O <sub>2</sub> . . . . .	3.10 „

The interatomic distances within the unit cell are given in table 4. All distances Cl—Cl, Sr—Sr and Sr—Cl are much larger than the sums of the corresponding ionic radii.



It is, however, noteworthy that the distance Sr — Sr along the C-axis 4,108 is about twice the atomic radius of uncharged Sr.

Even if this distance cannot be regarded as a contact it is a very small distance compared with the closest Sr — Cl

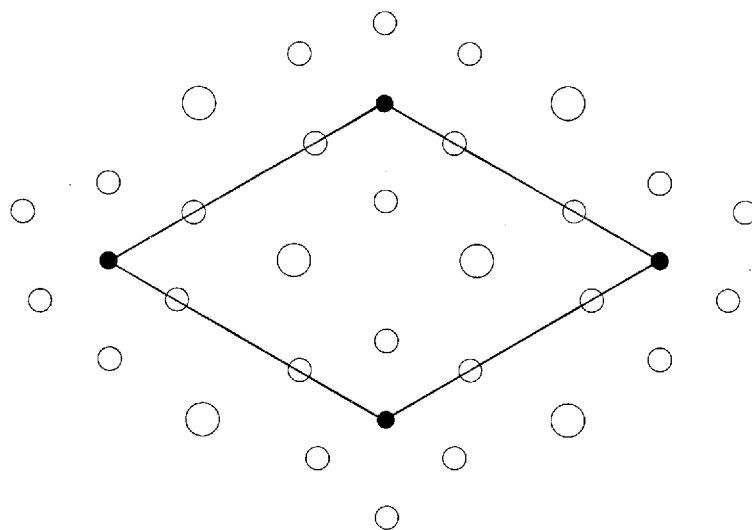


Fig. 9.  $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$  unit cell and some adjacent atoms projected on 0001.

distance and with the distance between a Sr atom and the nearest Sr in the a-b plane. Sr-O and Cl-O seem to be actual contacts. The distances are nearly the sum of the ionic radii and the radius of action of the water molecule as given by BRAGG<sup>1</sup>:

$$r_{\text{H}_2\text{O}} + r_{\text{Sr}^{++}} = 2 \cdot 65$$

$$r_{\text{H}_2\text{O}} + r_{\text{Cl}^-} = 3 \cdot 19.$$

The deviation from these distances are:

<sup>1</sup> W. L. BRAGG: "Atomic Structure of Minerals". Oxford Univ. Press 1937 p. 261.

$\text{H}_2\text{O}$  to  $\text{Sr}^{++}$ :  $+\cdot 16 \text{ \AA}$  and  $-\cdot 03 \text{ \AA}$

$\text{H}_2\text{O}$  to  $\text{Cl}^-$ :  $+\cdot 02 \text{ \AA}$  and  $-\cdot 09 \text{ \AA}$

and they do not seem serious.

The environments of the  $\text{H}_2\text{O}$  molecules are in agreement with their dipole character. The negatively charged

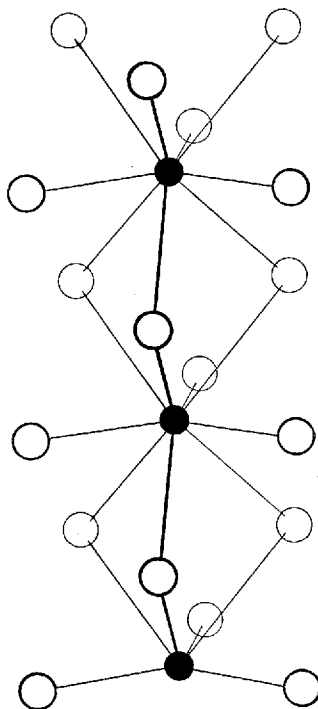


Fig. 10.  $\text{Sr} - \text{H}_2\text{O}$  column.

neighbours are on one side of the molecules, the positively charged ones on the opposite side.

The two kinds of oxygen atoms correspond roughly in environments to the two types of water molecules proposed by BERNAL and FOWLER<sup>1</sup>.  $\text{O}_1$  is "tetrahedral" and  $\text{O}_2$  of the "planar" type.

<sup>1</sup> J. D. BERNAL and R. H. FOWLER: J. Ch. Phys. I, 515, (1933).

The Cl atoms are surrounded by O atoms which form a distorted octahedron. The Sr atoms have 9 O atoms as nearest neighbours.

The peculiar columns of Sr atoms and  $\text{H}_2\text{O}$  molecules which are found in the structure are shown in fig. 10.

### Summary.

The structure of  $\text{SrCl}_2, 6\text{H}_2\text{O}$  which is typical of the trigonal hexahydrates of alkali earth halides has been determined by the method of successive Fourier approximations. Sr is surrounded by nine O atoms. Three touching no other Sr atoms, and two equivalent sets of 3 O atoms, each set also touching an adjacent Sr atom.

The 3 O's touching one Sr are of the "planar" type, the others of the "tetrahedral" type.

The nearest neighbours of a Cl atom are 6 O atoms forming a flat distorted octahedron.

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