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# THE STRUCTURE OF $SrCl_2, 2H_2O$

BY

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# INTRODUCTION

The salt hydrates in which both cation and anion are noble gas ions would form the best basis for a simple discussion of the chemical forces operating in solid hydrates. So far, only a few of such hydrates have been completely investigated by the methods of X-ray crystallography. The structures of the following compounds seem to be well established: $AlCl_3, 6H_2O$[1] with which $CrCl_3, 6H_2O$ is isomorphous, $MgCl_2, 6H_2O$ and the isomorphous bromide[2], $SrCl_2, 6H_2O$, and a long series of isomorphous Ca, Sr and Ba halide hexahydrates[3], the tetragonal mixed crystal of carnallite $KMgCl_3, 6H_2O$, and brom-carnallite $KMgBr, 6H_2O$[4]. In these hexahydrates the bi- or trivalent cations are completely surrounded by water molecules.

The atomic arrangement in a hydrate in which the number of water molecules per cation is so small that direct contact between cation and anion can be expected is of some interest. It shows whether the structure is in agreement with BERNAL and FOWLER's[5] ideas concerning the coordination of water molecules, a theory which has previously been confirmed by the present author in the case of hexahydrates.

## The Crystallography of $SrCl_2, 2H_2O$ and Related Compounds.

$SrCl_2, 2H_2O$ crystallizes from aqueous solutions at temperatures above 66.5°. Below that temperature, $SrCl_2, 6H_2O$ is the stable hydrate[6]. When crystallized from a hot aqueous solution

[1] K. R. ANDRESS and C. CARPENTER: Z. Krist. **A 87** (1934) 446.
[2] K. R. ANDRESS and J. GUNDERMANN: Z. Krist. **A 87** (1934) 345.
[3] A. TOVBORG JENSEN: D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVII, 9 (1940).
[4] K. R. ANDRESS and O. SAFFE: Z. Krist. **A 101** (1939) 451.
[5] D. BERNAL and R. H. FOWLER: J. chem. Phys. **1** (1933), 515.
[6] TILDEN: J. Chem. Soc. **45** (1884), 269.

it appears according to the author's experience as thin fragile plates. According to WULFF and HEIGL[1], the crystals show double refraction, they are "biaxial and non-orthogonal". $SrCl_2, 2\,H_2O$ may also be prepared by precipitating a saturated solution of $SrCl_2, 6\,H_2O$ with concentrated HCl, or by dehydrating $SrCl_2, 6\,H_2O$ at a suitable water vapour tension. Powder specimens were prepared in the two last mentioned ways at several temperatures. They gave identical powder diagrams (i. e. identical apart from minor differences in intensity due to the fact that $SrCl_2, 2\,H_2O$ precipitated by HCl forms thin flaky crystals, while prepared by dehydration it shows no developed faces). The correct composition of all preparations was ascertained by titration with $AgNO_3$. The powder diagrams could be indexed with the lattice constants found on single crystals prepared in the first mentioned way. Hence, all three methods of preparation led to identical hydrates.

$SrCl_2, 2\,H_2O$ is neither isomorphous with $CaCl_2, 2\,H_2O$ nor with $BaBr_2, 2\,H_2O$, since these compounds showed totally different powder diagrams. Nor is it isomorphous with $BaCl_2, 2\,H_2O$, as may be seen by comparing its cell dimensions with those of $BaCl_2, 2\,H_2O$ (cf. NARÁY-SZABÓ and SASVÁRI[2]). Moreover, the mixed crystals of $BaCl_2, 2\,H_2O$ and $BaBr_2, 2\,H_2O$ are of a fifth type, as follows from the crystallographic data for $BaBr_2, 2\,H_2O$ and $Ba(Cl, Br)_2, 2\,H_2O$[3]. Powder diagrams of these compounds were also taken and were found to lack any resemblance to each other.

Some attempts to prepare mixed crystals of $SrCl_2, 2\,H_2O$ and $BaCl_2, 2\,H_2O$ (LEHMANN's „Kristalle ähnlich den wasserärmeren von Chlorbarium, doch weit schöner ausgebildet, somit wahrscheinlich isomorphe Mischungen"[4]), which might have been useful for the determination of the structure of $BaCl_2, 2\,H_2O$ by Fourier methods proved quite unsuccessful. Crystallization by evaporation or cooling of solutions containing 5 mols of $SrCl_2$ to 1 mol of $BaCl_2$ always gave ordinary crystals of $BaCl_2, 2\,H_2O$ which, in semi-quantitative analyses, were found to contain far less than 5 per cent of $SrCl_2, 2\,H_2O$. It may be mentioned on

[1] Z. Krist. 77 (1931), 99.
[2] Z. Krist. 97 (1937), 235—37.
[3] Gmelins Handb. 30, Ba, 225 and 235.
[4] Z. Krist. 8 (1884), 451.



this occasion that LEHMANN described his experiments but briefly, and they seem, moreover, to have been made in a somewhat casual way. His observations are not completed by quantitative optical or chemical data; but they only inform us of what the microscope reveals.

From the information collected above it is obvious that the problem is of a perplexing diversity as compared, for instance, with the hexahydrates of the same alkaline earth halides.

## Determination of Crystal System, Unit Cell, and Space Group of $SrCl_2, 2\,H_2O$.

The single crystals of $SrCl_2, 2\,H_2O$ prepared by evaporation from a solution at 80° were thin plates and presented no other crystallographic elements. They were far from perfect, since they had to be broken off, removed from the mother liquor, and wiped with filter paper as rapidly as possible, because while cooling the adhering mother liquor solidifies to a mass of hexahydrate crystals.

Of a plate of $SrCl_2, 2\,H_2O$ 80 KV Laue photographs were taken with the primary beam perpendicular to the developed face. The diagram, plate I, Fig. 1, shows that a plane of symmetry is present in the crystal. Another diagram was taken with the primary beam perpendicular to the plane of symmetry found. The diagram, plate I, Fig. 2, shows a twofold axis, only. Hence, the crystal belongs to the monoclinic system with the b-(ortho)axis parallel to the developed face. A small fragment of the crystal was mounted on the goniometer head and was orientated with the b-axis as axis of rotation by aid of a number of Laue-photographs. From oscillation photographs, the length of the b-axis was found to be 6.44 Å. The h0l plane of the reciprocal lattice was constructed[1] by means of a Weissenberg diagram.

From the reciprocal net the crystal lattice dimensions were found to be $\beta = 72°$[2], b = 3.33 Å, a = 5.87 Å. According to WULFF and HEIGL (loc. cit.) d = 2.6715. This gives Z = 0.996.

[1] The Bernal reciprocal lattice. Proc. Roy. Soc. A 113 (1926) 117.
The diagrams were taken with a Buerger-Weissenberg goniometer. Z. Krist. A 94 (1936) 87—99.
[2] The angles between the reciprocal axes were taken to be > 90°. Hence, all indexes and fractional coordinates refer to a cell with $\beta = 72°$.

A h11 Weissenberg photograph revealed that the $a$ and $c$ axes were twice the axes first obtained, and the number of mols in the true unit cell must be 4. The h11 and h21 nets were constructed from Weissenberg diagrams, and the following reflections were found to be present:

$$\left.\begin{array}{lll} \text{in} & \text{h0l} & \text{h} = 2\text{n},\ \text{l} = 2\text{n} \\ & \text{h1l} & \text{h}+\text{l} = 2\text{n}+1 \\ & \text{h2l} & \text{h}+\text{l} = 2\text{n} \end{array}\right\} \text{h}+\text{k}+\text{l} = 2\text{n}.$$

With the axes chosen, the lattice is body-centered. The condition $h+k+l = 2n$ was also fulfilled in the hk0 and the hk1 Weissenberg diagrams, and in the powder diagrams. Cu-radiation was used for the Weissenberg diagrams, Cr-radiation for the powder diagrams. The space group has glide planes with the translations a, c, and n. Conventionally, a is included in its symbol, but not c or n, which with the axes mentioned above leads to the following orientated space groups for $SrCl_2, 2\,H_2O$:

$I\,2/a\,(C_{6h}^2)$ which is centrosymmetrical and
$I\,a\,(C_S^4)$ which is not centrosymmetrical.

The complete structure shows that $I\,a\,(C_S^4)$ is the correct space group.

## Bragg-Fourier projection on 010.

The visually estimated intensities from 48 reflections on the h0l diagram were employed in the usual way[1] to give a projection of the structure on 010 (Figs. 3 and 4). The unit area contains only one mol of $SrCl_2, 2\,H_2O$ and, since the Sr atom with 38 of the total of 92 electrons is per definitionem at the origin of the projection to be calculated, all reflections stronger than "very weak" could safely be assumed to be positive. The unit of projection (of which

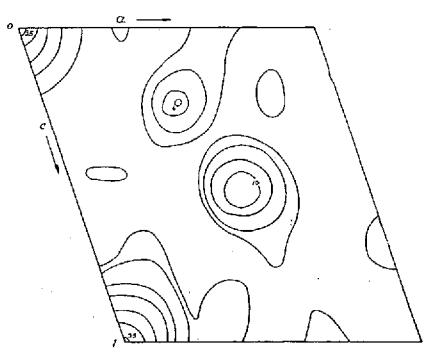


Fig. 3. Bragg-Fourier projection on 010 in $SrCl_2, 2\,H_2O$.

[1] Cf. $SrCl_2, 6\,H_2O$. D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVII. 9. 1940.



Fig. 3 is the left half) contains—apart from the heavy atom at the origin, which was assumed in order to determine the signs of the F's—two medium and two light atoms, in accordance with the formula $SrCl_2, 2\,H_2O$. The knowledge of this formula has, however, nowhere been applied to the calculations. The peaks are practically circular; moreover, the number of peaks is correct and their relative heights are reasonable. This shows that the atomic arrangement when projected on 010 is centrosymmetrical or at least very close to it with the origin as center of symmetry. However, it will be shown later that the centrosymmetry does not extend to the spatial arrangement of the atoms. The x- and z-coordinates referring to the unit of projection are

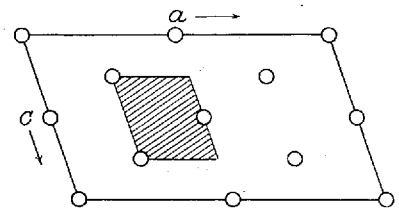


Fig. 4. Symmetry elements in 010 projection of $SrCl_2, 2\,H_2O$. The density was calculated in the shaded area, only.

| | | |
|---|---|---|
| Cl | x = 0.287 | z = 0.510 etc. |
| O | x = 0.226 | z = 0.240 etc. |

and referring to the larger unit cell with Sr at $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$ as has been chosen later

| | | |
|---|---|---|
| Cl | x = 0.106 | z = 0.005 |
| O | x = 0.137 | z = 0.130. |

Table 1 shows the very satisfactory agreement between calculated and observed intensities.

As should be expected, the lowest orders of reflection from the only developed face, (100), are registered with an abnormally high intensity.

If the structure had been based on the space group $I\,2/a$ $(C_{2h}^6)$ it would have been determined by 3 Cl parameters, 3 O parameters, and one or no Sr parameter[1].

Of these six or seven parameters, four were accurately known from the Fourier synthesis. Numerous attempts were now made

[1] Cf. Intern. Tabellen z. Best. v. Kristallstrukturen p. 102, where the orientation, however, is C 2/c.

Table 1.

Calculated and observed intensities in the h0l zone of $SrCl_2, 2\,H_2O$.

| hl | sin | obs. int. | calc. int. | hl | sin | obs. int. | calc. int. |
|---|---|---|---|---|---|---|---|
| 20 | 0.14 | s | 65 | 46 | 0.70 | w-m, m | 12 |
| 22 | 0.22 | m-s | 24 | 06 | 0.72 | 0 | 0.6 |
| 02 | 0.24 | w | 1.0 | $6\bar{4}$ | 0.72 | w-m | 7.4 |
| 40 | 0.28 | w, w-m | 0.6 | 104 | 0.73 | 0 | 0 |
| 42 | 0.30 | m-s, s | 62 | 86 | 0.76 | 0 | 0.2 |
| $2\bar{2}$ | 0.31 | m-s | 55 | $2\bar{6}$ | 0.78 | v | 2.0 |
| 60 | 0.41 | s | 18 | $10\bar{2}$ | 0.79 | m, m-s | 9.4 |
| 62 | 0.41 | w-m, m | 10 | 122 | 0.79 | w-m | 2.9 |
| $4\bar{2}$ | 0.42 | m-s | 38 | 120 | 0.82 | w | 1.1 |
| 24 | 0.45 | w-m | 4.9 | 124 | 0.82 | w-m, m | 2.1 |
| 44 | 0.47 | w-m | 3.4 | 106 | 0.83 | w-m | 8.9 |
| 04 | 0.48 | m-s | 16 | $8\bar{4}$ | 0.83 | w, w-m | 4.8 |
| $6\bar{2}$ | 0.53 | 0 | 0.4 | $4\bar{6}$ | 0.85 | w-m | 8.0 |
| 64 | 0.53 | m-s | 17 | 126 | 0.92 | w-m | 10.3 |
| 82 | 0.53 | w-m, m | 3.2 | 68 | 0.93 | w-m | 6.4 |
| $2\bar{4}$ | 0.55 | w-m | 3.9 | 144 | 0.93 | m-s | 26 |
| 80 | 0.55 | m-s | 19 | $10\bar{4}$ | 0.93 | 0 | 0.5 |
| $4\bar{4}$ | 0.60 | 0 | 1.9 | 142 | 0.94 | 0 | 1.1 |
| 84 | 0.62 | w-m | 7.3 | $12\bar{2}$ | 0.96 | w-m, m | 13 |
| $8\bar{2}$ | 0.66 | 0 | 0.2 | 140 | 0.96 | w-m | 13 |
| 102 | 0.66 | m-s | 7.1 | 08 | 0.96 | w-m, m | 21 |
| 66 | 0.67 | 0 | 0.4 | 28 | 0.96 | 0 | 2.5 |
| 100 | 0.68 | v, 0 | 1.8 | 48 | 0.96 | 0 | 1.5 |
| 26 | 0.70 | w-m | 7.0 | 88 | 0.97 | w-m | 10 |

on the basis of these parameters and of space considerations to build up a structure of the crystal. However, all attempts were unsuccessful. It was not possible to find an arrangement which led to reasonable distances between the atoms. It was deemed necessary to find the still unknown parameters independently, thereby settling the question whether the higher or the lower space group is the true one.

## Patterson-Fourier projection on 001.

The material was a hk0 Weissenberg diagram. The tabulated intensities showed the expected symmetry properties of reflections



from Cmm. A set of approximate $F^2$'s was obtained from visually estimated spot entensities, and a Patterson synthesis was performed (Figs. 5 and 6). In order to interpret this vector diagram in terms of atomic coordinates, I 2/a and I a as well as their projections on 001 must be considered.

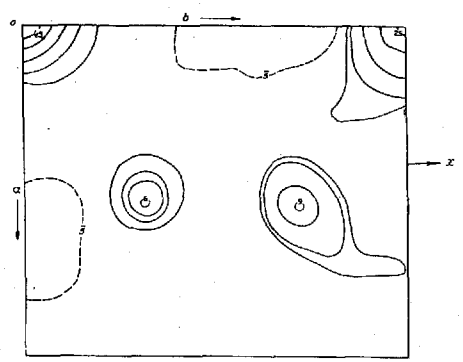


Fig. 5. Patterson-Fourier projection on 001 in $SrCl_2, 2\,H_2O$.

I 2/a point positions: $\left(000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}\right)+$

4: (a) $000;\ 00\frac{1}{2}$ (b) $0\frac{1}{2}0;\ 0\frac{1}{2}\frac{1}{2}$

(c) $\frac{1}{4}\frac{1}{4}\frac{3}{4};\ \frac{3}{4}\frac{1}{4}\frac{3}{4}$ (d) $\frac{1}{4}\frac{1}{4}\frac{1}{4};\ \frac{3}{4}\frac{1}{4}\frac{1}{4}$

(e) $0y\frac{1}{4};\ 0\bar{y}\frac{3}{4}$

8: (f) $xyz;\ \bar{x}\bar{y}\bar{z};\ \bar{x}, y, \frac{1}{2}-z;\ x, \bar{y}, \frac{1}{2}+z.$

Its general point projects on 001 in

$$\left(00;\ \frac{1}{2}\frac{1}{2}\right)+xy;\ \bar{x}\bar{y};\ \bar{x}y;\ x\bar{y}$$

which is the general point of the plane group Cmm (Patterson: $C_{2v}^{IV}$)[1]

[1] Bragg and Lipson. Z. Krist. (A) **95** (1936) 238. Patterson ib. **90** (1935) 546.

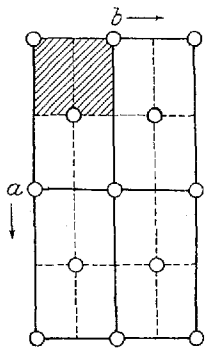


Fig. 6. Symmetry elements of 001 Patterson vector map.

Cmm contains the following special points

2: (a) $00; \frac{1}{2}\frac{1}{2}$ (b) $\frac{1}{2}\,0; 0\,\frac{1}{2}$

4: (c) $\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}$

(d) $x0; \bar{x}0; \frac{1}{2}+x, \frac{1}{2}; \frac{1}{2}-x, \frac{1}{2}$

(e) $0y; 0\bar{y}; \frac{1}{2}, \frac{1}{2}+y; \frac{1}{2}, \frac{1}{2}-y.$

(d) is not a projection of a four-fold position in the space group I 2/a. The interatomic vectors (Patterson peaks) corresponding to (a) and (b) are at 00 and $\frac{1}{2}\frac{1}{2}$. The Patterson peaks, corresponding to (c), (d), and (e), are shown in Fig. 7.

Apart from the very large peaks at 00 and $\frac{1}{2}\frac{1}{2}$ which must always be present, the Patterson projection Fig. 5 shows a large peak at $x = 0$ $y = \frac{1}{2}$, about half the size of the 0 0 peak. This peak corresponds to the smaller peak in Fig. 5 (c)[1] and must be

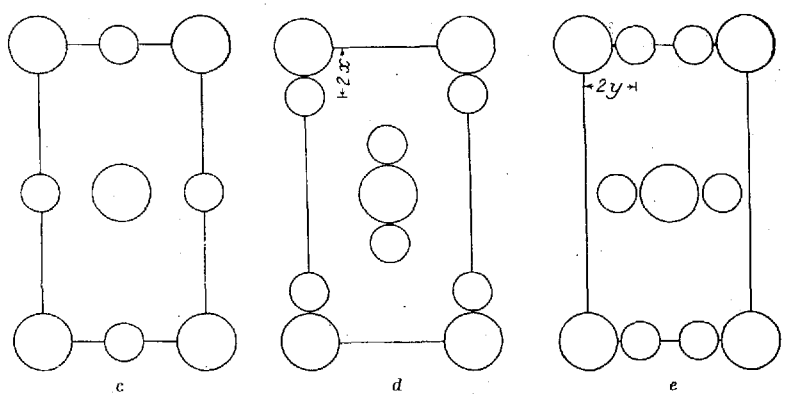


Fig. 7. Interatomic vectors (Patterson peaks) corresponding to the special positions (c), (d) and (e) in the plane group Cmm.

[1] It should be mentioned that Fig. 5 may also be interpreted as analogous to Fig. 7 (d) or (e) with the special value of $\frac{1}{4}$ of the variable parameter; however, this represents no new solution, but only a change of the origin of the coordinate system, even when the corresponding special positions in space (I 2/a) are considered.



the Sr — Sr peak. Still assuming the space group to be I 2/a, we have now to look for the next largest peaks which are due to interaction between 4 Sr at (c) and 8 Cl in the general position (f)

$$xy;\ \bar{x}y;\ x\bar{y};\ \bar{x}\bar{y};\ \frac{1}{2}+x, \frac{1}{2}+y;\ \frac{1}{2}-x, \frac{1}{2}+y;\ \frac{1}{2}+x, \frac{1}{2}-y;\ \frac{1}{2}-x, \frac{1}{2}-y$$

As possible coordinates for Cl, the special positions may be discarded, since they would lead to absurd atomic arrangements. The 64 interatomic vectors between (c) and (f) consist of 16 different sets of coordinates, every set occurring 4 times. The 16 peaks are situated as shown in Fig. 8. They form groups of four around the coordinates of the Sr atoms $\frac{1}{4}\frac{1}{4}$ etc., and they are displaced from $\frac{1}{4}\frac{1}{4}$ etc. by xy, $x\bar{y}$, $\bar{x}y$ and $\bar{x}\bar{y}$, respectively.

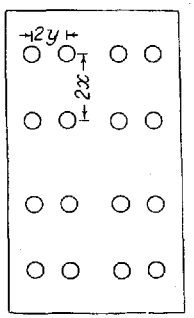


Fig. 8. Interatomic vectors between 4 atoms at $\frac{1}{4}\frac{1}{4}$ etc. and 8 at xy in Cmm.

The projection, Fig. 8, actually shows 16 peaks, much smaller than the Sr—Sr peaks, arranged in sets of four around $\frac{1}{4}\frac{1}{4}$ etc. These are the Sr—Cl peaks, situated at a distance of $x = 0.109$ and $y = 0.100$ from $\frac{1}{4}\frac{1}{4}$ etc. $x = 0.109$ $y = 0.100$ would be the Cl-coordinates in the unit cell, and $x = 0.100$ agrees well with $x = 0.106$ found independently by Fourier projection on 010.

The solution $xy = 0.11; 0.10$ is not the only one possible. $xy = 0.11; 0.40$ is another solution, but it corresponds to 0.11; 0.10 and a shift of the origin. So far, no objection to a structure built on the higher space group has been encountered. A set of calculated intensity contributions from Sr and 2 Cl with the coordinates found did not agree very well with the observed values. The non-included oxygen contributions were made responsible for this failure, and the calculated Sr + 2 Cl contributions were employed to determine the sign of the F (hko)'s; a Bragg-Fourier synthesis was performed which is reproduced in Fig. 7, although it represents a false track. It is interesting to note that the erroneous assumption of centrosymmetry appears in the projection. The peaks occur at other values of xy than expected,

they are badly shaped, and the background is very far from smooth.

What was expected when it proved impossible to find the y parameters by space considerations now becomes apparent, viz. the structure is definitely not based on I 2/a, and therefore the acentric group Ia has to be discussed.

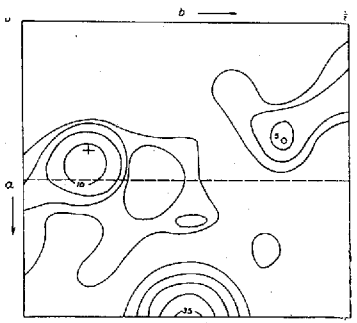

Fig. 9. Bragg-Fourier synthesis on 001 based upon the incorrect assumption of a centrosymmetrical space group. The large peak is a Sr atom. + indicates where the upper Cl peak should appear according to the 001 Patterson projection. The dotted line indicates where the 0 peak should be expected according to the 010 Bragg projection.

The group Ia has no special points and its general point is

$$xyz;\ x, \bar{y}, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}-y, z$$

which projects onto 001 in

$$xy;\ x\bar{y};\ \frac{1}{2}+x, \frac{1}{2}+y;\ \frac{1}{2}+x, \frac{1}{2}-y$$

the latter being the general point of the plane group Cm in the orientation C1m[1].

[1] Bragg and Lipson. Z. Krist. A **95** (1936) 327, Patterson. Z. Krist. A **90** (1935) 545. Patterson's table contains an error, viz. $\bar{x}, \bar{y}; \frac{1}{2}-x, \frac{1}{2}-y$, should read $\bar{x}, y; \frac{1}{2}-x, \frac{1}{2}+y$. Another error was found on p. 546. $C_{2v}^{II}$ (c) where $\bar{x}, y+\frac{1}{2}$ should read $\frac{1}{2}-x, \frac{1}{2}+y$. In view of the great applicability of the Patterson tables and because they have already been incorporated uncorrected into the handbook of Halla-Mark, the author ventures to draw the reader's attention to these errors.



A Sr atom in general position in C1m will give rise to the following interatomic peaks in a Patterson projection

| xy | Weight |
|---|---|
| 00 | $4z^2$ |
| $\frac{1}{2}\frac{1}{2}$ | $4z^2$ |
| $0, 2y$ | $2z^2$ |
| $0, \overline{2y}$ | $2z^2$ |
| $\frac{1}{2}, \frac{1}{2}+2y$ | $2z^2$ |
| $\frac{1}{2}, \frac{1}{2}-2y$ | $2z^2$ |

} Fig 7.

The positions of the large peaks in Fig. 5 also agree well with I a. $y_{Sr}$ is found to be $\frac{1}{4}$. In Ia, x and z for the first atom may be chosen at will, thereby fixing the origin of the coordinate system; taking $xz = \frac{1}{4}\frac{1}{4}$, we obtain the same set of coordinates for Sr as previously found in I 2/a. The special position (a) in the plane group C1m may be disregarded. It would give Sr—Sr peaks at 00 and $\frac{1}{2}\frac{1}{2}$ only, and the peak at $0\frac{1}{2}$ is too large to be due to interaction between Cl and Sr or Cl and Cl.

A Sr atom at $\frac{1}{4}\frac{1}{4}$ etc. and a Cl atom at the general point xy etc. give rise to 16 Patterson peaks of weight $2Z_{Sr}Z_{Cl}$ arranged in sets of four at distances of $x_{Cl}y_{Cl}$, $\bar{x}_{Cl}y_{Cl}$, $x_{Cl}\bar{y}_{Cl}$, $\bar{x}_{Cl}\bar{y}_{Cl}$ from $\frac{1}{4}\frac{1}{4}$ etc. The 16 peaks of secondary size found in the Patterson synthesis were—when I 2/a was discussed—interpreted as interatomic peaks from 4 Sr at $\frac{1}{4}\frac{1}{4}$ etc., and 8 Cl at xy etc. (Cmm). In Ia, they must be considered to be superpositions of 2 sets of 16, each set originating from the interaction of 4 Sr at $\frac{1}{4}\frac{1}{4}$ etc., and Cl at xy etc. in Cm. Any one of the 16 peaks in Fig. 3 is at distances of 0.14, 0.15 from $\frac{1}{4}\frac{1}{4}$ etc. This leads to the following 4 equations for $x_{Cl}$

$$\left.\begin{array}{ll} \frac{1}{4}-x & \frac{1}{4}+x \\ \frac{3}{4}-x & \frac{3}{4}+x \end{array}\right\} = 0.14$$

but only x = 0.11 and 0.39 are independent solutions. In y, all four solutions are independent. y = 0.90; 0.10; 0.40; 0.60. From

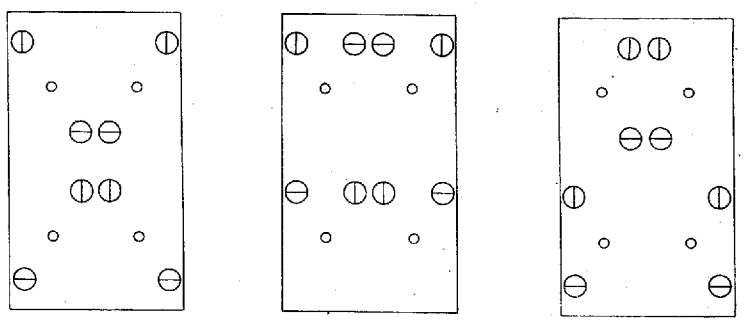

Fig. 10. The three projections of Sr and Cl on 001 according to a Patterson-Fourier synthesis.

○ Sr ⊕ $Cl_I$ ⊖ $Cl_{II}$

(a) is the Cmm solution previously discarded, in (b) both axes are divided by 2, only (c) is possible.

these equations, the coordinates of $Cl_I$ and $Cl_{II}$ are determined. If mirror images etc. are eliminated, the number of independent solutions (atomic arrangements) is reduced to 3 shown in Fig. 10.

(a) is the Cmm solution previously found to be incorrect. In (b) the cell is no longer primitive, both axes are halved so this solution cannot be correct; it would mean that all reflections with h and k odd were due to oxygen atoms only, which is not the case, since a number of them are fairly strong.

(c) is the only remaining possibility. The Cl contributions were calculated according to (c).

$$Cl_I \; xy = 0.11 \; 0.10$$
$$Cl_{II} \; xy = 0.39 \; 0.10$$

Structure factor for Clm: $A = 4 \cos 2\pi hx \cos 2\pi ky$

$B = 4 \sin 2\pi hx \cos 2\pi ky$



and they were found to be a very definite improvement of the Cmm solution. All more striking discrepancies were removed.

The new arrangement agrees with the Cl parameter x = 0.106 from the 010 projection just as satisfactorily as did the discarded one.

The Patterson diagram Fig. 5 can also yield some information as to the O coordinates. According to the projection on 010 $x_0 = 0.14$. Sr—O peaks in the Patterson diagram should be

Table 2.

Calculated and observed intensities in the hko zone of $SrCl_2, 2\,H_2O$.

| hk | sin | obs. int. | calc. int. | hk | sin | obs. int. | calc. int. |
|---|---|---|---|---|---|---|---|
| 20 | 0.14 | vs | 65 | 93 | 0.73 | v | 0 |
| 11 | 0.14 | v, w | 3.4 | 06 | 0.73 | m-s | 10.4 |
| 31 | 0.24 | m-s | 6.2 | 26 | 0.74 | w-m, m | 2.7 |
| 02 | 0.26 | m-s | 11 | 84 | 0.75 | w, w-m | 0.5 |
| 40 | 0.28 | w-m | 0.9 | 111 | 0.77 | w-m, m | 1.1 |
| 22 | 0.29 | s | 29 | 75 | 0.78 | w-m | 1.2 |
| 13 | 0.38 | 0 | 0 | 46 | 0.78 | 0 | 0.1 |
| 42 | 0.38 | s | 27 | 120 | 0.83 | w-m | 1.0 |
| 51 | 0.38 | v | 0.2 | 66 | 0.84 | m | 4.1 |
| 33 | 0.42 | w | 0.3 | 113 | 0.84 | v | 0.1 |
| 60 | 0.41 | vs | 17 | 17 | 0.85 | 0 | 0 |
| 62 | 0.49 | m-s | 5.6 | 104 | 0.85 | m-s, s | 5.1 |
| 04 | 0.49 | w | 0 | 122 | 0.86 | m-s | 4.3 |
| 71 | 0.50 | m, m-s | 2.5 | 95 | 0.87 | v | 0.3 |
| 24 | 0.51 | m-s | 7.8 | 37 | 0.88 | w | 0 |
| 53 | 0.53 | 0 | 0 | 86 | 0.91 | s | 9.9 |
| 80 | 0.55 | s, vs | 19.3 | 131 | 0.91 | w-m, m | 0.7 |
| 44 | 0.56 | s | 18.8 | 57 | 0.92 | 0 | 0 |
| 82 | 0.60 | m | 2.5 | 08 | 0.96 | m-s | 10.5 |
| 15 | 0.62 | w-m | 0.1 | 140 | 0.96 | m-s | 14.4 |
| 73 | 0.62 | v | 0.2 | 133 | 0.96 | 0 | 0 |
| 91 | 0.63 | w-m | 0.5 | 124 | 0.96 | m-s | 11.3 |
| 64 | 0.64 | w-m, m | 2.8 | 77 | 0.97 | 0 | 0 |
| 35 | 0.64 | v | 0.9 | 115 | 0.97 | w-m | 3.1 |
| 100 | 0.70 | w, w-m | 1.6 | 142 | 0.98 | m-s | 7.8 |
| 55 | 0.70 | v | 0 | 28 | 0.98 | m-s | 9.1 |
| 102 | 0.73 | m-s | 3.7 | | | | |

Table 3.

Atomic parameters xyz for $SrCl_2, 2\,H_2O$.

Space group Ia ($C_S^4$), all atoms in general position:

xyz; $x\bar{y}\left(\frac{1}{2}+z\right)$; $\left(\frac{1}{2}+x\right)\left(\frac{1}{2}+y\right)\left(\frac{1}{2}+z\right)$; $\left(\frac{1}{2}+x\right)\left(\frac{1}{2}-y\right)z$.

| | | | | |
|---|---|---|---|---|
| Sr | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | etc. |
| $Cl_I$ | 0.11 | 0.10 | 0.00 | etc. |
| $Cl_{II}$ | 0.39 | 0.10 | 0.50 | etc. |
| $O^I$ | 0.14 | 0.40 | 0.63 | etc. |
| $O_{II}$ | 0.36 | 0.40 | 0.87 | etc. |

looked for at x = 0.11. The line x = 0.11 is seen to cut the upper parts of the two peaks of which the larger part is due to Sr and Cl. In fact, the slopes of the upper areas fall off more slowly than those of the lower areas, thus indicating other influences than Sr and Cl. The peak on the left extends from 0.13 to 0.18, the peak on the right from 0.32 to 0.39 at x = 0.11. Yo in the crystal hence must lie somewhere between 0.13 and 0.07; 0.10 was taken as best value.

A discussion similar to that in the case of Cl shows that there are only two possible sets of coordinates for the O atoms, provided they cannot be placed almost on top of the Cl atoms; the length of the c-axis 6.36 Å allows no such arrangement. The coordinates are

$$O_I \quad xy = 0.14\ 0.60 \text{ etc.}$$
$$O_{II} \quad xy = 0.36\ 0.60 \text{ etc.}$$

The assignment of proper z-coordinates to $O_I$ $O_{II}$ $Cl_I$ and $Cl_{II}$ is the next problem. In the full projection on 010 we have O-atoms at z = 0.13 0.27 0.63 0.77 and Cl atoms at x = 0.00 and 0.50; but only the arrangement whose full set of coordinates are given in table 3 was possible without almost superimposing atoms in several places.

Calculated and observed intensities are given in table 2.



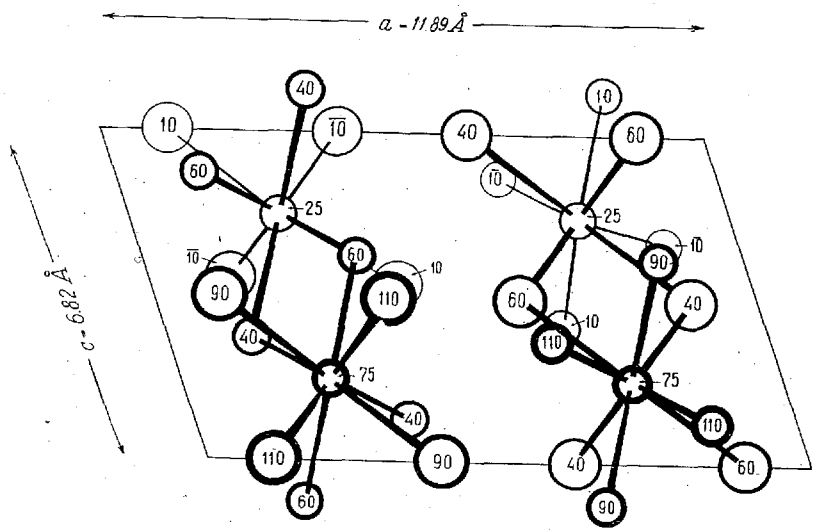


Fig. 11 $SrCl_2, 2\,H_2O$ projected on 010, only bonds within the layers parallel to 100 are drawn. Where two atoms are superimposed, the lower one is slightly displaced in the figure.

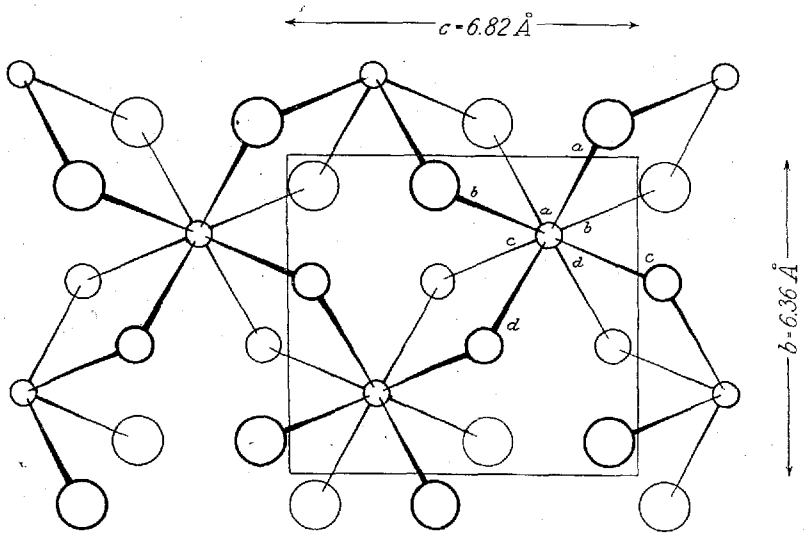


Fig. 12 A layer of $SrCl_2, 2\,H_2O$ projected on 100. Sr atoms lie in the plane of the drawing. Cl atoms 1.59 ÅU above and below. O atoms 1.23 ÅU above and below.

## Description of the structure.

Fig. 11 shows the structure projected on 010. It is built up of identical sheets of a thicknees of $\frac{a}{2}$, every sheet displaced $\frac{b}{2}$ and $\frac{c}{2}$ with respect to the foregoing sheet. The way in which two consecutive sheets are fitted together does not correspond to any simple kind of packing of spheres. Fig. 12 depicts a single sheet of the structure projected on 100 (not on a plane perpendicular to the a-axis). Every sheet is a complete $(SrCl_2, 2\,H_2O)_{n^2}$ "giant molecule" as far as purely geometrical aspects are concerned. Every Sr atom is surrounded by 4 O and by 4 Cl atoms and any Cl and any O atom links the Sr atom to a neighbouring Sr. The 8 neighbours of a Sr atom form an acentric but very neat cluster around the Sr, a cluster of which the surrounding atoms of any adjacent Sr form the mirror image.

Table 4 gives some of the interatomic distances. The distances from Sr to Cl (2.88 and 2.99 Å) are somewhat below the distance 3.02 Å found in $SrCl_2$[1]. This contraction is to be expected, since $SrCl_2$ crystallizes in the fluorite lattice with its 8—4 coordination, while Cl in $SrCl_2, 2\,H_2O$ has only two charged neighbours. The distances Sr—O are 2.83 and 2.71 Å and they agree with the distance 2.80 Å found in $SrCl_2, 6\,H_2O$ for a water oxygen linking together two Sr atoms. It is not clear whether the difference in distance for the S—Cl bonds a and b and the Sr—O distances c and d are of physical significance. A change of parameters within the experimental error (which may be estimated to be about 0.01, except for the y parameters of O where it is higher) might cause equal Sr—Cl distances and Sr—O distances.

Some of the Cl atoms in the sheet are in actual contact, they are 3.64 and 3.57 Å apart. This is almost exactly twice the ionic radius of $Cl^-$ which is 1.81 Å.

The distances between oxygen atoms are all large compared with 2.76 Å which, according to W. L. Bragg, is twice the radius of a water molecule; however, one distance from O to Cl of

[1] H. Ott: Z. Krist. **63** (1926) 222. Strukturberichte **1** 187.



Table 4.

Environment and interatomic distances in $SrCl_2, 2\,H_2O$.

| Central Atom | Surrounding Atoms: Nature | Surrounding Atoms: Number | Separation in Å | |
|---|---|---|---|---|
| Sr | $Cl_{(a)}$ | 2 | 2.99 | |
| | $Cl_{(b)}$ | 2 | 2.88 | |
| | $O_{(c)}$ | 2 | 2.71 | |
| | $O_{(d)}$ | 2 | 2.83 | |
| $Cl_{(I)}$[1] | $Sr_{(a)}$ | 1 | 2.99 | in the same layer |
| | $Sr_{(b)}$ | 1 | 2.88 | |
| | $Cl_{(II)}$ | 1 | 3.57 | |
| | $Cl_{(I)}$ | 2 | 3.64 | |
| | $Cl_{(II)}$ | 1 | 3.98 | |
| | $O_{(I)}$ | 1 | 3.10 | |
| | $O_{(II)}$ | 2 | 3.35 | |
| | $Cl_{(II)}$ | 2 | 4.11 | in the adjacent layer |
| | $O_{(II)}$ | 1 | 3.34 | |
| | $O_{(II)}$ | 1 | 3.50 | |
| $O_{(I)}$[1] | $Sr_{(c)}$ | 1 | 2.71 | in the same layer |
| | $Sr_{(d)}$ | 1 | 2.83 | |
| | $Cl_{(I)}$ | 1 | 3.10 | |
| | $Cl_{(II)}$ | 2 | 3.35 | |
| | $O_{(I)}$ | 2 | 3.64 | |
| | $O_{(II)}$ | 1 | 2.97 | |
| | $O_{(II)}$ | 1 | 3.48 | |
| | $Cl_{(II)}$ | 1 | 3.34 | in the adjacent layer |
| | $Cl_{(II)}$ | 1 | 3.50 | |

[1] The special values of the atomic parameters make the environment description somewhat cumbrous. Particulary, it should be noted that a $Cl_{(II)}$ atom has the same environments as a $Cl_{(I)}$ atom, an $O_{(II)}$ atom the same environments as an $O_{(I)}$ atom.

3.10 Å is rather short compared with $r_{Cl^-} + r_{H_2O} = 3.19$ Å which seems to indicate a (repulsing) contact.

The interatomic distances from one layer to the next are large compared with the sums of the radii which are $2\,r_{Cl^-} = 3.62$ Å, $r_{Cl^-} + r_{H_2O} = 3.19$ Å, but they are not improbable, since the lattice is decidedly a layer lattice. The layers are parallel to the only face developed; unfortunately, it has, however, not been

Table 5.

Calculated and observed intensities in the powder diagram of $SrCl_2, 2\,H_2O$. CrK$\alpha$ radiation.

| hkl | $\sin^2$ calc. | $\sin^2$ obs. | obs. int. | calc. int. |
|---|---|---|---|---|
| 211 | 0.0838 | 0.0846 | m-s | 83 |
| 202 | 0.1244 | 0.1258 | m | 36.4 |
| 310 | 0.1250 | | | 26.4 |
| 002 | 0.1272 | .. | 0 | 1.5 |
| $\bar{2}11$ | 0.1276 | 0.1284 | vs | 204 |
| 020 | 0.1281 | | | 22 |
| 112 | 0.1495 | .. | 0 | 5.4 |
| 121 | 0.1597 | 0.1602 | w-m, m | 28 |
| 400 | 0.1654 | .. | 0 | 12 |
| 220 | 0.1695 | 0.1700 | m-s | 88 |
| $\bar{1}21$ | 0.1814 | 0.1824 | m | 71 |
| 411 | 0.1859 | 0.1868 | vs | 241 |
| 312 | 0.1884 | 0.1889 | m | 53 |
| $\bar{1}12$ | 0.1930 | 0.1940 | w-m | 29 |
| 402 | 0.2069 | 0.2071 | m-s, s | 71 |
| $\bar{2}02$ | 0.2143 | 0.2149 | m-s, s | 70 |
| 321 | 0.2205 | 0.2211 | w-m, m | 29 |
| 222 | 0.2548 | 0.2550 | s | 46 |
| 022 | 0.2572 | 0.2577 | s | 61 |
| $\bar{4}11$ | 0.2736 | 0.2746 | m-s | 31 |
| $\bar{3}21$ | 0.2863 | .. | (v) | 7 |
| 510 | 0.2905 | .. | 0 | 0.4 |
| 420 | 0.2936 | 0.2944 | s | 60 |
| 213 | 0.2981 | 0.2982 | s-vs | 87 |
| 130 | 0.2986 | .. | 0 | 0.2 |
| 512 | 0.3100 | .. | 0 | 0.6 |
| $\bar{3}12$ | 0.3200 | .. | 0 | 2.4 |
| 031 | 0.3206 | 0.3215 | m-s, s broad | 47 |
| 013 | 0.3226 | | | 38 |
| 422 | 0.3350 | 0.3350 | w-m | 18 |
| 231 | 0.3400 | 0.3399 | s | 59 |
| $\bar{2}22$ | 0.3430 | .. | (w-m) | 17 |
| 413 | 0.3554 | 0.3557 | w | 12 |
| 521 | 0.3657 | 0.3648 | v | 6.5 |
| 602 | 0.3698 | 0.3726 | s, broad | 9.0 |
| 611 | 0.3708 | | | 42 |
| 600 | 0.3722 | | | 16 |
| 330 | 0.3813 | .. | 0 | 0.5 |
| $\bar{4}02$ | 0.3822 | 0.3832 | m-s | 37 |
| $\bar{2}31$ | 0.3838 | .. | 0 | 6.6 |
| 132 | 0.4050 | .. | 0 | 0.1 |
| 323 | 0.4130 | .. | 0 | 4.9 |



possible to ascertain how perfect the cleavage is, parallel to the layers. The crystals were too thin and too fragile as to permit an investigation of this kind.

A more detailed discussion of the bonding and dynamics of the lattice will be given in a later communication.

## Powder photographs.

In the derivation of the structure, no reflections of the general type hkl have been employed. For a final check, the observed intensities of powder photographs were compared with a set of intensities calculated from the set of parameters found. The powder photographs were taken with the focussing cameras of PHRAGMÉN-HÄGG with Cr-radiation. The reflections from low to medium orders, only, have been indexed. The difficult indexing of the few and feeble lines found at higher angles was considered unnecessary. The work of refining 15 parameters by trial and error would have been very great, however, the agreement between calculated and observed intensities is good enough to show the fundamental correctness of the structure.

The structure factor of $C_S^4$ in the orientation Ia (= Ic = In) is

$$\left.\begin{array}{r} h+k+l=2n+1 \end{array}\right\} \; A = B = 0$$

$$\left.\begin{array}{r} h+k+l=2n \\ l=2n \end{array}\right\} \; \begin{array}{l} A = 4\cos 2\pi(hx+lz)\cos 2\pi ky \\ B = 4\sin 2\pi(hx+lz)\cos 2\pi ky \end{array}$$

$$\left.\begin{array}{r} h+k+l=2n \\ l=2n+1 \end{array}\right\} \; \begin{array}{l} A = -4\sin 2\pi(hx+lz)\sin 2\pi ky \\ B = 4\cos 2\pi(hx+lz)\sin 2\pi ky \end{array}$$

The accurate lattice constants found were: $a = 11.76$ ÅU. $b = 6.38$ ÅU. $c = 6.66$ ÅU. $\beta = 72.9°$

## Summary.

$SrCl_2, 2\,H_2O$ prepared in different ways always crystallizes in the same lattice.

Its structure has been determined from Weissenberg photographs by Bragg- and Patterson-Fourier syntheses. The structure is determined by 15 parameters and is a layer lattice. Every layer is a two-dimensional giant molecule of $SrCl_2, 2\,H_2O$ in which every Sr is surrounded by 4 Cl and 4 O atoms. Every

Cl and every O link two Sr atoms. The interatomic distances show that the forces within the layers are strong, from layer to layer, however, relatively weak.

I am indebted to Professor GUNNAR HÄGG and the University of Uppsala for the hospitality granted me during the spring term of 1940 when the early part of the present work was done, and moreover to Professor HÄGG for many helpful discussions. My stay at Uppsala was made possible by a grant from K. A. LARSSEN'S Legat, for which I express my sincere thanks.

Indleveret til Selskabet den 26. Maj 1942.
Færdig fra Trykkeriet den 14. December 1942.



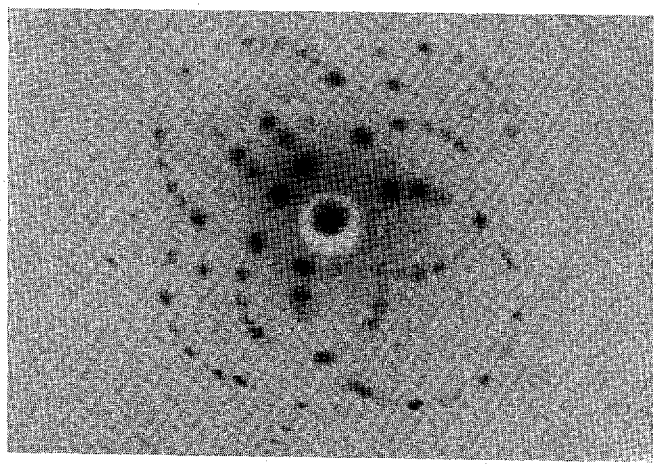

Fig. 1. Laue photograph of $SrCl_2$, 2 $H_2O$. Beam perpendicular to developed face.

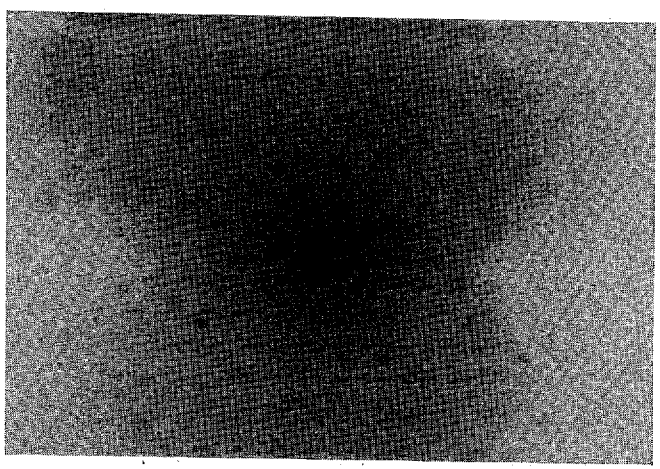

Fig. 2. Laue photograph of $SrCl_2$, 2 $H_2O$. Beam perpendicular to symmetry plane.