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The crystal structure of SnCl₂. By J. M. VAN DEN BERG, *Laboratory of Inorganic Chemistry, University of Leiden, The Netherlands*

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Preparation

SnCl₂ is prepared by heating Sn in a flow of gaseous HCl. It is obtained as a fine powder. Single crystals were prepared by sublimation in a vacuum-sealed tube at 300 °C. The crystals, thin needles, appeared in the upper part of the tube.

Crystallographic investigation

Photographs were taken about the *c*- and *a*-axis, both with Cu Kα and Mo Kα radiation.

From oscillation and Weissenberg photographs the space group was found to be *Pnam* or *Pna*.

The cell constants are:

$$a = 7.793, b = 9.207, c = 4.43 \text{ \AA}.$$

Since the crystals are very sensitive to atmospheric influence, it was difficult to measure their density. From the density of the liquid, 3.39 g.cm.⁻³, the density of the solid was assumed to be about 4 g.cm.⁻³. From this value the number of molecules per unit cell was found to be 4; this gives a calculated density of 3.91 g.cm.⁻³.

On the Weissenberg diagram *Ok*l, it was noticed that intensities *Ok*l + 2 are equal to *Ok*l, apart from *LP* factor and normal decline. It was concluded that all atoms in the cell lie on two planes parallel to (001), at a distance of $\frac{1}{2}c$. Thus the space group *Pnam* could be assumed. Then Sn has a fourfold position and Cl has two fourfold positions:

$$x, y, \frac{1}{4}; \bar{x}, \bar{y}, \frac{3}{4}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4}; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4}.$$

Weissenberg photographs about the *c*-axis—needle axis—of a very thin crystal served as a basis for this structure determination (zero- and first level).

The *hk*0 and *hk*1 intensities were measured on a photometer, and corrected for the Lorentz-polarization factor and absorption, treating the needle as a cylinder.

The initial parameters for Sn and Cl were obtained from a Patterson projection on the (001) plane.

The structure was improved first by an electron-density projection along [001]. After scaling of the *hk*0 and *hk*1 structure factors to the calculated values, a generalized projection:

$$\rho(xy) = \sum_{h+k=2n} F(hk0) \cos hx \cos ky - \sum_{h+k=2n+1} F(hk0) \sin hx \sin ky \\ - \sum_{h+k=2n} F(hk1) \sin hx \cos ky - \sum_{h+k=2n+1} F(hk1) \cos hx \sin ky$$

was computed (Zachariasen, 1954). Since all atoms lie in the planes $z = \frac{1}{4}$ and $z = \frac{3}{4}$, this is equivalent to the section at $z = \frac{1}{4}$. Then a difference map of the same generalized projection was made. In this summation, and in all subsequent work, the strong low-order reflections were omitted because extinction was suspected. The following parameters were obtained:

	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0.231	0.074	0.250
Cl _I	0.022	-0.155	0.250
Cl _{II}	0.644	0.075	0.250

With these parameters and an overall isotropic temperature factor $B = 1.8 \text{ \AA}^2$, the value of

$$R = \frac{\sum |F_c| - |F_o|}{\sum |F_o|}$$

was 13%. The difference map indicated that Sn had more thermal motion than assumed and Cl less. When individual isotropic temperature factors for Sn and Cl of 2.2 and 1.2 Å² respectively were used the *R* factor dropped to 11%. A second difference map showed that these temperature factors are essentially correct.

Discussion

A projection of the structure along [001] is shown in Fig. 1. Atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$ are distinguished by heavy and light circles.

The structure is isomorphous with PbCl₂ and PbBr₂ (Nieuwenkamp & Bijvoet, 1932).

The Sn atom at $z = \frac{1}{4}$ has three Cl atoms as nearest neighbours in the same plane at distances of 3.22, 3.26 and 3.30 Å, and two Cl atoms at distances of 2.78, two at 3.06 and two at 3.86 Å in the planes $z = \frac{3}{4}$ and $z = -\frac{1}{4}$.

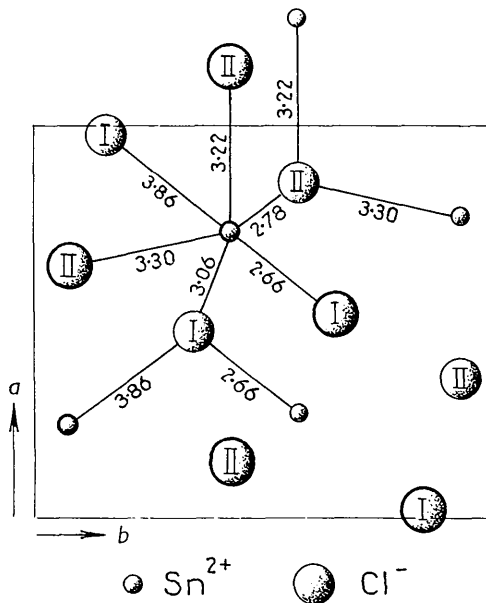


Fig. 1. Projection along [001]. Heavy circles: atoms at $z = \frac{1}{4}$. Light circles: atoms at $z = \frac{3}{4}$.

Cl_{II} is tetrahedrally surrounded by Sn; Cl_I has three Sn atoms at a shorter distance, and two Sn atoms at a longer distance. Chlorine-chlorine nearest neighbour-distances vary from 3.45 to 4.43 Å.

That B_{Sn} is larger than B_{Cl} could perhaps be ascribed to the irregular manner in which the Sn atom is surrounded by the Cl atoms.

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References

- NIEUWENKAMP, W. & BLIJVOET, J. M. (1932). *Z. Kristallogr.* **84**, 49.
 ZACHARIASEN, W. H. (1954). *Acta Cryst.* **7**, 305.

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Relation of symmetry to structure in twinning. II. By K. DORNBERGER-SCHIFF, *Deutsche Akademie der Wissenschaften zu Berlin, Institut für Strukturforchung Berlin-Adlershof, Deutschland*

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Twin structures, which may be characterized as consisting of two equivalent crystals with a layer periodic in two dimensions—the boundary layer—common to both, have been considered by Holser (1958) and Dornberger-Schiff (1959).

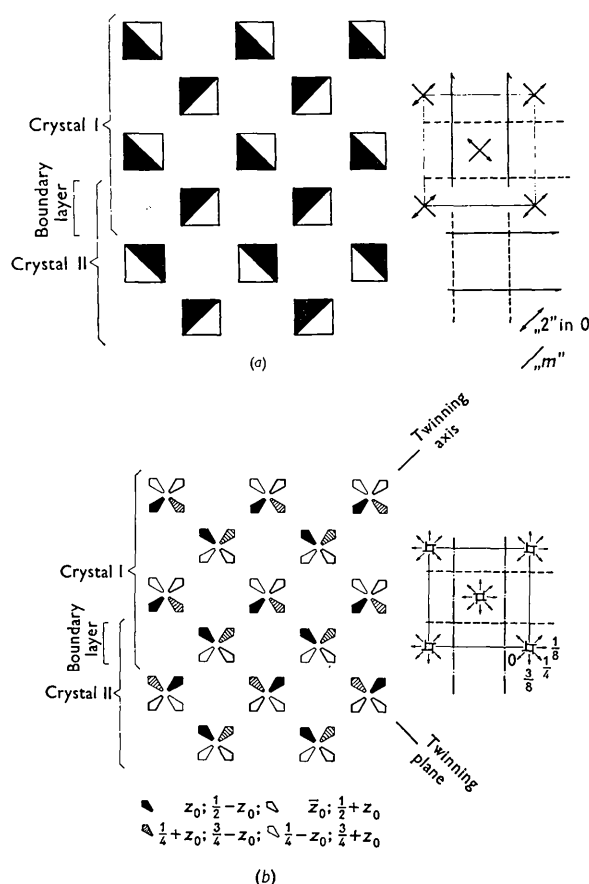


Fig. 1. Two schematic examples of OD structures built of equivalent rods extending perpendicular to the plane of drawing, each representing a twin structure consisting of two equivalent twin individuals with a common boundary layer.

a = example 1, b = example 2.

In the latter note it was erroneously asserted that any such structure may be looked upon as a member of a family of OD structures built of layers periodic in two dimensions (for a definition of the term 'OD structure' see Dornberger-Schiff & Grell-Niemann, 1961). Although, certainly, this description is true for a great many (if not most) of the known twin structures of this kind, it is now known not to be a necessary condition. Recent work has shown that there are some twin structures characterized as above which are OD structures built of rods periodic in one dimension only.

Two schematic examples are shown in Fig. 1(a), (b). A projection along the rod direction c is shown in each case. In either example, each rod has 4 nearest neighbours and any pair of adjacent rods is equivalent to any other pair of adjacent rods. The symmetry of the rods is such that a description of the symmetry of the boundary layer with the help of one of the 80 plane groups in 3 dimensions does not give all the symmetry operations of the linear group in three dimensions of the single rod, although these symmetry operations are essential for the equivalence of pairs of adjacent rods. Thus, in example 1, if A, B are the centres of adjacent rods, there is a rotation diad parallel to AB and a mirror plane perpendicular to it; both these are at 45° to the boundary layer, and therefore cannot be elements of the symmetry group of the boundary layer. In example 2 it is the 4_1 axis parallel to the boundary layer which—for obvious reasons—cannot be an element of its symmetry. In both examples the twin plane or twin axis is at 45° to the boundary plane which is the composition plane.

I should not like to predict, at the present stage, whether all twins, consisting of two equivalent crystals with a boundary layer in common, may be looked upon as members of families of OD structures built of either layers periodic in two dimensions or of rods periodic in one dimension (all alike or of several different kinds). It may very well be that the case of OD structures built of non-periodic blocks has also to be considered.

References

- DORNBERGER-SCHIFF, K. (1959). *Acta Cryst.* **12**, 246.
 DORNBERGER-SCHIFF, K. & GRELL-NIEMANN, H. (1961). *Acta Cryst.* **14**, 167.
 HOLSER, W. T. (1958). *Z. Kristallogr.* **110**, 249.