Acta Cryst. (1955). **8**, 343

The Crystal Structure of Tin Tetraiodide

By F. Meller and I. Fankuchen

Polytechnic Institute of Brooklyn, Brooklyn 1, *N.Y., U.S.A.*

(*Received* 2 *March* 1954 *and in revised form* 19 *March* 1954)

This redetermination of the crystal structure of tin tetraiodide shows that the data can be explained in terms of a simpler distortion of the ideal structure than that used in the earlier work of Dickinson.

The crystal structure of tin tetraiodide was determined by Dickinson (1923). The unit cell is cubic with $a_0 = 12{\cdot}26$ Å (Dickinson's $a_0 = 12{\cdot}23$ Å); there are eight molecules per unit cell. The space group is T_h^6–$Pa3$. The structure, as described by Dickinson, can be visualized in terms of small deviations from an 'ideal' structure consisting of tin atoms occupying one-eighth of the tetrahedral interstices in a cubic close packing of iodine atoms. In the 'ideal' structure the tin atoms and one of the iodine atoms of each SnI_4 tetrahedron would be located on one of the threefold cube axes; the other three iodine atoms of the tetrahedron would lie in a plane perpendicular to this axis.

Assuming that the regular tetrahedral coordination of the SnI_4 group is maintained, three shifts from the 'ideal' may be considered: (*a*) The tetrahedron may be translated along the threefold axis; (*b*) the tetrahedron may be contracted or expanded; (*c*) the iodine atoms in general positions may be rotated about the threefold axis.

Dickinson permitted all three types of deviations from the 'ideal' structure in addition to possible distortion of the tetrahedron. In terms of the unit-cell edge the magnitudes of these shifts were 0·004 for type (*a*), 0·001 for contraction of type (*b*), and 3° for type (*c*). His determination was based on analysis of Laue diagrams and spectral photographs, and the parameters (Table 1) were obtained by a systematic trial-and-error procedure.

Table 1. *Atomic parameters for the 'ideal' (Dickinson) and present structures for one* SnI_4 *tetrahedron*

Sn at (u, u, u); I at (v, v, v), (x, y, z), (y, z, x), (z, x, y).

	'Ideal'	Dickinson	This paper
u	0·125	0·129	0·125
v	0·250	0·253	0·252
x	0	0·009	−0·002
y	0	0·001	−0·002
z	0	0·253	0·252

Since the structure of tin tetraiodide is considered a prototype, it was thought desirable to reinvestigate it, using present day techniques. Compounds of the SnI_4-type structure include SiI_4, $TiBr_4$, TiI_4, $Ni(CO)_4$, etc.

Normally tin tetraiodide grows from solution in the form of needles with [111] as the needle axis. Crystals with this orientation were grown from carbon tetrachloride solution, and diffraction data were obtained. It was soon found that a reliable set of $hk0$ intensity data was needed. For this purpose single crystals aligned along a cube axis were grown from the melt in thin-walled pyrex glass capillary tubes 0·07 mm. in diameter. Weissenberg and precession photographs were taken of these specimens. The absorption correction for cylindrical specimens, developed by Bradley (1935), was applied to data obtained with copper radiation.

The space group $Pa3$ permits only those $\{hk0\}$ reflections for which h is even, and causes no further restrictions. However, further apparently systematic extinctions were observed for this zone for SnI_4. Only the following types of reflections were observed (Fig. 1): (1) Reflections whose indices h and k were both divisible by 4; all of these had relatively high intensities. (2) Reflections for which h was even, not

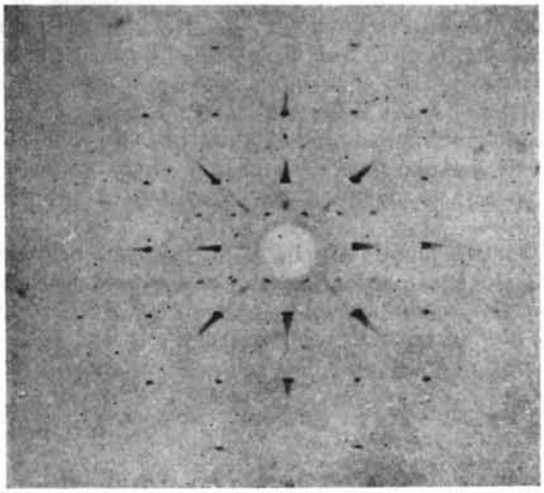

Fig. 1. Precession diagram of the $hk0$ zone of SnI_4; 48 hr.; Mo $K\alpha$ radiation.

divisible by 4, and *k* was odd; all of these were comparatively weak.

Measurements of intensities were made by visual comparison with calibrated standards. The usual Lorentz and polarization corrections were applied.

Structure factors for the *hk*0 reflections were calculated for the 'ideal' structure. Only reflections of types (1) and (2) would be observed if the structure were 'ideal'. A study of the observed intensities, however, indicated a shift from the 'ideal'.

Computations of structure factors were carried out in terms of shifts from the 'ideal' positions. Any deviation other than one of type (*b*) would cause the appearance of types of reflections not observed, i.e. those with indices other than *h* and *k* divisible by 4, or *h* even not divisible by 4 and *k* odd. Deviations of type (*a*) as small as 0·001 of the unit-cell edge, of type (*c*) of 1°, as well as small combinations of all three types of shift, would give rise to a number of reflections whose intensity would be comparable to some of the weaker reflections which were actually observed.

A Fourier summation was carried out for a projection on (001). The signs for F values of the 'ideal' structure were used. The electron-density map showed a small expansion of the SnI_4 tetrahedra and a displacement of the maximum of the tin atom peak off the threefold axis. A 'control' Fourier summation of the same set of terms, using as coefficients the temperature-corrected computed structure factors for the 'ideal' structure, was also carried out. Corrections based on this Fourier returned the tin atom to the 'ideal' position and moved the iodine atoms to a location corresponding to a slight expansion of 0·002 of the unit-cell edge.

In structure-factor calculations certain reflections, such as (290), (2,11,0), (2,13,0), (650), (670), (690), were very sensitive to small displacements of the iodine atoms in shifts of type (*b*). The above expansion of the SnI_4 tetrahedron was verified by a study of the variation of $|F_c-F_o|$ for a small number of such reflections; these differences were computed for expansions of the SnI_4 tetrahedron of 0·001–0·005. The best fit was obtained for a change of the iodine atom parameters of 0·002 in an expansion of the 'ideal' structure.

Structure factors for the *hk*0 terms were calculated, using the parameters (Table 1) of this proposed structure. The reliability coefficient for all $F(hk0)$ values was 10·8%; for the 'ideal' structure it was 13%. On the basis of observed values only, the coefficients were:

*hk*0 group	'Ideal' structure	Dickinson structure	This paper
h and *k* divisible by 4	8·0%	7·6%	7·0%
h even not divisible by 4, *k* odd	34·1%	25·2%	23·4%

Interatomic distances, based on $a_0 = 12·26$ Å, are: Sn–I (intramolecular): 2·69±0·02 Å.

Separation of iodine atoms within a tetrahedron: 4·41 Å.

Closest approach between iodine atoms: 4·30 Å.

The sum of Pauling (1944) radii for singly covalently bonded tin and iodine atoms is 2·73 Å. The van der Waals radius for the iodine atom, listed by Pauling (1944), is 2·15 Å.

This structure differs only very slightly from that reported by Dickinson. The latter permits three types of shifts from the 'ideal' structure (types (*a*), (*b*) and (*c*), above); in the present investigation it was found that only deviations of type (*b*) need be postulated to account for the observed reflections. The actual shifts are very small in both cases. However, the Dickinson structure would give rise to reflections not observed in this work; these include a number, such as (890), (8,10,0), (12,5,0), (12,6,0), etc., whose calculated structure factors are comparable in magnitude to many reflections which were observed. A 48-hr. precession diagram of the *hk*0 zone (Fig. 1) was taken to check on such reflections. With the possible exception of 810, no such reflections were observed. Shifts from the 'ideal' structure, of types (*a*) and (*c*), which would give rise to these unobserved reflections, are therefore very slight, if they exist at all. It should be emphasized that our data do not rule out the possibility that such weak reflections occur. This communication confirms Dickinson's interesting original finding that the distortion from the ideal structure is slight. It, however, suggests a simpler distortion as adequate to explain our data. Assuming the tetrahedra to remain regular, a small expansion gives satisfactory agreement with the observed intensities.

We are greatly indebted to Prof. Pauling for some very stimulating discussions of Dickinson's work and helpful criticisms of ours.

References

BRADLEY, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.

DICKINSON, R. G. (1923). *J. Amer. Chem. Soc.* **45**, 958.

PAULING, L. (19440). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.