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THE CRYSTAL STRUCTURE OF TIN TETRA-IODIDE

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Introduction

Previous X-ray investigations of inorganic substances have been carried out with metals or with strongly polar compounds; it has, therefore, been considered of interest to attempt the determination of the crystal structure of a somewhat non-polar compound. Tin tetra-iodide, SnI_4, has a comparatively low melting point (146°) and appreciable solubility in a great variety of organic solvents. It crystallizes readily from carbon disulfide solution giving isotropic crystals[2] whose face development is clearly that of the paramorphic hemihedry T_h (pyrites class). The X-ray data used here came from spectral photographs and Laue photographs obtained and treated as previously described.[3]

The Unit of Structure

As no organic liquid was found which does not dissolve tin tetra-iodide to some extent, the density was determined[4] by weighing the powdered solid under conc. sulfuric acid (after evacuating to remove air), the value[5] found being 4.46. Reflections of the rhodium line, K_α ($\lambda = 0.6121$ Å.), were obtained from (111) at the following angles: 2° 29′, 4° 59′, 9° 59′, 15° 4′. The usual calculation of n^3/m for these reflections shows that there are 8 SnI_4 in the unit of structure having $d_{100} = 12.23$ Å., and that the orders of the observed reflections are 1, 2, 4 and 6, respectively. The density conversely calculated from the angles of reflection is 4.52.

The Laue photographic data did not necessitate the assumption of a unit containing more than 8 SnI_4; for, using $d_{100} = 12.23$, no values of $n\lambda$ were found smaller than the wave lengths known to be present in the X-rays used. In addition to the Laue spots several larger and much more diffuse spots were obtained on each photograph. No definite indices could be assigned to these by the usual methods of treatment. It is possible that they are connected with the phenomena described by Clarke and Duane[6] and by McKeehan;[7] the diffuse patches are being investigated further.

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[1] National Research Fellow in Chemistry.

[2] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. **1**, p. 231.

[3] Dickinson, THIS JOURNAL, **44**, 276 (1922).

[4] A similar method has recently been used on germanium tetra-iodide by Dennis and Hance, *ibid*, **44**, 2856 (1922).

[5] This is somewhat lower than the older value 4.696 quoted by Groth (Ref. 2).

[6] Clarke and Duane, *Proc. Nat. Acad. Sci.*, **8**, 90 (1922).

[7] McKeehan, *J. Opt. Soc. Am.*, **6**, 989 (1922).

The Space Group Symmetry

The Laue photographs showed that in general the planes (*hkl*) and (*khl*) reflected unequally strongly at the same wave length. This fact shows that the space-group symmetry must be isomorphous with that of one of the point groups T or T_h. The fact that planes having 1, 2 or 3 odd indices were found reflecting in the first order shows that the lattice underlying the space group must be the simple cubic one, T_c. The possible space groups are thus limited to T^1, T^4, T_h^1, T_h^2, and T_h^6. Since the largest number of equivalent positions in the unit given by any of these space groups is 24, and since 32 iodine atoms must be disposed in the unit, it follows immediately that *all of the iodine atoms cannot be in equivalent positions.*

It is, however, possible to determine the space-group symmetry without any definite assumption as to the nature of the non-equivalence of the iodine atoms. The examination of 3 different Laue photographs (2 at different inclinations to a (100) section and 1 through a (111) section) revealed only the following forms[8] having one index zero and reflecting in the first order: {902}, {702}, {11·0·2}, {3·0·10}, {106}, {108}, {506}, {504}, {11·0·6}, {304}, {13·0·2}, {1·0·10}. In all of these forms *h* is odd and *l* even; no first order reflections were found from forms having *k* zero, and *h* even and *l* odd, or *h* and *l* both odd. The presence of these reflections excludes[9] the space group T_h^2 since no arrangement with this symmetry is capable of producing any first order reflections from these forms.

At least 32 of the 40 atoms in the unit must be in positions which involve one or more parameters. For the space groups T^1, T^4, and T_h^1, it can be shown that any arrangement involving parameters (and consequently any combination of such arrangements, since the parameters are presumably independent of one another) gives in general first order reflections from all planes with the exception of (100) in the case of T^4. The complete absence of the classes noted above is not accounted for by any of these space groups; but arrangements with the symmetry T_h^6 cause all first-order reflections from planes having one index zero to vanish except from {*h*0*l*} when *h* is odd and *l* is even. It is therefore extremely probable that T_h^6 is the correct space group.

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[8] The same choice of axes on each photograph was insured by taking the axes so that {942} was present and {492} absent in the first order in each case.

[9] Wyckoff, *Am. J. Sci.*, **4,** 175 (1922), has given criteria for distinguishing between these space groups in case atoms of appreciable scattering power are in the general position; in the present instance it is not necessary to assume that any atoms are so located, although this is found to be the case. The coördinate positions upon which the present discussion is based may be found in Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, **1922.**

The Arrangement of the Atoms

With 8 SnI_4 in the unit and with the symmetry T_h^6, the following arrangement is the only one that permits surrounding each tin atom closely by 4 iodine atoms, and is also the only one not requiring either more than one kind of position for the tin atoms or more than two kinds for the iodine atoms.

8 Sn atoms at	(u,u,u)	$(\frac{1}{2}+u, \frac{1}{2}-u, \bar{u})$	$(\bar{u}, \frac{1}{2}+u, \frac{1}{2}-u)$	$(\frac{1}{2}-u, \bar{u}, \frac{1}{2}+u)$
	$(\bar{u},\bar{u},\bar{u})$	$(\frac{1}{2}-u, \frac{1}{2}+u, u)$	$(u, \frac{1}{2}-u, \frac{1}{2}+u)$	$(\frac{1}{2}+u, u, \frac{1}{2}-u)$

8 I atoms at a similar set of coördinates in v.

24 I atoms at:	(xyz)	$(\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$	$(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	$(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$
	(zxy)	$(\bar{z}, \frac{1}{2}+x, \frac{1}{2}-y)$	$(\frac{1}{2}-z, \bar{x}, \frac{1}{2}+y)$	$(\frac{1}{2}+z, \frac{1}{2}-x, \bar{y})$
	(yzx)	$(\frac{1}{2}-y, \bar{z}, \frac{1}{2}+x)$	$(\frac{1}{2}+y, \frac{1}{2}-z, \bar{x})$	$(\bar{y}, \frac{1}{2}+z, \frac{1}{2}-x)$
	$(\bar{x}\bar{y}\bar{z})$	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	$(\frac{1}{2}+x, y, \frac{1}{2}-z)$
	$(\bar{z}\bar{x}\bar{y})$	$(z, \frac{1}{2}-x, \frac{1}{2}+y)$	$(\frac{1}{2}+z, x, \frac{1}{2}-y)$	$(\frac{1}{2}-z, \frac{1}{2}+x, y)$
	$(\bar{y}\bar{z}\bar{x})$	$(\frac{1}{2}+y, z, \frac{1}{2}-x)$	$(\frac{1}{2}-y, \frac{1}{2}+z, x)$	$(y, \frac{1}{2}-z, \frac{1}{2}+x)$

Since 5 parameters occur in this structure, a systematic determination of their values seems hardly practicable. It is worth while, nevertheless, to point out a set of probable values found by trial. In Table I are given the relative intensities of the reflections from (100) and similar data for (110) and (111). These show striking peculiarities.

TABLE I

INTENSITIES OF THE SPECTRAL REFLECTIONS

Order, *n*	1	2	3	4	5	6	7	8
Obs. relative intensities for (100)............	abs.	abs.	abs.	strong	abs.	abs.	abs.	strong
$(A^2 + B^2)_2$ for (100).....	0	0.04	0	141	0	0.17	0	377
Obs. relative intensities for (110)............	abs.	abs.	abs.	strong	abs.	abs.	abs.	medium
$(A^2 + B^2)_2$ for (110).....	0	0.00	0	389	0	0.08	0	356
Obs. relative intensities for (111)............	faint	strong	abs.	medium	abs.	weak	...	...
$(A^2 + B^2)_2$ for (111).....	1.2	253	1.1	138	4.1	229	...	...

The absence of odd orders from (100) and (110) is accounted for by any T_h^6 arrangement. The other peculiarities, as well as many of the intensity relations derivable from the Laue photographic data, may be qualitatively accounted for by placing $u = {}^1/_8$, $v = {}^1/_4$, $x = 0$, $y = 0$, $z = {}^1/_4$. By changing these simple values of the parameters by small amounts,[10] it has been possible to account satisfactorily for the Laue photographic data given in Table II. Comparison of planes of the same form reflecting different wave lengths showed that wave lengths between 0.43 and 0.48 Å. were

[10] Since it was possible to keep these alterations small, they could be investigated fairly systematically by calculating roughly the partial derivatives of $(A^2 + B^2)$ with respect to each parameter for each reflection considered; 2 or 3 of the 5 derivatives were usually zero.

roughly equally effective under the conditions of this photograph. In the column headed S_2^2, equal to $(A^2 + B^2)_2$, are given the values of the structure factor calculated in the usual manner with u = 0.129, v = 0.253, x = 0.009, y = 0.001, z = 0.253; the reflecting powers of the tin and iodine atoms were assumed equal. For comparison, the values of the structure factor calculated with the simpler values of the parameters are given under S_1^2, equal to $(A^2 + B^2)_1$; it may be seen from these that the small alterations in the parameters produce in some cases large percentage changes in the values of the structure factor.

TABLE II

DATA FROM UNSYMMETRICAL (100) LAUE PHOTOGRAPH

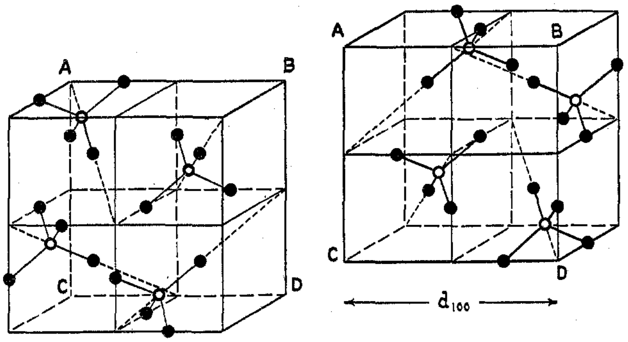
hkl	d_{hkl}	$n\lambda$	Estimated Intensity	S_1^2	S_2^2	*hkl*	d_{hkl}	$n\lambda$	Estimated Intensity	S_1^2	S_2^2
$2\bar{6}1$	1.91	0.47	0.1	0	0.5	$9\bar{2}2$	1.30	0.47	0.0	0	0.0
$6\bar{2}1$	1.91	0.46	0.1	0	0.4	$8\bar{5}2$	1.27	0.43	0.0	0	0.1
$5\bar{4}1$	1.89	0.43	0.4	0	1.2	$5\bar{8}2$	1.27	0.44	0.5	8	10.4
$4\bar{5}1$	1.89	0.44	0.4	0	1.1	$3\bar{9}2$	1.26	0.44	0.25	4	6.6
631	1.80	0.47	2.0	4	12.1	$9\bar{3}2$	1.26	0.43	faint	4	0.8
551	1.71	0.47	0.0	2	0.3	942	1.22	0.45	0.5	8	12.3
641	1.68	0.43	0.0	0	0.05	$\overline{49}2$	1.22	0.46	0.0	0	0.0
$\overline{46}1$	1.68	0.45	0.8	8	6.4	772	1.21	0.48	0.3	4	5.4
371	1.59	0.46	faint	2	1.1	952	1.17	0.44	faint	4	1.4
$\bar{7}31$	1.59	0.47	faint	2	1.1	592	1.17	0.47	0.15	4	2.7
081	1.52	0.46	0.2	0	2.0	$\overline{11}\cdot 0\cdot 2$	1.09	0.46	0.1	8	4.0
181	1.51	0.45	0.4	0	4.6	$\overline{11}\cdot\bar{1}\cdot 2$	1.09	0.45	0.1	4	4.5
$\bar{2}81$	1.47	0.46	0.0	0	0.2	$\bar{1}\cdot 11\cdot 2$	1.09	0.45	0.0	4	0.8
$\bar{8}21$	1.47	0.46	0.9	8	7.5	$10\cdot 5\cdot 3$	1.06	0.47	0.25	4	14.2
$\bar{6}61$	1.43	0.45	0.0	0	0.0	$5\cdot 10\cdot 3$	1.06	0.47	0.35	4	19.3
$\bar{3}81$	1.42	0.44	faint	0	1.8	$9\bar{7}3$	1.04	0.45	0.0	2	1.6
$\bar{8}31$	1.42	0.44	faint	0	1.8	$7\bar{9}3$	1.04	0.45	0.0	2	1.7
$\bar{5}71$	1.41	0.44	0.1	2	1.9	$9\cdot 10\cdot 4$	0.87	0.43	0.0	0	0.0
$\bar{7}51$	1.41	0.44	0.15	2	1.9	$10\cdot 9\cdot 4$	0.87	0.43	0.1	8	16.1

Discussion of the Structure

The structure obtained above is shown in the figure.

The final parameters given require that each tin atom be surrounded by four equidistant iodine atoms at the vertices of a regular tetrahedron, and that no other iodine atoms be located nearly so close to the tin atoms. The structure may therefore be considered to contain SnI_4 molecules. The tetrahedral molecules are arranged in pairs in a manner similar to the arrangement of the sulfur atoms in pyrites. The fact that one iodine atom is crystallographically non-equivalent to the other may be considered to arise from the arrangement of the molecules in the crystal rather than from any difference in the forces within the molecule between the tin atom and the iodine atoms.

The distance between the center of a tin atom and that of an adjacent iodine atom is calculated to be 2.63 Å. This is somewhat less than 2.80 Å., the sum of the corresponding Bragg radii.[11] The distance between an iodine atom of one molecule and the nearest one in another is 4.21 Å. This is much greater than 2.80 Å., the Bragg diameter of iodine, but in entire agreement with the distance[12] 4.21 Å. between adjacent iodine atoms in cadmium iodide (CdI_2).



Arrangement of the atoms in tin tetra-iodide; the unit cube has been divided along the plane ABCD to avoid superposition of the atoms in the figure.

It is likely that a number of other compounds possess the tin tetra-iodide structure, for example the tetra-iodides of carbon, silicon, titanium and germanium.

Summary

The crystal structure of tin tetra-iodide, SnI_4, has been investigated by means of Laue and spectral photographs. It has been found that there are 8 SnI_4 in a cubic unit having $d_{100} = 12.23$ Å., and that the iodine atoms cannot all be in equivalent positions. The space group symmetry is T_h^6. Probably the tin atoms are at points equivalent to (uuu) and the iodine atoms at points equivalent to (vvv) and (xyz). The values $u = 0.129$, $v = 0.253$, $x = 0.009$, $y = 0.001$, and $z = 0.253$ have been found to account for the intensity data, and to surround each tin atom tetrahedrally by iodine atoms. If these parameters are even approximately correct, the structure may be considered to be molecular.

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[11] W. L. Bragg, *Phil. Mag.*, **40,** 180 (1920).

[12] Bozorth, THIS JOURNAL, **44,** 2232 (1922).