On the Crystal Structure of the Antimony Oxychloride Sb₄O₅Cl₂ and Isomorphous Oxybromide

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X-ray crystallography and electron diffraction have shown that trivalent antimony forms in the oxides and the halides typical covalent bonds with definite valence angles.

The antimony halides SbX_3 form pyramidical molecules, with Sb at the top of the triangular pyramid and the three X in the base plane. This was shown by Gregg, Hampson, Jenkins, Jones and Sutton [1] and by Hassel and Sandbo [2] by electron diffraction investigations on SbX_3 in the gaseous state. Gregg *et al.* found the following distances Sb — X and valence angles X-Sb-X: $SbCl_3$: 2.37 ± 0.02 kX and $104° \pm 2°$, $SbBr_3$: 2.52 ± 0.02 kX and $96° \pm 2°$, SbI_3: 2.75 ± 0.02 kX and $98° \pm 2°$. Hassel and Sandbo found 2.47 kX and $98°$ for $SbBr_3$ and 2.70 kX and $99°$ for SbI_3. Byström and Westgren [3] have carried out an X-ray analysis on SbF_3 in the solid state. Their structure gives the angles of antimony as $81.9°$ and $104.3°$.

Trivalent antimony forms two types of oxides: the cubic, or low temperature modification, and the orthorhombic, or high temperature modification. They have been investigated by X-ray methods. Cubic Sb_2O_3 was first investigated by Bozorth [4], and was found to be built up from Sb_4O_6 molecules. The structure of orthorhombic Sb_2O_3 has been determined by Buerger and Hendricks [5]. It is composed of indefinitely long molecular chains of $(Sb_2O_3)\infty$. The smallest Sb-O distances within molecules are all 2.00 kX. The valence angles O-Sb-O are $81°$, $93°$, and $99°$, and the angles Sb-O-Sb are $116°$ and $132°$. Later on more exact determinations of the parameters of the cubic Sb_2O_3 were made by Almin and Westgren [6]. They found an Sb-O distance of 2.0 ± 0.1 kX, which agrees well with the distance found by Buerger and Hendricks for the orthorhombic form. From Almin and Westgren's values O-Sb-O angles may be calculated as $97.2°$ and the Sb-O-Sb angles as $130.5°$.

In the mineral nadorite, $PbSbO_2Cl$, however, antimony enters into MeO layers, where one antimony atom has four oxygen atoms as its nearest neighbours, which indicates an ionic binding [7]. Nadorite is closely related to the Me_2O_2X compounds which contain trivalent Bi, and which were investigated by Sillén [8]. These compounds form typical layer structures, which contain the same MeO layers as BiOX [9]. This suggests that antimony might form oxyhalides of the same types as does bismuth.

It therefore seemed of interest to investigate the oxyhalides of trivalent antimony, in order to obtain some idea of the bond character of antimony in these compounds.

PREPARATION

Antimony oxyhalides have been prepared by numerous workers. Among the earlier investigators are Sabanejew (1871) [10] and Cooke (1877) [11]. A detailed study of the system Sb_2O_3-HCl-H_2O was made by Lea and Wood [12]. They examined both the action of hydrochloric acid on hydrated antimonous oxide and the action of water on antimonious chloride. They found $SbOCl$, $Sb_4O_5Cl_2$ and Sb_2O_3 only to be stable solid compounds. Two metastable compounds were observed. One was assigned the formula $Sb_4O_3(OH)_5Cl$, and $Sb_4O_3(OH)_3Cl_3$ was suggested for the other.

In the present investigation solid SbX_3 (X = Cl, Br, or I) was hydrolysed with various amounts of water either at room temperature or at about 50° C. In some cases Sb_2O_3 was dissolved in HX and then various amounts of water added. A precipitate was obtained, which crystallised after some time when X was Cl or Br. The precipitates were filtered off with suction and dried in an exsiccator with concentrated H_2SO_4 or P_2O_5 and then washed free from adhering SbX_3. $SbCl_3$ was removed with ether and $SbBr_3$ and SbI_3 with carbon disulfide.

It was found that $Sb_4O_5Cl_2$ gave quite good crystals suitable for X-ray investigation. The best crystals were obtained when about 10 g $SbCl_3$ were dissolved in 20 ml concentrated HCl and then diluted with 110 to 150 ml water. When this mixture was kept in a conical flask with a stopper at 50° C, crystals of a size $\leq$ 1 mm were obtained within 5 to 10 days. The extension of the crystals was of about the same magnitude in the three dimensions. When the same mixtures were kept at room temperature, crystals appeared only after a very long time. These crystals formed fairly thin plates of a distorted hexagonal shape. After fourteen months plates of a length of more than 5 mm were obtained. These different types of crystals proved to give identical powder photographs.

It was more difficult to obtain crystals of $Sb_4O_5Br_2$ suitable for X-ray investigation. As a rule they were too small to give good rotation photographs. Sufficiently large crystals were obtained when Sb_2O_3 and HBr were sealed into a glass tube and kept first at about 180° C for 10 days and then at room temperature for 18 days.

It seemed of interest to investigate $Sb_4O_5I_2$ at the same time as $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$, as they might be isomorphous. It would then be possible to obtain more exact information on the positions of the X atoms from $Sb_4O_5I_2$. I have, however, not yet been able to obtain crystals of $Sb_4O_5I_2$, though such crystals are reported by Cooke [11]. I have tried methods similar to Cooke's and in addition several other methods. On one occasion

crystals in the form of hexagonal plates appeared and showed hexagonal symmetry from Laue photographs. The Weissenberg photographs were not very good, and a closer investigation and chemical analysis have not yet been carried out.

ANALYSES

Antimony was determined by titration with 0.1 n $KBrO_3$*. The oxyhalide was dissolved in 25 % HCl and titrated at about 60° C using methyl red as indicator. At the equivalence point the solution was colourless.

Halogen was determined by boiling the oxyhalide with Na_2CO_3 solution in a platinum dish. The filtrate was acidified with HNO_3 and precipitated by $AgNO_3$. The silver halide was then filtered off, dried, and weighed.

	Antimony %	Halogen %
Calc. for $Sb_4O_5Cl_2$	76.34	11.12
Obs.	76.0, 75.7	11.23, 11.15
Calc. for $Sb_4O_5Br_2$	67.01	21.99
Obs.	66.3, 66.5	22.34, 22.87

UNIT CELL AND SPACE GROUP

Single crystals of the oxychloride and the oxybromide were picked out and set, and rotation photographs and the following Weissenberg photographs were taken: the photographs $h0l$, $h1l$, $0kl$, $1kl$, $hk0$, and $hk1$ for $Sb_4O_5Cl_2$ and the photographs $h0l$, $h1l$, $hk0$, and $hk1$ for $Sb_4O_5Br_2$. The compounds proved to be monoclinic.

The cell dimensions were determined more accurately from the powder photographs. Thus

$$a = 6.229 \quad b = 5.107 \quad c = 13.50 \text{ kX} \quad \beta = 97.27° \text{ for } Sb_4O_5Cl_2$$
$$a = 6.593 \quad b = 5.133 \quad c = 13.43 \text{ kX} \quad \beta = 97.89° \text{ for } Sb_4O_5Br_2$$

with an accuracy of about $\pm$ 0.05 % for the axes, and $\pm$ 0.05° for the angles.

If two formula units are assumed per unit cell the density would be:

	$Sb_4O_5Cl_2$	$Sb_4O_5Br_2$
$d_{calc.}$	4.94	5.33
$d_{obs.}$	4.98, 4.94, 4.95	5.19, 5.15, 5.25

The agreement is quite good.

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* J. M. Kolthoff, Die Massanalyse, Berlin (1928) p. 443.

(Density determination: A sample was weighed in a small glass bulb, first in air and then in benzene. Air bubbles were driven out by evaporation. The temperature of the benzene was measured at each determination, and the corresponding density of benzene was used.)

In the Weissenberg photographs all reflections $h0l$ with l odd, and all reflections $0k0$ with k odd are absent. This is characteristic of the space group C_{2h}^5. It was observed that all reflections $h0l$ with $l = 2 + 4n$ are very weak.

STRUCTURE ANALYSIS

Patterson analysis

In order to obtain the positions of the eight antimony atoms of the cell, it seemed appropriate to apply Patterson analysis to $Sb_4O_5Cl_2$, where antimony is much heavier than the other atoms of the cell. The Patterson xz-projection and yz-projection were calculated. The values of $I(h0l)$ and $I(0kl)$ were estimated visually from the Weissenberg photographs in question. These I values were used instead of the F^2 values. Spots with large Θ were not taken into account (cf. Sillén) [13].

Because of the symmetry of space group C_{2h}^5, the parameters need only to be varied within the limits: $0 \leq x \leq 1$, $0 \leq y \leq \frac{1}{2}$, and $0 \leq z \leq \frac{1}{2}$. If positions 4(e) only are considered, it would be possible to make the limits even narrower for one set of parameters, thus for instance: $0 \leq x_1 \leq \frac{1}{2}$, $0 \leq y_1 \leq \frac{1}{4}$, $0 \leq z_1 \leq \frac{1}{4}$ and $0 \leq x_2 \leq 1$, $0 \leq y_2 \leq \frac{1}{2}$, $0 \leq z_2 \leq \frac{1}{2}$.

The xz-projection

In the xz-projection of space group C_{2h}^5 the following point positions are possible: 2(a) or 2(c): 00, $0\frac{1}{2}$; 2(b) or 2(d): $\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}$; 4(e): $\pm (x,z)$, $\pm (x, \frac{1}{2} + z)$.

The Patterson xz-projection actually found is given in fig. 1, which is referred to during the following discussion.

On account of the symmetry it is necessary to calculate only the area $0 \leq x \leq \frac{1}{2}$, $0 \leq z \leq \frac{1}{2}$.

For the eight antimony atoms in the unit cell, all combinations involving twofold positions of different kinds can be excluded, as there is no peak in the projection corresponding to an interatomic vector at $(\frac{1}{2} \frac{1}{2})$. On the other hand, two twofold positions of the same kind may be regarded as a special case of 4(e). Therefore, only a combination of two fourfold positions 4(e) need be considered. Thus

3
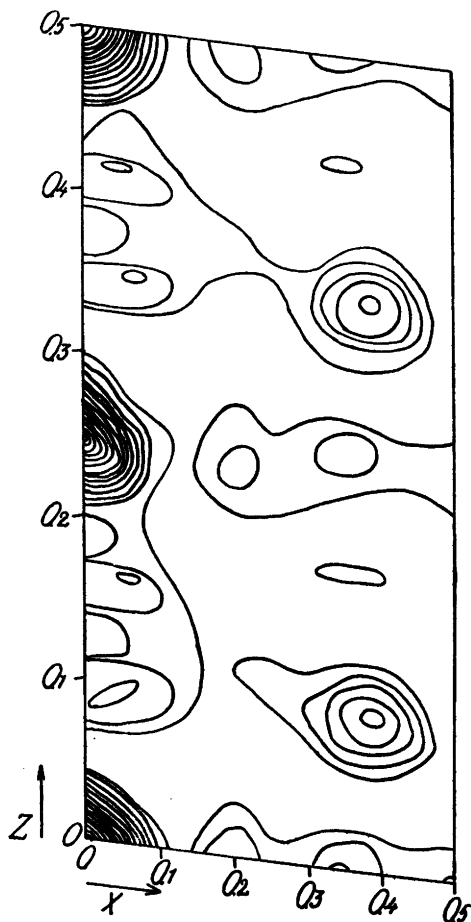
Fig. 1. Patterson projection $P(xpz)$ for $Sb_4O_5Cl_2$
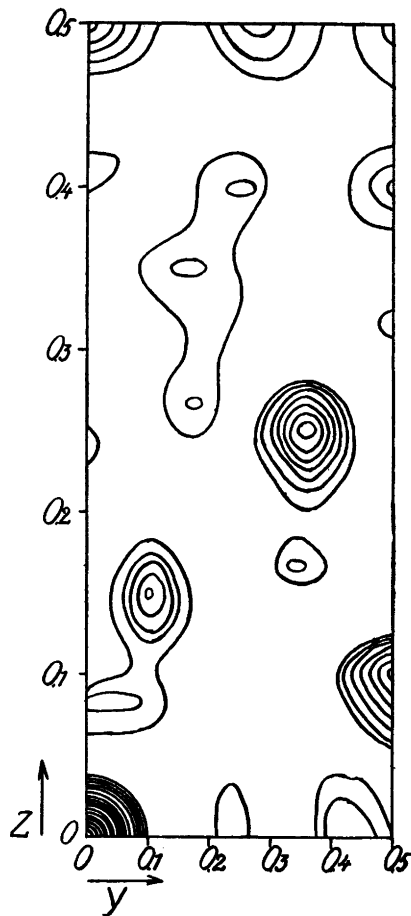
Fig. 2. Patterson projection $P(pyz)$ for $Sb_4O_5Cl_2$.

$$4Sb_1 \text{ in } x_1,z_1 \quad \bar{x}_1,z_1 \quad \bar{x}_1,\tfrac{1}{2}-z_1 \quad x_1,\tfrac{1}{2}+z_1$$
$$4Sb_2 \text{ in } x_2,z_2 \quad \bar{x}_2,\bar{z}_2 \quad \bar{x}_2,\tfrac{1}{2}-z_2 \quad x_2,\tfrac{1}{2}+z_2$$

Peaks in the Patterson projection corresponding to interatomic vectors can be expected at the following points:

Distances $Sb_1 - Sb_1$ and $Sb_2 - Sb_2$:

$$\begin{aligned}
&\text{I of weight 2} && \pm (2x_1, \ 2z_1) \\
& && \pm (2x_2, \ 2z_2) \\
&\text{II of weight 2} && \pm (2x_1, \ 2z_1 - \tfrac{1}{2}) \\
& && \pm (2x_2, \ 2z_2 - \tfrac{1}{2}) \\
&\text{III together of weight 8} && \pm (0 \ \tfrac{1}{2})
\end{aligned}$$

Distances $Sb_1 - Sb_2$

IV of weight 4 $\pm (x_1 - x_2, z_1 - z_2)$ $\pm (x_1 - x_2, z_1 - z_2 - \frac{1}{2})$

$\pm (x_1 + x_2, z_1 + z_2)$ $\pm (x_1 + x_2, z_1 + z_2 - \frac{1}{2})$

On inspecting more closely the limits of the parameters necessary to explain a Patterson xz-projection of space group C_{2h}^5, it was found from the symmetry that only x-parameters between 0 and $\frac{1}{2}$ need be considered, and that one z-parameter can be limited to $0 \leq z_2 \leq \frac{1}{4}$ and the other to $0 \leq z_1 \leq \frac{1}{2}$.

In the region $0 \leq x \leq \frac{1}{2}$, $0 \leq z \leq \frac{1}{2}$ two representatives of group I or II, two of group IV and the only vector of III will be found.

With the exception of the two high peaks at (00) and $(0\frac{1}{2})$, the Patterson projection reveals only three high peaks instead of the expected four. One is situated at $(0,\frac{1}{4})$ and is almost as high as the peaks at $(0,0)$ and $(0,\frac{1}{2})$, which indicates that its weight must be eight. The other two which are lower, are found at $x \approx 0.4$, $z \approx 0.1$ and $x \approx 0.4$, $z \approx 0.35$. They have the same height and are therefore assumed to have the weight four. As the z-values 0.1 and 0.35 cannot be transformed into each other by $\pm \frac{1}{2}$, both peaks cannot belong to group IV. This shows that $2x_1$ must almost coincide with $+ 2x_2$ or $- 2x_2$. The x values to be considered in the Patterson projection are 0, 0.4, 0.6, and 1.0.

The peak at $(0,\frac{1}{4})$ probably belongs to group IV, which will give it the weight 8, if $x_1 - x_2 = 0$ and $2x_1 \approx 2x_2 \approx 0.4$ or 0.6, which gives $x_1 \approx x_2 \approx 0.2$ or 0.3.

If it is assumed that $x_1 - x_2$, $z_1 - z_2$ is $(0, 0,25)$ which gives $z_1 \approx z_2 + 0.25$, solutions of the following two types are possible:

A. Assuming $x_1 + x_2$, $z_1 + z_2$ is $(0.4, 0.6)$ we have $x_1 \approx x_2 \approx 0.2$, $z_1 \approx 0.425$, $z_2 \approx 0.175$

B. Assuming $x_1 + x_2$, $z_1 + z_2$ is $(0.4, 0.35)$ we have $x_1 \approx x_2 \approx 0.2$, $z_1 \approx 0.3$, $z_2 \approx 0.05$

From the yz-projection it will later on be evident that only solutions of type B are possible.

The yz-projection

From the xz-projection it seems probable that the antimony atoms occupy two fourfold positions 4(e). This gives the following point positions in the yz-projection:

4 Sb_1 y_1, z_1 $\bar{y}_1, \bar{z}_1$ $\frac{1}{2} + y_1, \frac{1}{2} - z_1$ $\frac{1}{2} - y_1, \frac{1}{2} + z_1$

4 Sb_2 y_2, z_2 $\bar{y}_2, \bar{z}_2$ $\frac{1}{2} + y_2, \frac{1}{2} - z_2$ $\frac{1}{2} - y_2, \frac{1}{2} + z_2$

Using the same group notations as in the preceeding section the corresponding maxima in the vector space are:

Weight 1

I $\pm (2y_1, \pm 2z_1)$ $\qquad\qquad\qquad \pm (2y_2, \pm 2z_2)$

Weight 2

II $\pm (\frac{1}{2}, 2z_1 + \frac{1}{2})$ $\qquad\qquad \pm (\frac{1}{2}, 2z_2 + \frac{1}{2})$

III $\pm (2y_1 + \frac{1}{2}, \frac{1}{2})$ $\qquad\qquad \pm (2y_2 + \frac{1}{2}, \frac{1}{2})$

IV $\pm (y_1 - y_2, \pm (z_1 - z_2))$ $\qquad \pm (\frac{1}{2} + y_1 - y_2, \frac{1}{2} \pm (z_1 + z_2))$

$\pm (y_1 + y_2, \pm (z_1 + z_2))$ $\qquad \pm (\frac{1}{2} + y_1 + y_2, \frac{1}{2} \pm (z_1 - z_2))$

Just as for the xz-projection, it was found that the limits of the parameters for the Patterson yz-projection can be made narrower than for the spatial structure. Thus $0 \leq y_1 \leq \frac{1}{2}$, $0 \leq y_2 \leq \frac{1}{4}$, $0 \leq z_1 \leq \frac{1}{2}$ and $0 \leq z_2 \leq \frac{1}{4}$.

The Patterson projection was calculated for $0 \leq y \leq \frac{1}{2}$, $0 \leq z \leq \frac{1}{2}$. This area should contain eight peaks of weight 2 and two of weight 1. Now, excluding the high peak at (0,0) the projection contains four peaks, which are much higher than the others, namely at $(0, \frac{1}{2})$, $(\frac{1}{8}, 0.15)$, $(\frac{3}{8}, \frac{1}{4})$, $(\frac{1}{2}, 0.1)$, cf. fig. 2. The height of the last two seems to indicate a weight of 4, which was taken as a starting point.

At $y = \frac{1}{2}$ there are peaks at $z \approx 0.1$ (high), 0.4, 0.5, 0.6 and 0.9 (high), which should correspond to vectors of group II. Accordingly, possible values of z_1 and z_2 would be about 0, 0.05, 0.2, 0.3, 0.45 or 0.5. The xz-projection could be explained only by assuming $z_1 - z_2 \approx 0.25$ or $z_1 + z_2 \approx 0.25$ or 0.75 *. This excludes the z-values 0 and 0.5. The possible z-combinations are therefore, $z_1 \approx 0.05$ or 0.45 $z_2 \approx 0.2$ or 0.3.

At $z = \frac{1}{2}$ there are peaks at $y \approx 0$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and 1.0, which should correspond to vectors of group III. This gives y_1 and $y_2 \approx 0$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{3}{8}$, or $\frac{1}{2}$.

The high peak at about $(\frac{3}{8}, \frac{1}{4})$, which, according to the possible z-values, must be of group IV and thus contain the sum or the difference between y_1 and y_2, indicates a combination of $y \approx \frac{1}{8}$ or $\frac{3}{8}$ with $y \approx 0$, $\frac{1}{4}$ or $\frac{1}{2}$. As the peaks at $y = \frac{1}{2}$ are not of the same height, it seems probable that one peak of group I coincides with (0.5, 0.1) or (0.5, 0.9). This would be possible if $y_1 \approx \frac{1}{4}$. From the previous discussion on the limits of the parameters, it is clear that we need only consider $y_2 \approx \frac{1}{8}$. The possible combinations are:

$$y_1 \approx \frac{1}{4} \quad z_1 \approx 0.05 \text{ or } 0.45$$
$$y_2 \approx \frac{1}{8} \quad z_2 \approx 0.2$$

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* In the xz-projection the possibility of $z_1 + z_2 \approx 0.25$ or 0.75 was not discussed, as this would give x-parameters outside the given limits.

As $y_1 + y_2 \approx \frac{3}{8}$, the z-values 0.25 or 0.75 of the Patterson projection must be equal to $\pm (z_1 + z_2)$. This is only possible if $z_1 \approx 0.05$ and $z_2 \approx 0.2$. Thus we obtain: $y_1 \approx \frac{1}{4} \quad z_1 \approx 0.05$

$$y_2 \approx \tfrac{1}{8} \quad z_2 \approx 0.2$$

Now the parameter values from the two projections have to be combined into a structure in space. As the two Patterson projections can be explained independently the indices of the parameters were chosen arbitrarily. In combining the two projections the numerically equal z-values must be taken and not those with the same index. It should also be observed that the limits of the parameters are larger in space than in the Patterson projections. The parameter limits were discussed in the introductory part of the Patterson analysis. The narrowest space limits need not, of course, all belong to the same fourfold position.

From the xz-projection we obtain only two alternatives

$$x_1 \approx 0.2 \quad z_1 \approx 0.3 \qquad\qquad x_1 \approx 0.8 \quad z_1 \approx 0.2$$
$$x_2 \approx 0.2 \quad z_2 \approx 0.05 \quad \text{and} \quad x_2 \approx 0.2 \quad z_2 \approx 0.05$$

and from the yz-projection only one

$$y_1 \approx \tfrac{1}{4} \quad z_1 \approx 0.05$$
$$y_2 \approx \tfrac{1}{8} \quad z_2 \approx 0.2$$

(Other combinations give both z_1 and z_2 or both y_1 and y_2 larger than $\frac{1}{4}$). Thus we obtain as the only possible combination

$$x_1 \approx 0.2 \quad y_1 \approx \tfrac{1}{4} \quad z_1 \approx 0.05$$
$$x_2 \approx 0.8 \quad y_2 \approx \tfrac{1}{8} \quad z_2 \approx 0.2$$

where the indices are the same as in the yz-projection.

DISCUSSION OF INTENSITIES

In order to get more exact values for the parameters, these were varied around the approximate values obtained from the Patterson analysis, and the intensities were calculated. At first the influence of the halogen and the oxygen atoms was neglected.

For $h00$ the structure factor is

$$\frac{F_{\text{Sb}}}{4f_{\text{Sb}}} = \cos 2 \pi h x_1 + \cos 2 \pi h x_2.$$

As $|x_1| \approx |x_2| \approx 0.2$, it is simpler to write $\xi_1 = \dfrac{|x_1| + |x_2|}{2}$ and $\xi_2 = \dfrac{|x_1| - |x_2|}{2}$, thus giving $\dfrac{F_{Sb}}{4f_{Sb}} = 2 \cos 2\pi h \xi_1 \cos 2\pi h \xi_2$.

It is possible to fix ξ_1 to within fairly narrow limits as 0.197 for the oxychloride, whereas ξ_2 is more difficult to determine. Presumably $0 \le \xi_2 \le 0.015$. At first ξ_2 was assumed to be 0.

It is obvious that the antimony atoms are situated in two layers at $x \approx 0.2$ and $x \approx 0.8$. I thought it then probable that the ten oxygen and the four halogen atoms are also situated in layers, as, for instance, in the Me_2O_2X-compounds investigated by Sillén. Considerations of space as well as a rough intensity calculation of $h00$ for $Sb_4O_5Br_2$ make it probable that the four halogens are situated at $x \approx \frac{1}{2}$. However, they must occupy a fourfold position, as 2(b) and 2(d) with $x = \frac{1}{2}$ would give a distance halogen — halogen equal to $\frac{1}{2}b$ or about 2.5 kX, which seems very improbable. Then there is no room for oxygen atoms at $0.2 < x < 0.8$. It seems most probable that $x_0 \approx 0$. The ten oxygen atoms must then occupy one twofold position with $x = 0$, and two fourfold positions 4(e).

Assuming $\xi_2 \approx 0$, all Br at $x \approx \frac{1}{2}$, and all oxygen at $x \approx 0$, ξ_1 was determined to be about 0.181 for the oxybromide. Then the Br- and the Sb-parameters were varied alternately to obtain the best intensity agreement. When the intensities were calculated from $I \sim \dfrac{1 + \cos^2 2\Theta}{\sin 2\Theta} F^2$ it proved very difficult to obtain a satisfactory agreement for $I(100)$ and $I(200)$, which are fairly weak and seem to have almost the same intensities. On assuming all the ten oxygens at $x = 0$, $I(200)_{calc.}$ was much weaker than $I(100)_{calc.}$. The influence of varying the oxygen x-parameters was then examined. It was assumed that the two x_0 are nearly equal, as the two x_{Sb} seemed to be equal, and it would be difficult to make separate variations of the former, considering their low contribution to the intensities. The best intensity agreement was obtained with $\xi_1 = 0.185$, $x_{Br} = 0.515 \ (0.485)$, 2 O at $x = 0$ and 8 O at $x = 0.11$, ξ_2 was assumed to be $= 0$.

The x-parameters of the oxychloride were then inspected more closely, which led to the conclusion that $\xi_1 = 0.197$, $0 < \xi_2 < 0.01$, $x_{Cl} = 0.515$ (0.485) and 2 O at $x = 0$, 8 O at $x = 0.13$.

For $00l$ the structure factor is

$$\frac{F_{Sb}}{4f_{Sb}} = \cos 2\pi l z_1 + \cos 2\pi l z_2.$$

As the y- and the z-axes of $Sb_4O_5Br_2$ are almost equal to those of $Sb_4O_5Cl_2$, it was assumed that the y- and z-parameters of the two compounds are nearly equal. Considering antimony only, the best agreement was preliminarily obtained with $z_1 = 0.049$ and $z_2 = 0.201$ for the oxychloride. As the reflections $h0l$ with $l = 2 + 4n$ are very weak for both the oxychloride and the oxybromide, it was assumed that the halogens cannot contribute much to these reflections. This would indicate $z_{hal.} \approx \frac{1}{8}$.

To determine the y-parameters of Sb more accurately, the reflections $0kl$ from a Weissenberg photograph of $Sb_4O_5Cl_2$ were used, as the few reflections $0k0$ were not sufficient. Assuming $y_1 = \frac{1}{4}$ and $y_2 = \frac{1}{8}$ we have $I(043)_{calc} \sim 0$. As the observed intensity is between medium and strong, this reflection cannot depend only on Cl and O. The best agreement was obtained with $y_1 = 0.225$ and $y_2 = 0.113$.

The $hk0$ reflection of $Sb_4O_5Br_2$ were then scrutinized. Here the contribution of Br to the intensities cannot be entirely neglected. A variation in the y-parameters of Sb indicates $y_{1Sb} = 0.220$ and $y_{2Sb} = 0.12$, when considering $0k0$ reflections, if it is assumed at the same time (1) that $F_{Br} \approx - F_{Sb}$ for 040, which is absent, and $F_{Br} \approx 0$ for 060, and (2) that F_{Br} and F_{Sb} have the same sign (negative) for 020. It seemed desirable to obtain as high a calculated intensity of 020 as possible. Values of y_{Br} fulfilling the conditions (1) are approximately 0.045, 0.205, 0.295, 0.455, 0.545, 0.705, 0.795 and 0.955. Of these values only 0.205, 0.295, 0.705 and 0.795 fulfil condition (2). If $y_{hal.} \approx 0.205$ and 0.295 are used for the oxychloride, and at the same time we assume $z_{Cl} \approx \frac{1}{8}$, $x_{Cl} \approx \frac{1}{2}$, a distance 2.1 kX (with more preliminary parameters 1.9 — 2.0 kX) is obtained for Sb —Cl, which is too small, as Sb — Cl is 2.37 ± 0.02 kX in $SbCl_3$[1]. These y-values were therefore rejected.

It is not possible to distinguish between $y_{Br} = 0.705$ and 0.795 by means of $hk0$. It is, however, possible to do so by means of hkl with l odd. When the other parameters were more definitely fixed, the influence of oxygen is, however, of little importance, a comparison was made between $I(012)$ and $I(013)$. $I(012)_{obs}$ was stronger than $I(013)_{obs}$. Taking the polarizing factor into account, the calculated values were:

1. $y_{Br} = 0.705 : I(012) \sim 17.1,\ I(013) \sim 8.6.$
2. $y_{Br} = 0.795 : I(012) \sim 17.1,\ I(013) \sim 25.6.$

This favours $y = 0.705$. When fixing the oxygen atoms, space considerations also seemed to favour $y = 0.705$.

THE OXYGEN POSITIONS

The rough parameter values of antimony and halogen were now used to determine the oxygen positions, which would render possible a more exact calculation of the parameters.

The Sb-O distance was assumed to be the same as in Sb_2O_3, where it is 2.0 kX, (cf. p. 178), and the sum of the ionic radii of oxygen and halogen are:

$$
\begin{array}{lllll}
\text{O—Cl} & 3.13 \text{ kX (Goldschmidt)}, & 3.21 \text{ kX (Pauling)}, \\
\text{O—Br} & 3.28 \text{ »} & \text{»} & 3.35 \text{ »} & \text{»} \\
\text{O—O} & 2.64 \text{ »} & \text{»} & 2.80 \text{ »} & \text{»}
\end{array}
$$

(Values of ionic radii are taken from *Internationale Tabellen* [14].)

Spheres of appropriate radii, inside which no oxygen ions could occur, were then drawn around the Sb and Cl (Br) centers, and cuts were made at $x = 0$ and $x = 0.13$ (chloride) $x = 0.11$ (bromide), since these x-parameters seemed probable for oxygen from the intensities of $h00$.

Cut $x = 0$. There are two twofold positions with $x = 0$, 2(a): (000), $(0\frac{1}{2}\frac{1}{2})$ and 2(c): $(00\frac{1}{2})$, $(0\frac{1}{2}0)$. This cut shows that only 2(c) is possible. It also seems as if some O — O distances would be rather short, if all oxygen atoms were placed at $x = 0$.

Cut $x = 0.11$ (0.72 kX) (bromide). Fig. 3 (The coordinates are referred to an orthogonal coordinate system, where the directions of the y- and the z-axis of the monoclinic cell and the orthogonal system coincide.) Possible oxygen
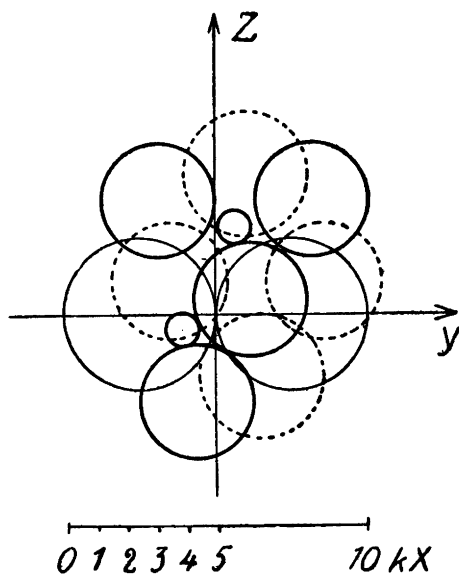

Fig. 3. $Sb_4O_5Br_2$. Spheres of appropriate radii are drawn around the Sb, Br, and O centers. Cut at $x = 0.11$. Thick circle = the Sb-O distance, dotted circle = the Br-O distance and thin circle = the O-O distance. Possible oxygen positions are approximatly: I $y - 0.3$ kx $z \approx -0.9$ kx, II $y \approx 0$, $z \approx 3$ kx and III $y \approx 1.5$ kx $z \approx 2.5$ kx.

positions are approximately I. $y \approx -0.3$ kX, $z \approx -0.9$ kX, II. $y \approx 0$, $z \approx$ 3 kX and III. $y \approx 1.5$ kX, $z \approx 2.5$ kX. It does not seem possible to combine II and III. With the preliminary coordinates there would be a distance $O - O$ about 1.6 kX. The oxygen can, however, be moved, so that this distance will become larger or about 2.25 kX. It might be possible to make it even larger, but this does not seem to be of interest, as these oxygen positions appear to give a rather improbable coordination around Sb_1. It is seen from fig. 4 that between two adjacent Sb_1 (distance between them 3.4 kX) there are no other negative charges than Br at distances 3.3 and 3.5 kX.
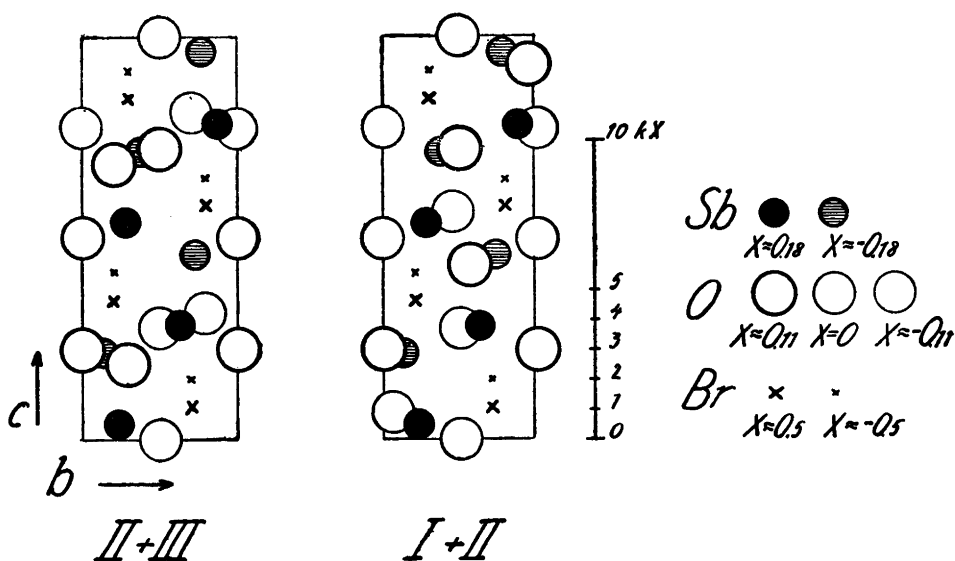
Fig. 4. *Orthogonal projections of the unit cell of* $Sb_4O_5Br_2$, *giving the possible oxygen positions which could later on be excluded.*

This would mean that only a combination of I and II or I and III is possible. Now the distance between two oxygen atoms of O_I would be about 2.4 kX, which seems rather short. If O_I is moved to $x \approx 0.6$, $y \approx 0.2$ and $z \approx -1.2$ kX, this distance will be better (about 2.7 kX), though the distance O_I-Br will be a little short. This was however thought to be less objectionable, as the halogens are more easily deformed. If I is combined with II the $O - O$ distance of two adjacent oxygens of I and II would be about 2.6 kX, if the coordinates $x \approx 0.72$, $y \approx -0.3$, $z \approx -0.9$ kX are used for O_I, and about 2.2 kX with the coordinates $x \approx 0.6$, $y \approx 0.2$, $z \approx -1.2$ kX. There seems to be some difficulty in obtaining good $O - O$ distances with a combination of I and II. A projection of this configuration is shown in fig. 4.
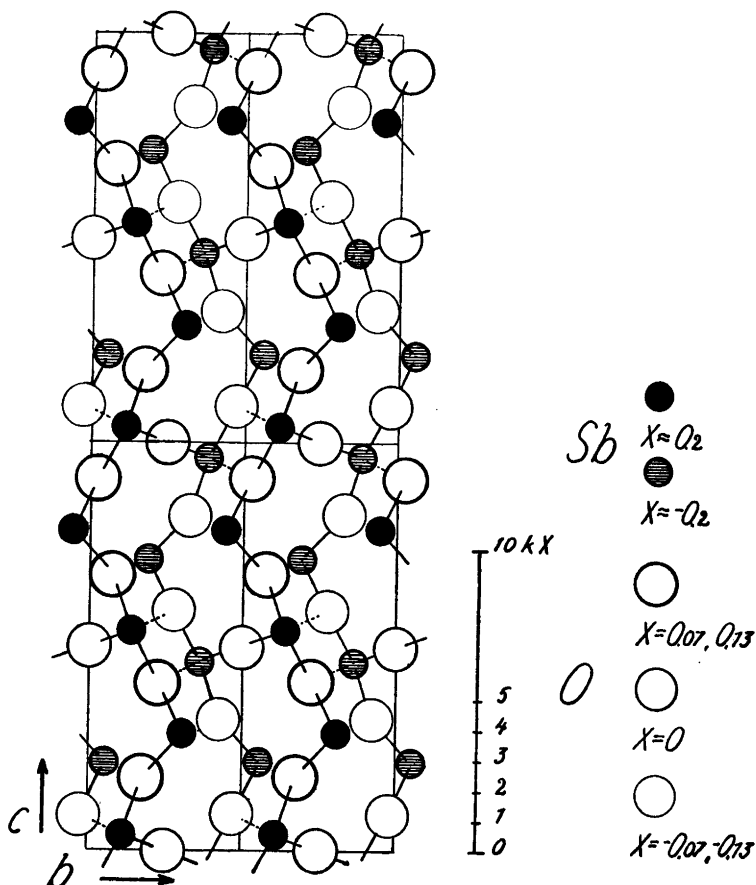
Fig. 5. *Orthogonal projection of four adjecent unit cells of* $Sb_4O_5Cl_2$ *on* $x = 0$, *showing the Sb-O layer. The Cl-atoms have been omitted, to make the Sb-O chains more obvious.*

A combination of I and III gives quite reasonable O — O distances. The shortest distance $O_I — O_{III}$ is about 2.5 kX for both positions of O_I. A projection of this configuration is shown in fig. s 5 and 6. (This is for $Sb_4O_5Cl_2$ with the final parameters).

In I + II there will be no oxygen or halogen atoms immediately between Sb_1 and Sb_2. In I + III, however, there is one oxygen between them. This seems to favour I + III, especially as Sb — O chains will be formed in I + III, which seems fairly plausible, as the antimony atoms do in fact appear to form chains.

To fix the x-parameters better, cuts were later on made at $z \approx 2.4$ kX and $z \approx — 1.2$ kX, when the other atomic positions had been determined more accurately. This gave the following oxygen positions:
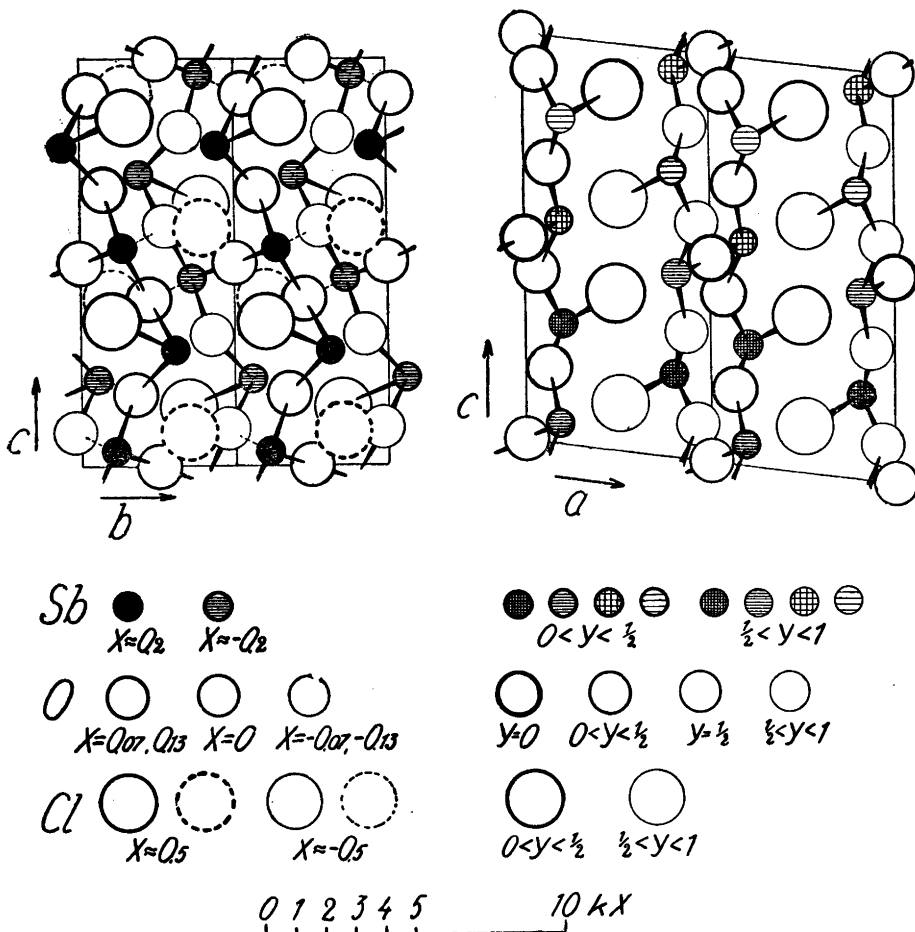
Fig. 6. *Orthogonal projections of the structure of* $Sb_4O_5Cl_2$ *on* $x = 0$ $(-\frac{1}{2} \lesssim x \lesssim \frac{1}{2})$ *and on the* xz-*plane.*

$Sb_4O_5Br_2$: O_1 2 (c) $(00\frac{1}{2})$, $(0\frac{1}{2}0)$ O_2 4 (e) $x = 0.13$, $y = 0.37$, $z = 0.187$ O_3 4 (e) $x = 0.08$, $y = 0.04$, $z = -0.084$.

and similarly

$Sb_4O_5Cl_2$: O_1 2 (c) $(00\frac{1}{2})$, $(0\frac{1}{2}0)$ O_2 4 (e) $x = 0.13$, $y = 0.35$, $z = 0.185$ O_3 4 (e) $x = 0.07$, $y = 0.05$, $z = -0.085$.

FURTHER DISCUSSION OF INTENSITIES

When a more exact intensity calculation was carried out for $hk0$ of $Sb_4O_5Br_2$, it was found impossible to obtain good agreement for the weak

reflections $h10$ as long as it was assumed that $|x_{1Sb}| = |x_{2Sb}|$. Assuming them to be unequal, the best agreement was obtained with:

$$Sb_1 \quad at \quad x = 0.174, \qquad y = 0.225$$
$$Sb_2 \quad at \quad x = -0.194, \qquad y = 0.125$$
$$Br \quad at \quad x = 0.51, \qquad y = 0.705$$

Table 1 shows that the agreement between observed and calculated intensities for the Weissenberg photograph $hk0$ is quite good.

Table 1. Calculated and observed intensities of hk0 from Weissenberg photograph of $Sb_4O_5Br_2$. CuKa radiation.

k	0k0	1k0	2k0	3k0	4k0	5k0	6k0	7k0	8k0
0		1.9 m.+	2.8 m.+	64 v.st.	1.2 w.+	9.2 st.—	41 st.	9.4 m.	13 st.
1	— —	1.2 w.—	1.6 w.	1.8 w.—	1.4 w.	1.8 w.—	3.9 w.	4.1 m.—	3.1 m.
2	18 st.	0.7 v.w.	0.2 —	24 st.	0.4 —	0.3 —	21 st.	0.7 —	
3	— —	20 st.	10 st.—	2.5 w.+	29 st.—	4.2 m.—	5.5 m.	27 st.	
4	0.1 —	0.5 —	4.2 w.+	0 —	0 —	4.1 w.+	2.5 w.+		
5	— —	17 m.	11 m.	1.6 w.	17 st.—	2.9 m.+			
6	2.0 w.	0.9 —	2.1 w.+	2.8 m.+					

Similarly for $Sb_4O_5Cl_2$ (table 4):

$$Sb_1 \quad at \quad x = 0.186, \qquad y = 0.225$$
$$Sb_2 \quad at \quad x = -0.204, \qquad y = 0.113$$
$$Cl \quad at \quad x = 0.51, \qquad y = 0.703$$

Table 2. Calculated and observed intensities of h0l from Weissenberg photograph of $Sb_4O_5Br_2$. CuKa radiation.

l	00l	10l	20l	30l	40l	50l	60l	70l	80l
16	9.2 v.w.	23 m.—							
14	0 —	3.6 —	0.3 —	2.2 v.w.					
12	44 w.+	8,1 v.w.	18 w.+	35 w.+	22 m.—	17 m.			
10	1.9 —	0 —	0.7 —	0.3 —	0.7 —	0 —	0.8 w.		
8	11 w.	63 m.—	4.9 v.w.	16 w.+	44 m.—	17 w.+	15 m.—		
6	0.8 v.v.w.	0 —	0.7 —	0.4 —	0 —	3.1 v.v.w.	3.6 v.v.w.	0.8 v.w.	
4	0 —	4.1 w.—	51 m.	7.4 w.+	17 m.	45 m.+	14 w.+	15 m.—	
2	0 —	0.1 —	0.1 —	0 —	0.7 v.v.w.	1.3 v.v.w.	2.9 v.w.	4.8 v.w.	5.5 w.
0		1.9 w.	2.9 w.	64 st.	1.3 v.w.	9.2 m.—	41 m.	9.4 w.+	13 m.
—2		0 —	3.0 v.v.w.	0 —	0.4 —	8.5 w.	0.6 v.v.w.	2.2 v.w.	12 w.+
4		61 st.—	0.1 v.v.w.	5.2 v.w.	59 m.	1.5 —	13 w.+	46 m.	4.6 v.w.
6		0.1 —	0 —	7.1 v.w.	0 —	0.3 —	13 w.	2.5 —	5.0 w.
8		0.1 —	69 m.	4.9 —	0.8 —	45 w.+	0.2 —	8.1 w.+	
10	2.7 —	0 —	0.1 —	14 v.w.	0 —	0.1 —		21 m.—	
12	7.8 w.	0 —	58 w.+	4.1 —		3.0 —	49 m.—	0.5 —	
14	1.3 —	10 —	0 —	0.4 —		22 w.	0 —		
16		40 w.+	16 w.	0.8 —	40 m.				

Table 3. Calculated and observed intensities of h1l from Weissenberg photograph of $Sb_4O_5Br_2$. CuKa radiation.

l	01l	11l	21l	31l	41l	51l	61l	71l	81l
16	0.3 —	0.4 —							
15	3.5 w.	2.8 w.	1.2 v.w.						
14	13 w.+	33 m.—	11 m.	13 st.					
13	0.7 v.w.	4.2 w.	1.4 v.v.w.	2.9 w.	1.8 v.w.				
12	3.6 v.w.	0 —	0.7 —	1.2 v.w.	0.1 v.v.w.	1.3 v.w.			
11	0 —	3.5 w.	3.5 w.	1.4 v.w.	4.4 w.+	1.9 v.w.			
10	2.7 v.w.	8.5 w.+	34 m.+	13 m.	12 m.+	23 st.	24 st.		
9	0 —	3.0 w.	9.0 w.+	0.1 v.v.w.	2.1 w.	1.8 v.v.w.	4.4 w.+		
8	0.8 —	1.6 v.w.	0.4 v.w.	1.7 v.w.	0 —	1.6 w.+	2.6 w.		
7	8.3 m.	0 —	2.4 w.	2.8 w.—	2.4 w.	3.6 w.+	1.1 v.v.w.	4.6 m.	
6	52 v.st.	0.8 v.w.	6.4 m.	42 v.st.	6.9 m.	8.1 m.+	25 st.	17 st.	
5	4.4 m.	0.3 v.v.w.	3.1 w.+	5.3 m.	1.7 w.	5.9 m.	2.8 w.	4.5 w.+	
4	0 —	0.4 v.v.w.	0 —	0.6 w.	0.8 w.	0.4 —	3.0 w.+	2.3 w.+	
3	1.2 m.—	6.2 m.	0.1 —	2.6 m.	3.6 m.	2.0 w.	2.1 w.+	0.9 w.	
2	1.6 m.+	52 v.st.	0.8 w.	5.8 st.	44 v.st.	5.5 w.+	9.4 m.—	31 st.	11 st.
1		8.8 st.	0.2 v.v.w.	2.2 m.	5.8 m.	0.4 w.	3.0 w.+	0.6 w.	5.9 m.+
0		1.0 m.	1.4 m.—	1.6 m.—	1.5 w.	1.9 w.	4.1 w.	4.1 m.—	3.0 m.+
—1		1.4 w.	8.3 m.—	0 —	1.2 w.	2.3 w.	3.2 w.+	2.6 w.+	1.2 —
2		0.4 —	51 st.	0 —	3.1 m.	40 v.st.	2.7 w.	6.4 m.—	24 st.
3		0.6 v.w.	5.5 m.—	0.1 —	6.6 m.—	7.6 w.+	0.4 —	7.1 m.—	2.6 v.v.w.
4		1.0 v.v.w.	0.9 w.	0.3 v.v.w.	3.5 w.	2.6 w.	1.6 w.	7.1 m.—	7.2 m.—
5		0 —	1.5 w.	6.6 m.	0.4 —	1.8 w.	2.7 w.	2.9 w.	1.4 w.
6		2.8 m.—	0.2 —	51 st.—	0.2 —	3.1 w.	41 st.	0.5 —	5.5 m.
7		2.7 w.	0.6 v.w.	6.1 m.—	0.2 —	3.6 w.	3.5 w.	0.9 —	6.7 m.
8		0.3 —	6.7 w.	0.5 —	0.4 —	12 w.	1.4 v.w.	1.2 w.	
9		7.9 w.	0.4 —	0.4 —	5.5 v.w.	0.4 —	0.8 w.	1.4 w.	
10		42 m.	3.8 w.	0 —	41 w.+	0.7 —	2.3 w.	32 st.	
11		6.6 w.—	1.9 w.—	2.0 v.v.w.	7.2 w.—	0.1 —	7.4 w.+	7.2 m.+	
12		0.6 —	0 —	8.8 w.—	1.1 —	0.3 —	17 m.		
13		0 —	5.5 w.—	0.1 —	2.1 —	7.2 w.	0.4 —		
14		3.5 v.w.	37 w.+	7.7 w.—	0 —	34 st.—			
15		0.2 —	7.4 w.	3.5 w.—	1.2 —				
16		10 w.	0 —						

As the x-parameters now seemed to be fixed satisfactorily, the z-parameters were determined more accurately from the $h0l$ reflections in the Weissenberg photographs. It proved, however, rather difficult to obtain very satisfactory agreement. The reflections $00l$ with $l = 2 + 4n$, which are weak, could not be explained as depending entirely on oxygen. Therefore, $z_{1Sb} + z_{2Sb}$ could not be exactly 0.25 and $z_{hal.}$ could hardly be exactly ⅛. However, small variations of z_{1Sb} around 0.05 and z_{2Sb} around 0.20 do not influence the $00l$ reflections very much.

The intensities were calculated for different $z_{hal.}$, and it seemed probable that $z_{hal} < \frac{1}{8}$. Finally the parameters of the oxybromide giving the best calculated intensities were chosen as $z_{1Sb} = 0.051$, $z_{2Sb} = 0.203$ and $z_{Br} = 0.118$.

The calculated and observed intensities of $h0l$ from the Weissenberg photograph of the oxybromide are given in table 2. Considering the general weakening of all reflections in the vicinity of $00l$ the agreement is good.

The calculated and observed intensities of $h1l$ of the oxybromide are given in table 3. Here the agreement seems to be very satisfactory.

Table 4. Intensities of hk0 from Weissenberg photograph of $Sb_4O_5Cl_2$. CuKα radiation. The calculated intensity is given on the left of each column, and the intensity estimated for Patterson analysis on the right.

k	0k0		1k0		2k0		3k0		4k0		5k0		6k0		7k0	
0			4.6	50	12	60	38	90	3.0	8	24	50	13	17	21	50
1	—	—	1.8	17	2.1	3	0.4	—	1.8	3	2.2	3	0.2	—	5.3	17
2	8.1	100	0	—	1.9	17	12	50	0	—	2.2	8	8.5	22	1.1	5
3	—	—	25	100	9.8	50	8.8	30	33	60	0.6	3	19	50	17	60
4	0	—	0	—	1.7	6	0	—	0.4	3	0.6	3	3.2	15		
5	—	—	10	45	5.0	25	2.3	20	10	50	0.2	15				
6	7.9	22	1.3	1	7.6	30	6.4	40								

Table 5. Intensities of h0l from Weissenberg photograph of $Sb_4O_5Cl_2$. CuKα radiation. The calculated intensity is given on the left of each column, and the intensity estimated for Patterson analysis on the right.

l	00l		10l		20l		30l		40l		50l		60l		70l	
16	1.8	6	35	80	18	40										
14	0	—	1.0	2	0	—	2.9	7	0	—						
12	33	90	3.0	12	31	80	17	25	20	50	24	50				
10	1.0	5	0	—	0.3	—	0	—	1.1	3	0	—				
8	18	95	45	100	2.4	7	29	50	18	25	21	40	23	50		
6	0.2	5	0	—	0.9	—	0.5	—	0.1	—	3.5	5	1.0	—	1.6	7
4	1.7	40	12	15	31	60	6.7	25	32	95	17	40	22	40	21	50
2	0	—	0.1	—	0.2	—	0.1	3	0.1	2	2.1	5	4.2	7	0.7	—
0			4.6	50	12	60	38	90	3.0	8	24	50	13	17	21	40
—2			0.1	—	1.8	2	0	—	1.0	3	3.4	4	1.2	5	3.3	7
4			45	40	0.4	—	20	15	35	40	5.0	4	31	45	14	17
6			0.1	—	0.1	—	2.9	—	0.2	—	1.4	—	3.6	3	5.3	6
8			2.6	10	53	22	3.6	—	12	6	26	15	4.6	6	27	40
10			0.8	—	0	—	0.2	—	6.7	3	0.1	—	1.6	1	5.8	17
12			11	40	5.9	13	48	50	1.5	5	21	20	30	40		
14			0.2	5	4.4	5	0	—	0.3	—	9.6	15				
16			36	80	18	50	3.5	15								

Variations for the oxychloride gave $z_{1Sb} = 0,049$, $z_{2Sb} = 0.203$ and $z_{Cl} = 0.115$ as the most probable values. The calculated and observed intensities of $h0l$ from the Weissenberg photograph are given in table 5. There appeared at first to be a certain disagreement between the observed and calculated intensities of 004 and 104. $I(004)_{calc.} \sim 1.7$ and $I(104)_{calc.} \sim 12$, whereas $I(004)_{obs.}$ is definitely stronger than $I(104)_{obs.}$ in the Weissenberg photograph. This could not be overcome by small variations of the parameters since the indices were low. From the powder photograph (table 8), it was, however found that $I(004)$ must be lower than $I(104)$, in spite of the fact that their $\sin^2\Theta$ coincide with others. There seems to be a general enhancement of the observed intensities of $00l$, and a general weakening in other parts, especially in the neighbourhood of the zone n0$\overline{4}$n in the Weissenberg photograph. Taking these facts into consideration, the agreement between calculated and observed intensities is fairly satisfactory.

The $0kl$ intensities of the chloride were then calculated. Table 6 shows that the agreement between calculated and observed intensities is quite good.

Table 6. Intensities of $0kl$ from Weissenberg photograph of $Sb_4O_5Cl_2$. CuKa radiation. The calculated intensity is given on the left of each column, and the intensity estimated for Patterson analysis on the right.

l	$00l$		$01l$		$02l$		$03l$		$04l$		$05l$		$06l$	
0			—	—	8.3	40	—	—	0	—	—	—	7.9	20
1	—	—	1.0	15	9.8	90	1.4	14	0	—	0.2	9	1.9	18
2	0	—	4.8	15	6.2	90	0	2	25	115	0	—	0.1	3
3	—	—	1.9	6	0.7	4	0.2	1	9.6	65	16	85	18	110
4	1.7	50	0.1	—	0	1	29	115	0.2	3	11	85	1.3	4
5	—	—	3.4	6	1.2	4	5.5	60	2.6	14	4.8	40	3.1	40
6	0.2	6	36	40	1.0	3	0.2	3	2.4	14	0.7	—	0.3	—
7	—	—	8.4	40	2.8	6	4.4	14	0	3	0.8	2		
8	18	120	1.1	3	2.3	5	13	60	0.5	3	6.4	40		
9	—	—	0.2	—	3.6	14	0.8	7	2.5	14	20	80		
10	1.0	6	0	—	11	40	0.8	1	28	90	0.	1		
11	—	—	0	—	11	40	1.9	7	0.5	2	6.6	80		
12	33	115	1.4	4	9.0	40	8.8	40	0.2	6				
13	—	—	2.0	12	11	30	1.3	13	0.4	6				
14	0	—	18	80	5.0	12	0	—						
15	—	—	4.5	12	0.2	6	2.8	13						
16	1.8	7	0.2	—	1.2	6								

Tables 7 and 8 give the observed and calculated $\sin^2\Theta$ and intensities of the powder photographs of $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$.

Table 7. Powder photographs of $Sb_4O_5Br_2$. CrKa radiation.

hkl	sin²Θ calc.	sin²Θ obs.	I calc.	I obs.	hkl	sin²Θ calc.	sin²Θ obs.	I calc.	I obs.
012	0.0791	0.0790	3.0	v.v.w.	12$\bar{3}$	.2837	(.2856)	39	(w. +)
110	.0803		2.4		115	.2858		0.8	
11$\bar{1}$	.0836	.0833	3.2	v.v.w.	123	.3082	.3097	6.7	v.w.
111	.0917	.0916	19	m—	21$\bar{5}$	.3163	(.3166)	3.4	(st.—)
11$\bar{2}$	.1016	—	0.5	—	016	.3163		105	
013	.1159	—	2.2	—	024	.3172		1.3	
004	.1178	.1181	0	st.	31$\bar{1}$	.3201		0	w.
112	.1179		106		22$\bar{1}$	.3203		8 2	
200	.1224	.1226	2.9	v.v.w.	220	.3211	.3216	0.3	
10$\bar{4}$	.1321	(.1321)	61	(st.)	106	.3217		0	
11$\bar{3}$	.1343	—	1.1	—	11$\bar{6}$	.3223		5.6	
20$\bar{2}$	.1355	—	3.0	—	214	.3232		0	
113	.1588	.1588	12	v.w.	310	.3250	(.3268)	3.5	(v.w.)
104	.1647	(.1647)	4.0	(v.w.)	302	.3295	—	0	—
014	.1675	—	0	—	31$\bar{2}$	.3301	—	0	—
202	.1681	—	0.2	—	12$\bar{4}$	.3314	.3320	44	m.
21$\bar{1}$	.1713	(.1711)	18	(w. +)	22$\bar{2}$	.3343	—	0.5	—
210	.1721		3.2		221	.3366	.3381	4.6	v.w.
11$\bar{4}$	.1818	—	1.6	—	20$\bar{6}$	.3399		0	
21$\bar{2}$	.1852	.1850	101	st.—	311	.3446	.3452	4.2	w.
211	.1876	—	0.6	—	30$\bar{4}$	.3447		5.2	
020	.1987	.1987	18	w.—	31$\bar{3}$	.3548	—	0.5	—
021	.2061	.2054	26	w.	22$\bar{3}$	.3632	—	0.5	—
20$\bar{4}$	.2076	—	0.1	—	124	.3641	—	0.7	—
21$\bar{3}$	.2139	(.2139)	10	(v.w.)	222	.3670	.3682	24	w.+
114	.2148		0.6		116	.3714	—	1.8	—
212	.2178	—	1.9	—	312	.3791	.3807	12	w.
022	.2282	(.2278)	9.3	(m.—)	025	.3838	—	1.1	—
120	.2293		1.5		21$\bar{6}$	.3895	—	0.5	—
12$\bar{1}$	.2326	(.2339)	0	(v.v.w.)	125	3940	(.3944)	39	(w. +)
015	.2338		7.4		31$\bar{4}$	.3944		0.5	
121	.2408	—	0	—	215	.3981	—	6.7	—
11$\bar{5}$	.2449	—	0	—	22$\bar{4}$	.4068	—	0.2	—
12$\bar{2}$	.2507	.2514	9.5	v.w.	223	.4122	(4129)	34	(m.—)
21$\bar{4}$	.2578	(.2579)	1.7	(v.v.w.)	017	.4125		17	
213	.2632	(.2628)	0.2	(w.)	11$\bar{7}$	.4145		5.8	
023	.2654	(.2671)	0.2	(v.w.)	313	.4284	(.4292)	4.4	(w.)
006	.2665		0.8		125	.4349	—	8.7	—
122	.2671		2.3		206	.4380	(.4396)	0.8	(v.w.)
10$\bar{6}$	.2726	—	0.1	—	304	.4429	(.4441)	7.4	(v.w.)
204	.2736	(.2760)	50	(st.)	31$\bar{5}$	.4487	(.4486)	13	(w.)
300	.2753		64		031	.4545	—	1.2	—
30$\bar{2}$	.2804	—	0	—	22$\bar{5}$	.4653	—	2.7	—
					026	.4653	—	3.4	—

hkl	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	I calc.	I obs.
$30\bar6$	.4683 ⎫		7.1 ⎧	
$3\bar21$	.4691 ⎬	(.4694)	27 ⎨	(w.)
$12\bar6$	.4713 ⎭		15 ⎩	
117	.4717	—	0	—
$10\bar8$	.4718	—	0.1	—
224	.4723 ⎫		47 ⎧	
$13\bar1$	.4736 ⎪		0.1 ⎪	
008	.4739 ⎬	.4739	11 ⎨	m.
320	.4740 ⎭		47 ⎩	
032	.4767	—	1.5	—
$2\bar17$	.4776 ⎫		1.1 ⎧	
130	.4777 ⎪		39 ⎪	
$32\bar2$	.4791 ⎬	.4789	18 ⎨	w.
131	.4818 ⎭		25 ⎩	
$40\bar2$	.4863	—	0.4	—
216	.4877 ⎫	.4894	13 ⎧	w.—
400	.4894 ⎭		1.3 ⎩	
314	.4925	—	1.2	—
321	.4937	.4944	20	w.—
$13\bar2$	.4991	(.4999)	4.0	(w.—)
$32\bar3$	.5038	—	1.7	—
033	.5137	—	0.4	—
132	.5155 ⎫	.5178	8.2 ⎧	m.
$3\bar16$	.5179 ⎭		100 ⎩	
126	.5204	—	13	—
$1\bar18$	.5215	—	0.7	—
018	.5236	—	1.6	—
322	.5284	—	12	—
$20\bar8$	.5292 ⎫		69 ⎧	
$4\bar11$	.5307 ⎬	.5305	2.2 ⎨	v.w.
$1\bar33$	.5310 ⎭		6.7 ⎩	
$4\bar12$	.5363 ⎫		6.1 ⎧	
108	.5364 ⎬	.5357	61 ⎨	w.
$22\bar6$	.5373 ⎭		10 ⎩	
410	.5398	—	2.9	—
$40\bar4$	.5423 ⎫	(.5423)	58 ⎧	(w.+)
$32\bar4$	.5427 ⎭		0.4 ⎩	
225	.5469	.5470	33	v.v.w.
402	.5528	—	0.7	—
133	.5558 ⎫	(.5565)	24 ⎧	(v.w.)
$4\bar13$	.5567 ⎭		14 ⎩	
027	.5603	—	2.3	—
$12\bar7$	.5620	—	0.2	—
411	.5637 ⎫	.5641	12 ⎧	w.
034	.5645 ⎭		49 ⎩	

hkl	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	I calc.	I obs.
$23\bar1$	.5680 ⎫	.5688	26 ⎧	w.
230	.5689 ⎭		20 ⎩	
315	.5720	—	10	—
323	.5778 ⎫		1.9 ⎧	
$13\bar4$	.5786 ⎬	(.5789)	2.2 ⎨	(v.v.w.)
$21\bar8$	.5788 ⎭		13 ⎩	
$23\bar2$	.5819	—	7.4	—
231	.5845	—	2.2	—
118	.5860	—	3.2	—
217	.5919 ⎫	.5918	4.6 ⎧	v.v.w.
$41\bar4$	.5919 ⎭		6.7 ⎩	
$32\bar5$	.5968	—	9.2	—
$31\bar7$	.6005	—	12	—
412	.6024	(.6030)	88	(m.—)
$23\bar3$	.6106 ⎫	.6117	31 ⎧	w.
134	.6117 ⎭		31 ⎩	
232	.6149	—	0.5	—
306	.6160	—	0.4	—
127	.6198	.6198	28	v.w.
$22\bar7$	.6250	.6250	30	w.—
035	.6310	.6320	26	v.v.w.
226	.6364	—	7.9	—
$13\bar5$	.6410 ⎫		1.4 ⎧	
$11\bar9$	.6413 ⎪		16 ⎪	
324	.6419 ⎬	(.6423)	1·5 ⎨	(v.w.)
$41\bar5$	.6419 ⎭		0.8 ⎩	
$30\bar8$	.6493	—	5.0	—
$23\bar4$	.6540 ⎫	(.6542)	45 ⎧	(w.)
413	.6559 ⎭		6.3 ⎩	
$40\bar6$	.6570	—	0	—
233	.6601	—	0	—
208	.6613	—	4.9	—
316	.6656 ⎫		83 ⎧	
$32\bar6$	.6657 ⎬	(.6662)	3.0 ⎨	(w.+)
$12\bar8$	.6687 ⎭		4.1 ⎩	
028	.6711	—	1.9	—
404	.6745	.6744	17	v.w.
019	.6779	—	0	—
$4\bar21$	.6795	—	2.5	—
135	.6823 ⎫	(.6845)	4.4 ⎧	(v.w.)
$4\bar22$	.6851 ⎭		6.3 ⎩	
420	.6886	—	0.8	—
$21\bar9$	.6961	—	0.8	—
$31\bar8$	.6989	(.6994)	1.0	(v.v.w.)
$4\bar23$	.7055 ⎫	.7053	22 ⎧	v.w.
$41\bar6$	.7066 ⎭		0.4 ⎩	

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Table 8. Powder photographs of $Sb_4O_5Cl_2$. CrKα radiation.

hkl	sin²Θ calc.	sin²Θ obs.	I calc.	I obs.	hkl	sin²Θ calc.	sin²Θ obs.	I calc.	I obs.
012	0.0790	(0.0790)	9.5	(m.—)	32̄4	.5771	—	1.6	—
110	.0842	.0838	3.5	v.w.	118	.5826	—	1.9	—
11̄1	.0874	(.0876)	5.8	(w.)	13̄4	.5858	—	0.1	—
111	.0954	.0954	17	m. +	23̄1	.5872	(.5879)	14	(w.)
11̄2	.1052	.1054	7	w.	230	.5879		20	
013	.1152	.1157	3.9	v.w.	41̄1	.5891	—	5.6	—
004	.1158		1.7		21̄8	.5894	—	5.6	—
112	.1210	.1212	68	v.st.	41̄2	.5950	.5949	24	m.—
104̄	.1342	.1342	45	st.	410	.5978	—	3.7	—
200	.1366	(.1366)	12	(st.)	217	.6000	(.6008)	7	(m.—)
11̄3	.1374		2.6		40̄4	.6003		35	
20̄2	.1498	.1502	1.9	v.v.w.	315	.6003		8.2	
113	.1612	.1612	11	w.	23̄2	.6010		0.8	
104̄	.1658	(.1658)	12	(m.)	231	.6032	—	1.8	—
014	.1659		0.2		402	.6088	—	0.1	—
202	.1814	.1813	0.2	v.v.w.	323	.6101	—	3.4	—
11̄4	.1842	—	0.2	—	41̄3	.6154	.6152	20	w.
21̄1	.1860	.1861	14	m.	134	.6178	.6198	33	w.
210	.1866		4.4		127	.6197		20	
21̄2	.1998	.2001	65	st.	411	.6211		6.7	
020	.2001		8.1		23̄3	.6295	.6319	13	w—
211	.2018	—	0.4	—	32̄5	.6307		16	
021	.2073	.2075	20	w.	31̄7	.6312		11	
114	.2158	—	0.7	—	232	.6330		0	
204̄	.2208	—	0.4	—	035	.6331		11	
21̄3	.2281	.2290	9.3	w.	22̄7	.6384	.6387	22	v.w.
022	.2290		12		11̄9	.6385		15	
015	.2310		7.0		019	.6403	—	0.3	—
212	.2314		0.6		306	.6424	—	0.5	—
321	.5278	(.5274)	11	(v.v.w.)	226	.6476	—	7.7	—
108	.5325	.5322	45	v.v.w.	13̄5	.6493	—	3.5	—
32̄3	.5381	.5394	6.5	w.	41̄4	.6504	—	0.6	—
13̄3	.5388		10		412	.6589	.6590	44	m.
20̄8	.5393		53		028	.6667	—	4.8	—
40̄2	.5449	—	1	—	208	.6672	—	2.4	—
400	.5477	(.5481)	3.0	(w.+)	12̄8	.6690	—	0.1	—
31̄6	.5485		67		41̄5	.6700	—	1.4	—
22̄6	.5517	—	15	—	23̄4	.6725	.6725	56	w.
027	.5574	—	5.8	—	324	.6731		0.2	
225	.5595	(.5593)	22	(v.w.)	233	.6774	—	0.7	—
322	.5616	—	9.8	—	30̄8	.6784	—	3.7	—
133	.5628	—	11	—	135	.6853	—	3	—
12̄7	.5637	—	2	—	316	.6925	.6918	43	m.
034	.5675	.5675	58	v.w.	32̄6	.6988	—	0.1	—

hkl	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	I calc.	I obs.	hkl	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	I calc.	I obs.
$2\bar{1}9$	.7052	—	1	—	$10\,\overline{10}$	.7228	—	0.8	—
119	.7105 ⎫	(.7108)	9.3 ⎫	(v.v.w.)	$13\bar{6}$	.7235	—	0	—
413	.7114 ⎭		2.9 ⎭		404	.7283 ⎫		32 ⎫	
036	.7132	—	0.5	—	$31\bar{8}$	.7285 ⎬	.7285	1.8 ⎬	w.+
$40\bar{6}$	.7140	—	0.2	—	0010	.7286 ⎭		1 ⎭	
218	.7173	—	2	—					

The intensities were calculated from $I \sim p \left[\dfrac{F}{4f_{Sb}} \right]^2$ for powder photographs, where p is the number of cooperating planes, and from $I \sim \left[\dfrac{F}{4f_{Sb}} \right]^2$ for Weissenberg photographs. Due consideration was given to the variation of $\dfrac{f_A}{f_{Sb}}$ with Θ, except in the Weissenberg photograph of hll of the oxybromide, where the average values $\dfrac{f_{Br}}{f_{Sb}} = 0.645, \dfrac{f_O}{f_{Sb}} = 0.1$ were used. In the lists of the powder photographs, the limits between the angular ranges of the three different focusing cameras are marked. Reflections systematically absent are omitted. The β-reflections have been omitted. If a tabulated reflection coincides with a β-reflection, the $\sin^2\Theta$ and the intensity of the resulting line are given in brackets. The observed intensities are indicated as follows: vst = very strong, st = strong, m = medium, w = weak, vw = very weak and vvw = very,very weak.

The atomic coordinates of $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$ are given in table 9.

Table 9. Atomic coordinates of $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$.

	$Sb_4O_5Cl_2$			$Sb_4O_5Br_2$		
	x	y	z	x	y	z
4 Sb_1	0.186 ± 0.005	0.225 ± 0.005	0.049 ± 0.003	0.174 ± 0.005	0.225 ± 0.005	0.051 ± 0.004
4 Sb_2	0.796 ± 0.005	0.113 ± 0.005	0.203 ± 0.003	0.806 ± 0.005	0.125 ± 0.005	0.203 ± 0.004
4 X	0.51 ± 0.01	0.703 ± 0.01	0.115 ± 0.005	0.51 ± 0.01	0.705 ± 0.01	0.118 ± 0.005
2 O_1	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0
	0	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$
4 O_2	0.13	0.35	0.185	0.13	0.37	0.187
4 O_3	0.07	0.05	0.915	0.08	0.04	0.916

DISCUSSION OF THE STRUCTURE

Projections of the structure of the oxychloride on the xz-plane and on the yz-plane are shown in fig. 6. The yz-projection is an orthogonal projection of the cell for $-\frac{1}{2} \lesssim x \lesssim +\frac{1}{2}$ on $x = 0$. It shows that the antimony atoms form zig-zag chains in two layers, with a distance of 2.4 kX between

the layers. The oxygen atoms enter between these layers, so that Sb — O chains seem to be formed, which are held together by the oxygen in 2(c), thus forming an Sb — O layer. This is more obvious from fig. 5, where the halogens are omitted. Between these layers, there are layers of halogen. As has been mentioned above, $Sb_4O_5Cl_2$ forms two types of crystals, one of which forms thin plates. In order to check the structure, suitable plates were selected and rotation photographs taken around the three axes. They showed that

Table 10. *Interatomic distances in* $Sb_4O_5X_2$. *kX units.*

	$Sb_4O_5Cl_2$				$Sb_4O_5Br_2$			
Within Sb—O chain								
Sb$_1$—2O	2.02	2.06			2.03	2.06		
Sb$_2$—2O	2.03	2.06			1.98	2.04		
Sb$_1$—Sb$_2$	3.88	3.83			3.88	3.87		
O$_2$—O$_3$ at »angle»	3.21				3.17			
O$_2$—O$_3$	3.93				3.98			
Between atoms in adjacent Sb—O chains								
Sb$_1$—O	2.22				2.25			
Sb$_2$—O	2.44				2.51			
Sb$_1$—Sb$_1$	3.43				3.41			
Sb$_1$—Sb$_2$	3.44				3.42			
Sb$_2$—Sb$_2$	3.71				3.72			
O$_2$—O$_3$	2.67				2.78			
O$_3$—O$_3$	2.61				2.65			
Sb$_1$—3O (4O)	1.89	2.02	2.06	(2.22)	1.89	2.03	2.06	(2.25)
Sb$_1$—3X	3.11	3.22	3.39		3.30	3.35	3.51	
Sb$_2$—2O (3O)	2.03	2.06	(2.44)		1.98	2.04	(2.51)	
Sb$_2$—X (3X)	2.91	(3.33	3.62)		3.03	(3.42	3.65)	
O$_1$—2Sb$_1$	1.89				1.89			
O$_2$—2Sb (3Sb)	2.02	2.03	(2.44)		2.03	1.98	(2.51)	
O$_3$—2Sb (3Sb)	2.06	2.06	(2.22)		2.04	2.06	(2.25)	
X—Sb (6Sb)	2.91	(3.11	3.22	3.33) 3.39 3.62)	3.03	(3.30	3.35	3.42 3.51 3.65)
X—X (4X)	3.72	(4.33	4.46	4.46)	3.79	(4.37	4.40	4.40)
X—3O (5O)	2.98	3.21	3.37	(3.51 3.74)	3.09	3.28	3.39	(3.65 3.94)
O$_1$—4X	3.51	3.74			3.65	3.94		
O$_2$—2X	3.21	3.37			3.28	3.39		
O$_3$—X	2.98				3.09			
O$_1$—4O (6O)	2.63	2.64	(3.09)		2.62	2.70	(3.06)	
O$_2$—2O (3O)	2.64	2.67	(3.21)		2.62	2.78	(3.17)	
O$_3$—3O (5O)	2.61	2.63	2.67	(3.09 3.21)	2.62	2.70	2.78	(3.06 3.17)

the y-and the z-axes lie in the plane of the plates, which supports the proposed structure.

The interatomic distances are given in table 10. It seems rather difficult to make a definite statement on the nature of the antimony bonds, as the oxygen positions, because of the method in which they have been determined are a little uncertain. Now there are two different kinds of antimony atoms, Sb_1 and Sb_2.

Sb_2 is adjacent to two oxygen atoms at 2.03 and 2.06 kX and a third oxygen atom at 2.44 kX. Even considering the uncertainty of the oxygen positions, the third distance seems to be too large to indicate an Sb — O bond. Sb_2 is also close to three chlorine atoms at distances 2.91, 3.33 and 3.62 kX (2.91 kX is the shortest Sb — Cl distance in the structure). This seems to indicate that Sb_2 is bound to two oxygen atoms and one chlorine atom at the distance 2.91 kX. This would give angles O — Sb — O 103°, O — Sb — Cl 84° and 71°. However, 2.91 kX for the distance Sb_2 — Cl seems rather large for a covalent bond, as the observed Sb — Cl distance in $SbCl_3$ is 2.37 kX [1]. Sb_1 has four oxygen atoms at distances 1.89, 2.02, 2.06 and 2.22 kX as nearest neighbours. Sb_1 is also fairly close to three chlorine atoms at 3.11, 3.22, 3.39 kX. If it is assumed that Sb_1 is bound only to the nearest three oxygens (1.9— 2.1 kX) valence angles of 83°, 84° and 149° are obtained, but 149° seems to be too great a distorsion of a valence angle expected to be 90°—100° (cf. p. 178). If the four oxygen atoms are considered the angles O—Sb—O for nearest neighbours of oxygen are 83°, 84°, 79°, 75°, and the »diagonal» angles 97° and 149°. The angles 97°, 83°, 84°, 79°, and 75° are of about the same magnitude as the valence angles of antimony. We can thus combine the »diagonal» angle 97° with two of the other four angles and obtain two possible valence configurations. One would have the angles 97°, 83°, and 75°, and the other the angles 97°, 84°, and 79°. From these values there does not seem to be any reason to prefer one set of angles before the other, so here the nature of the bonds has to be left open. In $Sb_4O_5X_2$ the Sb—X distances seem to be rather large. This is perhaps not so objectionable, as this is also the case for the Me— X distances in the layer structure Me_2O_2X [8]. In the latter structure the distances X—O are also a little large. In $Sb_4O_5Cl_2$, however, there seems to be contact between halogen and oxygen.

Within an antimony-oxygen chain the Sb—O—Sb angles are 147° and 137°.

It seems as if the antimony bonds in $Sb_4O_5X_2$ may be regarded as intermediate between covalent and ionic binding.

The fact that antimony and oxygen seem to form chains in the structure of $Sb_4O_5X_2$, may perhaps be of interest when considering the further hydrolysis of $SbCl_3$. According to Cooke [11] and Lea and Wood [12] needle-shaped crystals

are formed on further hydrolysis, Lea and Wood assigned to them the formula $Sb_4O_3(OH)_5Cl$. Crystal needles have also been obtained in the present investigation. A preliminary analysis does not seem to agree with Lea and Wood's formula, but there might of course have been impurities in the present preparations consisting of amorphous or microcrystalline material. It seems clear that they contain some water and less Cl than $Sb_4O_5Cl_2$. On further hydrolysis the orthorhombic modification of Sb_2O_3, containing chains of $(Sb_2O_3)\infty$ is formed, although this is normally the high temperature modification [15].

A determination of the crystal structure of the needle-shaped oxychloride seems to be of interest, and will if possible be carried out. An investigation of these and other antimony oxyhalides may perhaps give further knowledge regarding the oxygen positions in these compounds $(Sb_4O_5X_2)$.

SUMMARY

The isomorphous compounds $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$ have been investigated by X-ray crystallographic methods. They are monoclinic, space group C_{2h}^5, and the unit cell contains two formula units. Cell dimensions:

$$a = 6.229 \quad b = 5.107 \quad c = 13.50 \text{ kX} \quad \beta = 97.27° \quad \text{for } Sb_4O_5Cl_2$$
$$a = 6.593 \quad b = 5.133 \quad c = 13.43 \text{ kX} \quad \beta = 97.89° \quad \text{for } Sb_4O_5Br_2$$

The atomic coordinates are given in table 9.

These compounds form a new structure type. Projections of the structure are given in fig. s 5 and 6. It is a layer structure, in which antimony-oxygen sheets are connected by single halogen sheets. In the antimony-oxygen sheets there seem to be zig-zag chains of antimony and oxygen. There is, of course, some uncertainty in the oxygen positions. Further investigations of the antimony oxyhalides may perhaps give a more complete picture of the coordination of antimony.

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