nischen Verbindungen der Formel $A_m(XO_3)_n$ mit aus XO_4-Tetraedern aufgebauten Kettenanionen — ausgenommen die unter (1) genannten Strukturen — enthalten solche *Zweierketten.*

(3) Im Natriumpolyarsenat, in der Hochtemperaturform des Maddrellschen Salzes, $(NaPO_3)_x$ (I), und im β-Wollastonit, $CaSiO_3$, enthält die Identitätsperiode der Kette drei Tetraeder (Fig. 7(*c*)). Erst das vierte Tetraeder ist mit dem ersten identisch. Diese Art wäre danach als *Dreierkette* zu bezeichnen.

Über eine Reihe von anderen Verbindungen, die mit grosser Wahrscheinlichkeit auch Dreierketten enthalten, soll an anderer Stelle berichtet werden (Liebau, 1956).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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The crystal structures of thorium antimonides.

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The compounds considered here have been prepared by direct synthesis from the elements.

The thorium was obtained, in part, by electrolysis of fused $KThF_5$ and partly (in larger quantities) by reduction of ThO_2 with Ca. Its purity was, in any case, around 99·7%. The impurities were represented by oxygen in the form of ThO_2. The antimony employed was of a purity not less than 99·9%.

Proper mixtures of the powders of the two metals (in quantities of about 1–2 g.) were pressed (10^4 kg.cm.$^{-2}$) for the preparation of the various alloys, and the samples so obtained were closed in vacuum in silica ampullae and then heated at temperatures around 1000° C. (the total duration of the heating and subsequent cooling was 2–6 days). The samples thus obtained are compact, mechanically fairly resistant and only a little pyrophoric; they are etched by acids.

The roentgenographic examination of all the samples has proved the existence of the compounds ThSb, Th_3Sb_4 and $ThSb_2$, which represent the only phases present in the system under the above conditions of preparation.

The examination by X-rays was performed by the powder method, using Cu $K\alpha$ radiation ($\lambda(\text{Cu }K\alpha_1) =$ 1·537395 kX.).

ThSb

The preparation of this compound required heating at a fairly high temperature (1200–1300° C.), since, at lower temperatures, the reaction stops at the formation of Th_3Sb_4.

ThSb (65·59% Th) is cubic, NaCl type, with

$$a_0 = 6{\cdot}305 \text{ kX} .$$

The density, ϱ, is thus 9·32 g.cm.$^{-3}$. The Th–Sb distance is 3·15 kX.

Th_3Sb_4

The compound Th_3Sb_4 (58·84% Th) is body-centred cubic with

$$a_0 = 9{\cdot}353 \text{ kX.},\quad Z = 4,\quad \varrho = 9{\cdot}55 \text{ g.cm.}^{-3}.$$

The structure corresponds to the Th_3P_4 type (Meisel, 1939), $D7_3$ type, with:

Space group: T_d^6–$I\bar{4}3d$.

Atomic positions: 12 Th in (a) $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$
$\tfrac{3}{8}, 0, \tfrac{1}{4};\ \circlearrowleft$.
16 Sb in (c) $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$
$x, x, x;\ \circlearrowleft$ with $x = \tfrac{1}{12}$.

Each Th atom is surrounded by 8 Sb atoms at a distance of 3·24 kX.

$ThSb_2$

The powder photograph shows that $ThSb_2$ (48·80% Th) is tetragonal with:

$$a_1 = 4{\cdot}344,\quad a_3 = 9{\cdot}154 \text{ kX.},\quad a_3/a_1 = 2{\cdot}107$$

and, as $Z = 2$, we have $\varrho = 9{\cdot}09$ g.cm.$^{-3}$.

The calculation of the intensities has shown that the structure is of the $C38$ type:

Space group: D_{4h}^7–$P4/nmm$.

Atomic positions: 2 Sb_I in (a) $0, 0, 0;\ -\tfrac{1}{2}, \tfrac{1}{2}, 0$.
2 Sb_{II} in (c) $0, \tfrac{1}{2}, x;\ -\tfrac{1}{2}, 0, \bar{x}$
with $x = 0{\cdot}63_7$.
2 Th in (c') $0, \tfrac{1}{2}, t;\ -\tfrac{1}{2}, 0, \bar{t}$
with $t = 0{\cdot}27_5$.

The values indicated for the x and t parameters have been selected by repeating for quite a number of lines the calculation of the intensities with various pairs of values.

The most probable interatomic distances are therefore:

$$\text{Th–Sb}_\text{I} = 3{\cdot}32 \text{ kX. } (d)\ ,$$
$$\text{Th–Sb}_\text{II} = 3{\cdot}31 \text{ kX. } (d') \quad\text{or}\quad 3{\cdot}17 \text{ kX. } (d'')\ .$$

Each atom of Th is surrounded by 9 Sb atoms: 8 placed according to an antiprism (d and d'') and another isolated (d').

The smallest Sb–Sb distance is Sb_I–Sb_I = 3·07 kX.

Discussion

It is advisable, first of all, to point out the strict similarities existing between the Th–Sb system and the Th–As (Ferro, 1955*a*) and U–Sb (Ferro, 1952) systems. The compounds MX, M_3X_4 and MX_2 (which are isostructural with those described above) appear also in these two other systems. Also, in these other series of compounds there is a variation of interatomic distances which is similar to that of the Th–Sb compounds: the distances are large in the M_3X_4 compounds, smaller in the MX compounds, and included in a certain interval of values in MX_2. It should be pointed out, however, that, when passing from the Th–As compounds to the Th–Sb compounds, the various distances undergo a practically constant increase of 0·18 kX., which agrees well with the differences between the atomic radii of Sb and As (1·43 − 1·25 = 0·18 kX.) or between their ionic radii (2·08 − 1·91 = 0·17 kX.).

As regards the distances relating to the thorium, an average value of about 0·08 kX. higher than that relating to the distances of the uranium compounds is obtained from the comparison of the analogous compounds of thorium and uranium.

As far as the ThX compounds are concerned, a further remark may prove of interest: in fact the structure of the NaCl type is always present in the series ThP (Meisel, 1939), ThAs (Ferro, 1955*a*), ThSb and UP (Zumbusch, 1941), UAs (Iandelli, 1952), USb (Ferro, 1952), ThS (Zachariasen, 1949), ThSe (D'Eye, Sellman & Murray, 1952), US (Zachariasen, 1949), USe and UTe (Ferro, 1954), whilst when we arrive at ThTe (D'Eye & Sellman, 1954; Ferro, 1955*b*) then the structure of the CsCl type comes into being, although distances approaching those of ThSb are to be expected (for instance from the comparison with the similar compounds of uranium—see Table 1). That is to say, whilst the same structure remains in existence for USb and UTe (and as a matter of fact we have here possibility of solid solution (Ferro, 1954)), when passing from ThSb to ThTe the critical conditions for a higher stability of the CsCl-type structure appear to be reached suddenly.

Table 1. *Interatomic distances in* ThX *and* UX *compounds of the* NaCl-*type structure*

(Values in kX. units)

ThP	2·91	UP	2·79	ThS	2·83	US	2·73
ThAs	2·98	UAs	2·88	ThSe	2·93	USe	2·82
ThSb	3·15	USb	3·09	[ThTe]	3·31	UTe	3·07

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