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The crystal structures of thorium arsenides.

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The compounds under examination have been prepared by direct synthesis from the elements.

The thorium was obtained by electrolysis of very pure fused $KThF_5$ and had a unit-cell dimension of 5·073 kX.*; the only impurity in the metal was about 0·3% oxygen (mainly as ThO_2 mechanically mixed). The arsenic was purified by distillation.

The various samples were prepared by placing the powders of the two elements in small vacuum-sealed silica phials, heating slowly (exothermic reaction) to 800–900° C. and cooling slowly to room temperature.

The substances thus obtained are black-grey powders, fairly stable in air, which react rather strongly with nitric acid.

Under the above conditions of preparation, the roentgenographic examination (powder method, Cu $K\alpha$ radiation) has shown the existence of the compounds ThAs, Th_3As_4 and $ThAs_2$, all well defined as crystal phases.

ThAs

ThAs (Th = 75·60%) is cubic, NaCl-type, with

$$a_0 = 5{\cdot}960\ \text{kX}\,.$$

The specific gravity is thus $\varrho = 9{\cdot}57$. The Th–As distance is 2·980 kX.

Th_3As_4

Th_3As_4 (Th = 69·92%) is body-centred cubic with

$$a_0 = 8{\cdot}825\ \text{kX.},\ Z = 4,\ \varrho = 9{\cdot}56\,.$$

The structure is of the Th_3P_4 type ($D7_3$ type) (Meisel, 1939):

Space group: T_d^6–$I\bar{4}3d$.

Atomic positions:

12 Th in (*a*) $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + \tfrac{3}{8}, 0, \tfrac{1}{4};\ \circlearrowright$.
16 As in (*c*) $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + x, x, x;\ \circlearrowright$
with $x = \tfrac{1}{12}$.

The Debye intensities calculated on the basis of this hypothesis agree quite well with those observed.

The Th–As distance is 3·06 kX. Each thorium atom is surrounded by eight arsenic atoms at that same distance.

$ThAs_2$

$ThAs_2$ (Th = 60·77%) is tetragonal with

$$a_1 = 4{\cdot}078,\ a_3 = 8{\cdot}558\ \text{kX.},\ a_3/a_1 = 2{\cdot}098_5,$$
$$Z = 2,\ \varrho = 8{\cdot}85\,.$$

The structure is of the *C*38 type:

Space group: D_{4h}^7–$P4/nmm$.

Atomic positions:

2 As_{I} in (*a*) $0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0$.
2 As_{II} in (*c*) $0, \tfrac{1}{2}, x;\ \tfrac{1}{2}, 0, \bar{x}$ with $x = 0{\cdot}64$.
2 Th in (*c'*) $0, \tfrac{1}{2}, t;\ \tfrac{1}{2}, 0, \bar{t}$ with $t = 0{\cdot}28$.

The structure was checked by calculating the intensities for about 30 lines for 25 pairs of x and t values. With the indicated values a good correspondence was obtained between calculated and observed intensities for all reflexions.

The Th–As_{I} distance is 3·14 kX. (*d*); the Th–As_{II} distances are 3·08 kX. (*d'*) and 2·96 kX. (*d''*). Each thorium atom is thus bonded to nine arsenic atoms: 8 (forming an antiprism: *d* and *d''*)+1(*d'*).

The smallest As–As separation is As_{I}–As_{I} = 2·88 kX.

In conclusion, it is well to point out that a considerable similarity exists between the thorium and the uranium arsenides (Colani, 1907; Iandelli, 1952) as regards both the formulae and the structures, and also as regards the variations of the interatomic distances (rather low in the *M*As compounds, larger in the M_3As_4 compounds, and included within a fairly wide range of values in MAs_2 compounds).

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* All dimensions are given in kX. units and are based on λ (Cu $K\alpha_1$) = 1·537395 kX.

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Two charts for setting the Buerger precession camera.

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In my paper of the above title (King, 1955), no mention was made of the extended work of Fisher (1952, 1953) on the use of Buerger precession camera. These papers include charts for setting the precession camera, with essentially the same functions as Figs. 1 and 2 of my paper, but of a different design.

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