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**A modification of the logarithmic charts for the interpretation of powder photographs.** By  
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In Fig. 1 is suggested a slight variation of the plot of interplanar spacing against  $c/a$  in charts used for the interpretation of powder photographs (Hull & Davey (1921), Bjürström (1931), Bunn (1946), Bond (quoted by Azaroff & Buerger (1958) and Harrington (1938)).

The drawing (for the tetragonal system) is modified so that, on a double logarithmic scale, the  $hk0$  are represented by straight lines whose slope is fixed as  $S_{hk0} = 3/2$  (i.e.  $d \log c/a = 3/2 d \log \Sigma h_i^2 a_i^2$ ) while the  $00l$  are represented by straight lines also, the slope being  $S_{00l} = -\frac{1}{2} S_{hk0}$ . (All the other  $hkl$  curves, of course, are drawn accordingly.)

A possible advantage of this form of chart consists in the fact that, if the paper strip, on which are marked the observed values of  $d$ , is translated on the chart vertically without lateral displacements, all the matches

which are observed correspond to unit cells which (although with different  $c/a$ ) have the same volume. (The value of the volume in  $\text{\AA}^3$  can be read off the scale represented in the lower part of the drawing, by referring to the value  $d = 1 \text{\AA}$  marked on the paper strip of the film under examination.)

This fact can make more limited and systematic the attempts to index the film whenever it can be stated, from considerations of atomic volumes or from experimental measurements of density, that the unit-cell volume can be only some integral multiple of the molar volume. Moreover there is a possibility that a further limitation of possible volumes might be obtained, indicating (for the crystallographic system tried) the order of magnitude of the unit-cell dimensions from considerations of the number of lines present in the film (Lipson, 1949).

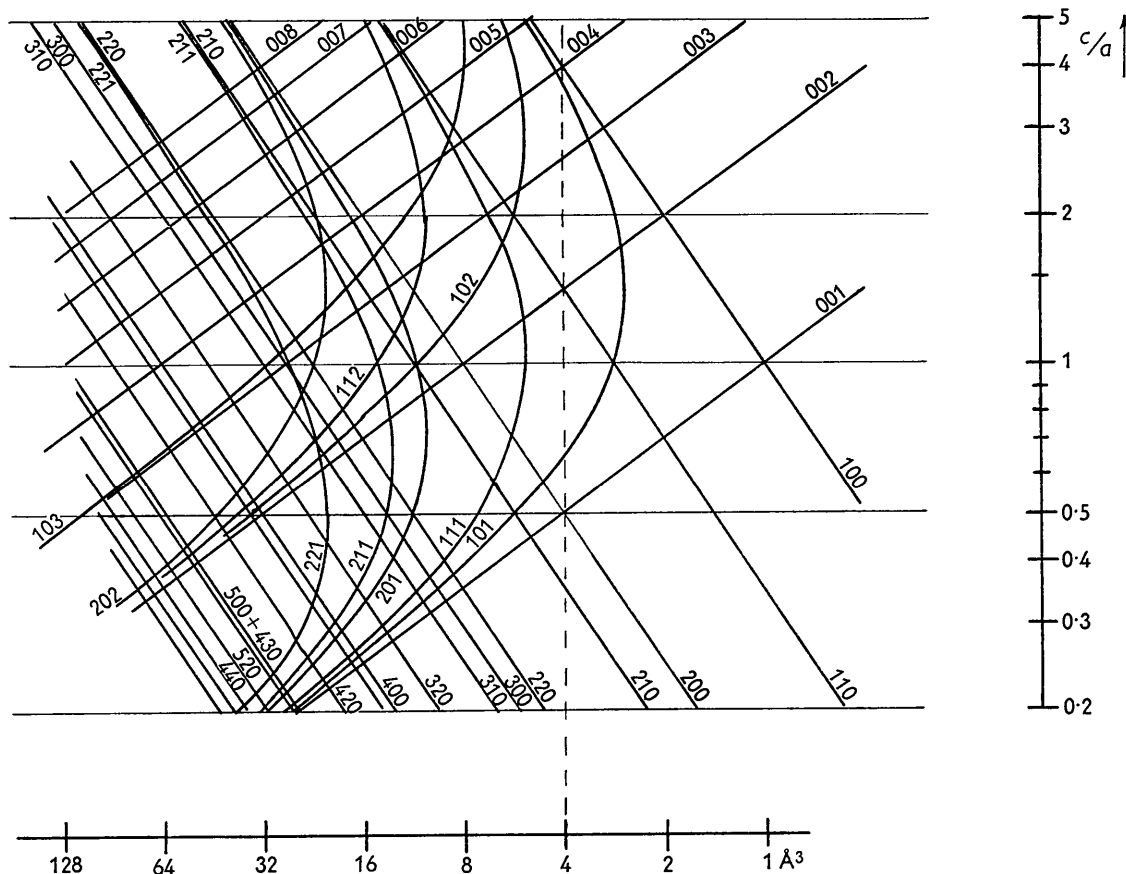


Fig. 1. Chart with double logarithmic scale for the tetragonal system. (Owing to the small size of the drawing, only a few indices are represented).—Let the paper strip translating on the chart maintain the mark of an observed value of  $d$  always on the dotted vertical line. All the possible unit cells correspond always to the same constant volume:  $V (= a^3 \cdot c/a) = 4d^3$ . Actually the selected line can have indices 210 (when  $c/a = 0.357_8$ , and  $a^3 \cdot c/a$  will be  $5\sqrt{5} \cdot d^3 \cdot 0.357_8 = 4d^3$ ), or it can be 200 (when  $c/a = 0.5$  and  $a^3 \cdot c/a = 8 \cdot d^3 \cdot 0.5 = 4d^3$ ) or 110 (for  $c/a = \sqrt{2}$ ); or again, it can have indices 101 either for  $c/a = 0.652_3$  (when  $a = 1.830_4 d$  and  $V = 4d^3$ ) or for  $c/a = 3.569$  ( $a = 1.038_3 d$  and  $V = 4d^3$ ), etc.

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**The phase D10<sub>2</sub> type in the thorium-rhodium alloy system.** By RICCARDO FERRO and GABRIELLA RAMBALDI, *General Chemistry Institute and Physical Chemistry Institute of Genoa University, Genoa, Italy*

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In this paper are reported the results obtained in the preparation of some thorium-rhodium alloys with high thorium percentages.

The thorium used was prepared by reduction of ThO<sub>2</sub> with Ca and had a purity of about 99.8% (main impurity oxygen as ThO<sub>2</sub>); the rhodium had a purity higher than 99.9%. The powders of the two metals, thoroughly mixed, were heated, in argon, up to 1800–1900 °C. (the synthesis appears to be strongly exothermic); the melted alloys were then slowly cooled and annealed for 1 day at 900 °C., for 1 week at 750 °C. and 2 weeks at 500 °C. The powders for the X-ray examination were further annealed for 50 hours at 500 °C.

The alloys, rather brittle and hard, were analyzed by the following method: the sample, finely ground, is treated with a mixture of HCl and H<sub>2</sub>O<sub>2</sub> which dissolves nearly all the thorium and a good part of the rhodium; the residue is then rendered soluble by mixing it with NaCl and heating, in a current of Cl<sub>2</sub>, up to 700 °C. After leaching with water, the rhodium is precipitated from the solution with H<sub>2</sub>S (in the filtrate thorium is determined by titration with sodium ethylenediaminetetraacetate or by double precipitation with H<sub>2</sub>O<sub>2</sub>): the rhodium sulphide, after re-solution with aqua regia, is then treated with NaBrO<sub>3</sub> and NaHCO<sub>3</sub>. The new precipitate, after ignition in H<sub>2</sub> atmosphere, is washed with dil. HCl, re-ignited in H<sub>2</sub> and, finally, weighed as Rh metal.

The micrographic examination was carried out, after dry polishing, by etching with HF + HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. The density was measured by use of a pycnometer which was filled with rectified benzene dried over sodium. The X-ray examination was carried out by the powder method (Straumanis arrangement) using chiefly Fe K $\alpha$  radiation ( $K\alpha_1$ ,  $\lambda = 1.93597$  Å).

An alloy which by analysis contained 81.5% Th and, in two determinations, 18.4<sub>9</sub> and 18.1<sub>5</sub>% Rh (i.e. very close to the theoretical composition for Th<sub>2</sub>Rh) appeared, under micrographic examination, clearly biphasic, in contrast to what one could expect by analogy with thorium-palladium alloys (Ferro & Capelli, 1961). On the other hand, the powder photograph of this alloy is identical with one of another alloy, nearly homogeneous under micrographic examination, containing 83.3<sub>3</sub>% Th and 16.6<sub>7</sub>–16.5<sub>5</sub>% Rh and having a density of 11.5 g.cm.<sup>-3</sup>.

The powder photographs of these alloys can be indexed with the following values for the constants (obtained by successive extrapolations with the function

$$\frac{1}{2} [\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta]:$$

$$a = 10.028, c = 6.293 \text{ \AA}, c/a = 0.627_5$$

(hexagonal axes).

The structure corresponds to the D10<sub>2</sub> type (Pearson, 1958) or Th<sub>7</sub>Fe<sub>3</sub> type (Florio *et al.*, 1956) with the following atomic positions referring to the ideal composition Th<sub>7</sub>Rh<sub>3</sub> (theor.: 15.97% Rh):

Space group  $C_{6v}^4$ .

$$2 \text{ Th}_I \text{ in } (b) \frac{1}{3}, \frac{2}{3}, u; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + u;$$

$$6 \text{ Th}_{II} \text{ in } (c) s, \bar{s}, v; \odot;$$

$$6 \text{ Th}_{III} \text{ in } (c) t, \bar{t}, w; \odot;$$

$$6 \text{ Rh} \text{ in } (c) x, \bar{x}, z; \odot.$$

(The calculated density is 11.7 g.cm.<sup>-3</sup> in good agreement with the pycnometric value previously mentioned).

The structure is confirmed by the good agreement between observed and calculated intensities (for ca. 150 reflexions possible with the Fe K $\alpha$  radiation). The calculated intensities were obtained taking, as a first approximation, the following values for the parameters, in analogy with other similar substances:

$$u = 0.06 (\text{Th}_I); s = 0.126, v = 0.25 (\text{Th}_{II});$$

$$t = 0.544, w = 0.03 (\text{Th}_{III}); x = 0.815, z = 0.31 (\text{Rh}).$$

This phase is, therefore, isostructural with a number of other similar compounds of thorium with several elements of group VIII (Florio, Baenziger & Rundle, 1956), the structural characteristics of which are summarized in Table 1. In the table are reported the constants (Å) and the molar volumes (cm.<sup>3</sup>) obtained both from crystallographica data ( $V_M$ ) and by adding the atomic volumes ( $\Sigma V_A$ ).

Table 1. *Structural data for Th<sub>7</sub>Me<sub>3</sub> compounds*

Th <sub>7</sub> Me <sub>3</sub>	a	c	c/a	V <sub>M</sub>	ΣV <sub>A</sub>
Th <sub>7</sub> Fe <sub>3</sub>	9.85	6.15	0.624	156	160
Th <sub>7</sub> Co <sub>3</sub>	9.83	6.17	0.628	156	159
Th <sub>7</sub> Ni <sub>3</sub>	9.86	6.23	0.632	158	159
Th <sub>7</sub> Rh <sub>3</sub>	10.02 <sub>3</sub>	6.29 <sub>3</sub>	0.627 <sub>5</sub>	165	164

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