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Compounds with the α-U_3O_8-type structure.*

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Zachariasen (1948) described the structure of α-UO_3 (orange, hexagonal, Type I of Katz & Rabinowitz, 1951, p. 278) and mentioned that α-U_3O_8 had a similar structure, with a pseudo-hexagonal orthorhombic unit cell. Hoekstra, Siegel, Fuchs & Katz (1955) found that α-U_3O_8 was truly hexagonal only above 400 C. On the other hand Milne (1951) decided from Weissenberg data that his 'crystal' of U_3O_8 was a composite of two truly hexagonal forms with the same c_0 (4·15 Å) and different a_0 (3·94 Å and 3·87 Å), the change in a_0 being due to different oxygen contents. Brooker & Nuffield (1952) likewise interpreted most of their data as two hexagonal cells.

According to Elson, Fried, Sellers & Zachariasen (1950), γ-Nb_2O_5 (*T*-form of Brauer, 1941), β-Ta_2O_5 (low-temperature form of Magneli & Lagergren, 1952) and one form of Pa_2O_5 are orthorhombic and isostructural with U_2O_5 or $UO_{2\cdot6}$, which is also homotypic (Megaw, 1946) with α-U_3O_8 and α-UO_3 (Baenziger, 1948; Hoekstra *et al.*, 1955). X-ray powder diffraction patterns, made in this laboratory, of γ-Nb_2O_5, β-Ta_2O_5 and α-U_3O_8 are all closely similar, in confirmation of published data. However, extension of Milne's interpretation of two hexagonal cells to the cases of Nb_2O_5 and Ta_2O_5 is inconsistent with the general chemistry of these elements, and with detailed knowledge of the Nb–O (Brauer, 1941) and Ta–O (Magneli & Lagergren, 1952) systems. Furthermore, detailed measurement and indexing of the powder diffraction patterns confirm the presence of an orthorhombic pseudo-hexagonal cell rather than two hexagonal cells (Table 1). Therefore, the orthorhombic type exists for all three compounds.

It should be noted that X-ray diffraction powder patterns of γ-Nb_2O_5 and β-Ta_2O_5 consistently show a few weak lines at about 3·35, 2·55, 2·10 and 1·5 Å. These cannot be indexed on the described hexagonal unit cells, the orthorhombic unit cell (Table 1), or the latter with the a_0, b_0 or c_0 parameter doubled. They apparently refer to a larger multiple cell, perhaps the very large cell found by Baenziger (1948) for $UO_{2\cdot6}$. Single-crystal work will be required to identify these lines.

Some of the X-ray powder diffraction patterns referred to above were kindly furnished by D. A. Vaughan and J. R. Bridge of Battelle Memorial Institute.

Table 1. *X-ray powder diffraction data for compounds with the* α-UO_3-*type structure*

Compound	a_0 (Å)	b_0 (Å)	c_0 (Å)	Non-hexagonal lines	References
U_3O_8*	6·70	3·97	4·14	(421) (600)	Grønwald (1948)
				(421) (600) (212)	
	6·71	3·96	4·15	(210) (211) (213) (302?) (320?)	Holser
γ-Nb_2O_5†	6·21	3·67	3·95	(211) (212)	Brauer (1941)
	6·19	3·65	3·94	(211)	Holser
β-Ta_2O_5†	6·18	3·65	3·88	(210) (320?)	Vermilyea (1953)
	6·20	3·67	3·90	(210) (211) (212) (120) (302) (320?) (421?)	Holser

* Milne's (1951) powder pattern (not taken on the same material for which he obtained Weissenberg data) does not even resolve some lines such as (110) and (111) which should be split in either interpretation, so it will not be considered further here. The General Electric pattern (ASTM card 2-0275) is nearly identical with Grønwald's data.

† The patterns by Peterson, Fassell & Wadsworth (1954, p. 1041) of Ta_2O_5 formed at temperatures between 500 and 1000 C. are poorly resolved, but two of them show the (211) line. Their pattern of 'ignited' Ta_2O_5 is the α (high-temperature) form. Hahn's (1951) patterns are also poorly resolved. There is a misprint apparent in his original publication, which is retained with added misprints on ASTM card 5-0258 and in Vermilyea (1953, p. 293). The pattern for Ta_2O_5 reported by Hanawalt *et al.* (1938) is a perovskite-type structure, apparently from soda contamination, as noted by Brauer for Nb_2O_5 and also experienced in this laboratory with Ta_2O_5.

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