a resistance furnace. Cold gas (nitrogen) is injected into a platinum tube to obtain a suitable temperature gradient. The single crystals are growing on the platinum tube.

Single crystals of thorium, neptunium, and plutonium dioxide have been grown as well as Np doped thorium dioxide.

The experimental conditions and results are summarized in Table I.

The average growth rate for all the actinide dioxides is about 1 mm/week. The single crystals have been characterized by X-ray diffraction (Debye-Scherrer, Gandolfi, Laue). A more complete characterization including the determination of the oxygen/metal ratio and a panoramic analysis of the impurities and the detection of inclusions is in progress.

1 B. M. Wanklyn, *J. Cryst. Growth, 7,* 368–370, (1970).
2 G. Garton, S. H. Smith and B. M. Wanklyn, *J. Cryst. Growth, 13/14,* 588–592 (1972).

D9

Phase Relations and Structures of Protactinium Hydrides

JOHN M. HASCHKE*, WILHELM BARTSCHER, JEAN REBIZANT and JOHN W. WARD

Commission of the European Communities, Joint Research Centre, Karlsruhe Establishment, European Institute for Transuranium Elments, Postfach 2266, D-7500 Karlsruhe, F.R.G.

The metal–hydrogen systems of the lighter actinides (Th–Am) have in general been well characterized, but a conspicuous gap occurs at Pa + H. Only the results of two X-ray diffraction studies have been described [1, 2]; Sellers *et al.* [1] reported that the elements reacted at 523 K to form a cubic β-UH_3-type hydride with a = 664.8 pm. Later work by Dod showed that the products formed between 373 and 573 K had the cubic α-UH_2-type structure with a = 415.4 pm, while that formed at 473 K gave a new diffraction pattern which was not indexed or correlated with a known structure. The present study was initiated after suitable quantities of ^{231}Pa (0.052 mass% impurity) were prepared in our institute.

Temperature–pressure–composition data were measured with a gold-lined Seivert's apparatus in the experimental range $373 < T < 795$ K and 10 μbar $< P < 45$ bar. Metal samples (0.15–0.21 g) were contained in a W cell. Samples for X-ray studies were prepared along hydriding and dehydriding isotherms and were cooled at constant composition. Diffraction data were obtained by the Debye–Scherrer method.

The pressue–composition isotherms measured during hydriding and dehydriding are similar, but large hysteresis effects are encountered. Results of extensive studies indicate that equilibrium is defined by the dehydriding pressures. At low H/Pa, hydrogen dissolves in the bct metal to form phase I. The hydrogen-saturated metal coexists with hydride for H/Pa < 1.3. Isotherms for T > 500 K show that the phase II hydride exists across the range $1.3 \leqslant$ H/Pa $\leqslant$ 1.7, and that a second diphasic region occurs for 1.7 < H/Pa < 2.0. Phase III forms in the range $2.0 \leqslant$ H/Pa $\leqslant 3.0$. At T < 500 K, a continuous solid solution designated phase IV exists across the entire range $1.3 \leqslant$ H/Pa $\leqslant 3.0$.

Diffraction data for phase II show that it is identical to the new hydride observed by Dod [2]. The reflections are indexable on fcc with parameters which vary from 914.4(6) pm at H/Pa = 1.3 to 919.8(2) pm at H/Pa = 1.7. Phases III and IV have β-UH_3-related and α-UH_3-related structures, repectively. The cubic parameter of phase III is 656.7(5) pm at H/Pa = 2.0 and 664.2(6) pm at H/Pa = 2.9. The parameters of phase II and III hydrides obtained along hydriding isotherms are consistently larger than those reported here for dehydriding samples. The phase IV parameter, 415.7(7) pm, is constant.

Metal atom coordinates for the phase II structure have been determined using powder intensities. The measured hydride density of 11.2 ± 1.2 g cm^{-3} is in good agreement with the 11.79 g cm^{-3} value calculated for Z = 24 formula units of $PaH_{1.67}$ per unit cell. The lattice parameters and intensities are similar to those of compounds with metal atoms in the $MgCu_2$(C15) arrangement, which served as a model. The d-values and calculated intensities for space group Fd3m with Pa on fixed positions 8 (a) and 16 (d) are presented with observed data in Table I.

Identification of this unique actinide hydride structure is particularly significant. The upper and lower boundaries of phase II correspond to the ideal stoichiometries Pa_3H_4 and Pa_3H_5, respectively, but it is not obvious why this complicated arrangement is stable in Pa + H at high temperatures. Protactinium occupies both Mg and Cu sites in the $MgCu_2$ arrangement, which is found for spinel, cubic AB_2 Laves hydrides and $ThZr_2H_7$. The behavior of Pa is most similar to that of the Th-Zr alloy in that neither metal exists in the $MgCu_2$ arrangement prior to reaction with hydrogen [3].

The two types of metal positions in Pa_3H_x are non-equivalent, and the phase must be looked upon as a 'pseudo-ternary' hydride. Each Pa on a Mg site is surrounded by 12 Pa on Cu sites at distances of 382.7 pm and by 4 Pa on Mg sites at 399.7 pm. Each metal on a Cu site is surrounded by 6 Pa on Cu sites at distances of 326.4 pm, which is similar to the inter-atomic distance in Pa metal (321.5 pm). The metals on Cu sites form an infinite three dimensional newwork composed of two-dimensional sheets having metal positions like those of the (110) planes of bct

TABLE I. Powder X-ray Diffraction Results for Phase II at H/Pa = 1.67.

hkl*	d(obs)	d(calc)	I(obs)$^+$	I(calc)
111	5.3282	5.3295	vw	5
220	3.2507	3.2637	m	26
311	2.7796	2.7833	vs	100
222	2.6630	2.6648	m	41
400	2.3067	2.3077	vw	5
331	–	2.1177	–	1
422	1.8831	1.8843	w	11
511	1.7766	1.7765	s	28
333				11
440	1.6311	1.6318	s	33
531	–	1.5603	–	1
442	–	1.5385	–	0
620	1.4593	1.4595	w	5
533	1.4073	1.4077	m	13
622	1.3889	1.3916	m	17
444	1.3364	1.3324	vw	1
551	–	1.2926	–	<1
711				<1
642	1.2338	1.2335	w	6
553	1.2018	1.2018	w	8
731				16

*Only low angle reflections are listed. $^+$s = strong, m = medium, w = weak, v = very.

protactinium. The spatial orientation of these sheets is defined by the faces of a regular tetrahedron, and their mutual intersection points lie at the centers of Pa_4 tetrahedra. The situation for phase II may well be similar to that of β-UH_3, which has two crystallographically different U atoms. One set occupies widely spaced bcc positions and is magnetic, while the other occupies closely-spaced (f-bonded) positions in the cubic faces and is metallic [4].

Three grossly nonstoichiometric hydrides are observed in Pa + H. In all cases, substoichiometry is attributed to hydrogen vacancies, and the possibilities of cluster formation and long range order exist. Since β-UH_3 is essentially stoichiometric at $T < 700$ K, the formation of an extended phase III solid solution is rather surprising. Phase IV is unusual because its lattice parameter is virtually constant across a stoichiometry range exceeding that of any other actinide hydride. Approximately 57% of the anion sites are vacant at its lower phase boundary.

The phase relations of Pa + H are established for $T > 500$ K where phases II and III are the stable high temperature hydrides, but the equilibrium state is not certain for the low temperature region where phase IV is observed. Although IV $\rightarrow$ II and IV $\rightarrow$ III transitions occur at high temperature, the reverse processes are not observed during cooling. No transition occurs when either phase II, III or IV is annealed at 423 K. It is not known whether phase IV is a metastable product or whether II $\rightarrow$ IV and III $\rightarrow$ IV processes are kinetically hindered at low temperatures. The situation is identical to that encountered for the α and β forms of UH_3 at low temperatures [5].

1 P. A. Sellers, S. Fried, R. E. Ellson and W. H. Zachariasen, *J. Am. Chem. Soc., 46* (1954) 5935.
2 R. L. Dod, USAEC Rept. LBL-659 (1972).
3 R. Van Houten and S. Bartram, *Metall. Trans., 2* (1971) 527.
4 J. W. Ward, L. E. Cox, J. L. Smith, G. R. Stewart and J. H. Wood, *J. Phys. (Paris), 40* (1975) C4–15.
5 Gmelin, 'Handbuch der Anorganischen Chemie' 55, Uran Erg.-Bd. C1, Springer Verlag, Berlin, 1977.

D10

Lanthanide Oxides: Yb_2O_3 Hydration

I. CARRIZOSA*, J. A. ODRIOZOLA and J. M. TRILLO

Inorganic Chemistry Department, Faculty of Pharmacy, University of Seville, Seville, Spain

Partial conversion to bulk hydroxycarbonate is attained by the heaviest 4f oxides when exposed to the air [1]. The low rate of this process has been related to a poisoning effect of the CO_2 from TPD and XPS data [2]. The aim of this work is the study of the uptake of H_2O vapour by Yb_2O_3 in the absence of CO_2, in the range of atmospheric conditions. Effect of pressure, temperature and time of exposure are examined. From TPD and IR data conclusions about the formed species are drawn.

Ytterbium hydroxycarbonate was precipited with NH_3 from nitrate solutions. Yb_2O_3 was finally prepared by calcining the precipitate in air at 873 K. The sample here studied was characterized by X-ray diffraction, thermogravimetric (TG) and differential thermal analyses (DTA), IR spectroscopy and pore size distribution. Data about preparation and characterization are reporded in [1]. The hydration of the samples was performed in a conventional vacuum system. The vacuum cell was designed in such a way that it also could be used as a TPD one. Details concerning the temperature programmed decomposition (TPD) device are given in [3]. All the experiments were carried out in helium flow (30 ml min^{-1}) at a heating rate of 8 K min^{-1}.

As the Yb_2O_3 samples were aged in air, previous activation is necessary in order to obtain an almost clean surface. Evacuation at 10^{-6} torr and 1173 K has been used, the specific surface being 21.6 m^2/g. The final state of samples after the thermal treatment has been described in [4].

The uptake of H_2O vapour at room temperature (RT) as a function of pressure has been carried out on an activated sample. Water pressures from 0 to