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
511 333	1.7766	1.7765	s	28 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
551 711	–	1.2926	–	<1 <1
642	1.2338	1.2335	w	6
553 731	1.2018	1.2018	w	8 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 → II and IV → 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 → IV and III → 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].

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D10

Lanthanide Oxides: Yb_2O_3 Hydration

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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

20 torr were admitted into the vacuum cell. It is noteworthy that at pressures below 8 torr the equilibrium was obtained in a few minutes, but no equilibrium was reached at pressures higher than 8 torr, even after several hours.

An adsorption process up to 8 torr and a water uptake at pressures higher than 8 torr, which surpass the surface monolayer capacity were found.

In Fig. 1 TPD chromatograms of water retained at 298 K are shown. The Yb_2O_3 sample was evacuated and water admitted into the reaction chamber at 3.0 torr during 24 hours, trace (a). Weakly adsorbed water was eliminated by free-zind with liquid N_2 and TPD running was carried out. A maximum at 390 K followed by a broad band centered at 670 K are observed. When water pressure is below 8 torr, i.r. data obtained in our laboratory [5] lends support to a dissociative adsorption with surface hydroxilation. Over this layer, weakly adsorbed H-bonded molecular water are found. TPD peak at 390 K is due to the later. At higher temperatures dehydroxilation takes place, firstly by interaction between vicinal OH groups and then by isolated ones. When the activated sample is exposed to H_2O pressures over 8 torr before the TPD running a different behaviour is observed. In Fig. 1(b) characteristic TPD trace of a sample exposed to 15 torr for 24 hours is shown. In order to eliminate the weakly adsorbed H_2O, TPD peak at 390 K in Fig. 1(a), a evacuation to 330 K was carried out until constant TPD trace. A well defined maximum at 440 K with a broad tail are explicited. Integration of TPD peak at 440 K leads to a coverage of 13.1 molec/nm^2 which largely exceeds the surface monolayer capacity and could be adscribed to bulk hydroxilation. The amount of water retained is now time dependent (Fig. 2) and after a short period of induction an appreciable rate of diffusion operates during 24 hours, at which a deceleration period begins. This bulk hydration process is prevented by the presence of CO_2 as has been described in [2]. On the other hand, when reaction with H_2O is carried out at 350—400 K and 15 torr TPD results show (Fig. 3) that only surface species are formed; therefore at these temperatures and pressures the bulk process is not thermodynamically favoured. It is interesting to point out that the same behaviour is found with samples which have been activated at 823 K.

Interaction type at room temperature of Yb_2O_3 with H_2O depend upon the water pressure. At pressures below 8 torr a surface process takes place. When pressures are raised over 8 torr, bulk hydration is found. The thermal decomposition of this phase takes place via vicinal OH groups elimination giving a TPD peak at 440 K. The bulk hydration proceeds at appreciable rate during the first 24 hours. By raising the reaction temperature at 350—400 K, the bulk hydration is prevented. This result is in accordance with the Touret et Queyroux ones [6]. On the other hand, the presence of CO_2 at RT has a poison effect also hindering the process [2].

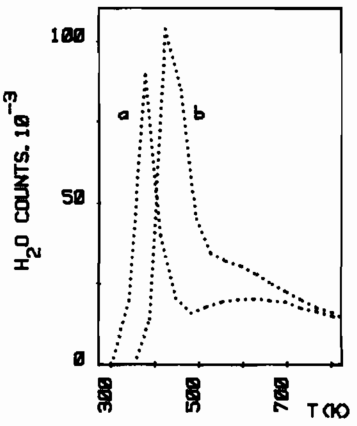

Fig. 1. TPD traces of water retained by Yb_2O_3 at 298 K during 24 hours: a) at 3 torr and b) at 15 torr.

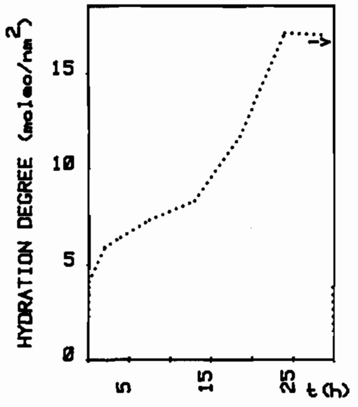

Fig. 2. H_2O uptake by Yb_2O_3 vs. time of exposure to it, at 15 torr and 298 K.

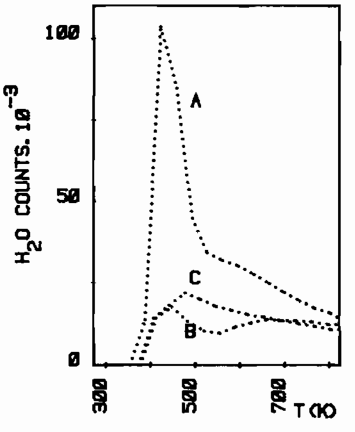

Fig. 3. TPD of hydrated Yb_2O_3 at 15 torr for 24 hours: A) at 298 K, B) at 353 K and C) at 400 K.

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D11

A Study of Decomposition of $Ce(In_{1-x}Sn_x)_3$ in Air Accompanied by Whisker Growth and Measurement of Electrical Resistivity

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$CeSn_3$ is an interesting compound which shows the mixed valence phenomena. One of the complexities in this sample is that it decomposes rapidly in air. For example, a contradiction in Mössbauer measurements by different groups on this sample was considered to originate from this decomposition [1]. Thus we must be careful in understanding its properties.

The purpose of the present study is to see how the decomposition of $CeSn_3$ and its pseudo-binary alloys, $Ce(In_{1-x}Sn_x)_3$, actually progresses, and to see how the decomposition is reflected on the electrical resistivity.

Ingots of samples are prepared by arc-melting in Ar atmosphere. X-ray powder diffraction showed that all samples of $Ce(In_{1-x}Sn_x)_3$ except pure $CeSn_3$ are of a single phase having a cubic Cu_3Au type crystal structure.

In the sample of $CeSn_3$, diffraction peaks due to β-Sn as an impurity phase were observed in addition. Content of β-Sn was found to change drastically with the time elapsed from the powder preparation. X-ray counts, at β-Sn diffraction position, of a quickly prepared powder are at the background level for the first several minutes and then gradually increase. Peak intensities of β-Sn are already comparable to those of $CeSn_3$ after a couple of hours. Peaks of $CeSn_3$ completely disappear and only those of β-Sn replace them after two days. The decomposition of $CeSn_3$ in air and the accompanying precipitation of β-Sn progress rapidly. Ce atoms are supposed to be oxidized and/or hydrated to form an amorphous material unobservable by X-ray diffraction. Decompositions of all samples $Ce(In_{1-x}Sn_x)_3$ except $CeSn_3$ are found to be much slower.

Ingots of $CeSn_3$ kept in a glass tube under a vacuum of 10^{-6} torr stay shiny for months. On the other hand, ingots of $CeSn_3$ in air lose rapidly the metallic lustre and in a few days they look like covered with fur or mould. Under an optical microscope, the ingots are seen to be covered with a flock of small fragments with irregular shapes mixed with strictly straight rods.

These rods were picked up and observed under a transmission electron microscope. They turned out to be β-Sn whiskers; electron diffraction patterns have tetragonal symmetry and lattice constants, *a* and *c*, agree with the reported values of β-Sn with the rod axis along [101] crystallographic direction. Size of these whiskers varies; the diameter is typically of 0.5–1.0 μm and the length is 1 mm at most. Thus, a part of β-Sn decomposed from $CeSn_3$ is found to exotically grow into whisker.

Ingots of $Ce(In_{1-x}Sn_x)_3$ whith $x \neq 0$ keep shiny for longer period. Rare whiskers are found on ingots of $CeIn_3$. Still rarer whiskers are found on ingots of $Ce(In_{1-x}Sn_x)_3$ with x neither 1 nor 0

We have also observed the ingot surface by a scanning electron microscope. Whiskers with length of several hundred μm are observed on a fresh surface of $CeSn_3$ cracked only several minutes before. This fact shows the rate of growth of the whiskers is very rapid. Besides, numerous eruptions with diameter of about 1 μm are observed on the fresh surface of $CeSn_3$ as well as all other samples of $Ce(In_{1-x}Sn_x)_3$. They look like pebbles under the scanning electron microscope. Probably some eruptions somehow gain their heights and are thought to develop into whiskers.

We have measured electrical resistivity ρ of $Ce(In_{1-x}Sn_x)_3$. Samples of a typical dimension 1 X 1 X 15 mm^3 are cut from the ingots. Measurements were made by the standard dc four prove method. As the decrease of temperature, ρ of all samples $Ce(In_{1-x}Sn_x)_3$ was found to decrease sharply at a critical temperature around 4.2 K. Fig. 1 shows several examples. $Ce(In_{0.4}Sn_{0.6})_3$ looks like as if it were

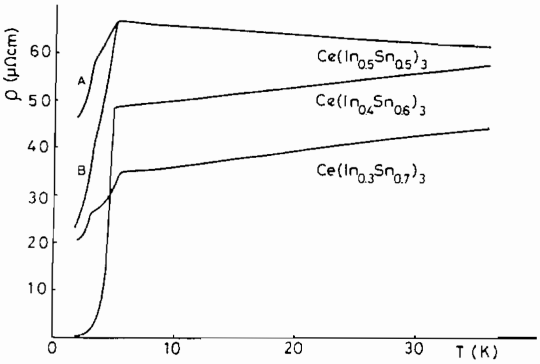

Fig. 1. Electrical resistivity ρ of three samples of $Ce(In_{1-x}Sn_x)_3$ plotted as a function of temperature T.