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HIGH PRESSURE DIFFRACTION STUDIES OF YbH_2 UP TO 28 GPa

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It is expected that Yb in orthorhombic YbH_2 should undergo a phase transition, at moderate pressure, from the divalent to a trivalent state, and that this transition might be followed by a change to the fluorite structure characteristic of the trivalent rare-earth hydrides.
For these reasons high pressure neutron and X-ray diffraction studies of YbH_2 have been undertaken.

Neutron diffraction measurements up to 4 GPa and preliminary X-ray results up 11 GPa have shown no structural changes. Very recent X-ray diffraction experiments up to 28 GPa using synchrotron radiation have shown a clear structural change at about 14 GPa from the orthorhombic phase to a hexagonal close packed with $c/a = 1.34$. The transition is accompanied by a 5.4% decrease in volume. A preliminary interpretation of the transition is given.

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1. INTRODUCTION

In several rare-earth compounds and intermetallics the valence state of the rare-earth ion may be changed between the $4f^n(5d6s)^2$ and $4f^{n-1}(5d6s)^3$ configurations by chemical manipulations or by application of high pressure (1). By now quite a number of such unstable valence systems have been studied, although the main emphasis has been on chemically manipulated systems rather than on compressed systems. Furthermore, no attention has been directed towards those cases where the valence change may be accompanied by a change in crystal structure.

It can be expected that the rare-earth dihydride, YbH_2, is such a system. At zero pressure it shares the orthorhombic structure with EuH_2, and in both compounds the ground state configuration is $4f^n(5d6s)^2$. In contrast, the ground state configuration of the other rare-earth dihydrides is $4f^{n-1}(5d6s)^3$, and they all form in the fcc fluorite structure. Hence, when the valence state of Yb is changed to $4f^{n-1}(5d6s)^3$ under pressure one would expect YbH_2 to transform into an fcc structure.

Following these considerations we have undertaken high pressure experiments with YbH_2.

The preliminary measurements were performed at Risø National Laboratory (Denmark) using the neutron powder diffraction technique and the high pressure cell described in ref. (2). At pressures up to 4 GPa no phase transformation was observed. At the same time an attempt to find the expected phase transformation was made by means of a diamond anvil cell and the x-ray white beam energy-dispersive technique (3). Measurements up to 11 GPa performed at Physics Laboratory II, University of Copenhagen, using an X-ray tube did not show any phase transformation either.

Only very recently experiments at pressures up to 28 GPa have clearly demonstrated a phase transformation at about 14 GPa. A preliminary account on these experiments and the obtained results, followed by a discussion is the subject of this paper.

2. EXPERIMENT

A diamond anvil high pressure cell was used and an Ytterbium dihydride powder sample 2oo µm in diameter and 8o µm thick was enclosed in an Inconel gasket. A 4:1 methanol-ethanol mixture and a ruby were added to the powder to allow for hydrostatic pressure conditions and a proper calibration of pressure, respectively.

The X-ray diffraction studies were performed at the electron storage ring DORIS at DESY-HASYLAB in Hamburg. The electron energy was 4 GeV (critical wavelength 1.o6 Å) and the time averaged electron current produced by 2o bunches was usually between 2o and 4o mA. The white beam energy-dispersive diffractometer (4) and the triple axis spectrometer (5) working in the energy dispersive mode were used. By applying very fine slits (loo µm× loo µm) in the incident beam we avoided the diffraction by the gasket. The very good collimation of the incident beam, the small size of the illuminated part of the sample, the relative large distance (35 cm) between the sample and the detector, and a 2oo µm slit in front of the detector resulted in a small geometrical contribution to the total resolution. The pure Germanium solid state detector had an energy resolution of 15o eV (FWHM) at 5.9 KeV. With a scattering angle of $2\Theta = 14.51^{\circ}$, used in this experiment, the FWHM of a diffraction peak at 2o KeV was 3oo eV, corresponding to lo channels.

The energy analysis of the diffracted X-rays was carried out by means of a 2o48-cannel analyser covering the range from lo keV to 7o keV. The exposure time was usually 5oo s. The diffraction patterns were recorded on an x-y plotter and on paper tape or a floppy disk. The centroids of the diffraction maxima were determined by the Jupiter multichannel analyser system or by computer fitting.

The scattering angle was determined by fitting the spectra at zero pressure to the known structure of the sample. For this preliminary report this fitting and the ones reported below were done in a simplified way described in the next section. A more careful fitting will be done later, but it cannot change the basic results presented in this paper. However, the absolute values of the lattice constants may differ slightly from those presented here.

The pressure was determined by measurements of the frequencies of the two ruby lines, which could be clearly seen up to highest pressures. The accuracy of frequency determination corresponds to an uncertainty in the pressure less than o,2 GPa. However, the uncertainty in the pressure of the sample might be larger due to pressure gradients in the cell.

3. RESULTS

Before presenting our results we recall the literature data concerning the structure of YbH_2 at atmospheric pressure. It is generally accepted that the structure is orthorhombic of space group Pnma (4 units YbH_2). Korst and Warf (6) on the basis of an X-ray study on $YbD_{1.98}$ found that with the origin at $\bar{1}$ the Yb atoms are in positions 4(c) with x = o.24o and z = o.llo. The lattice constants measured by various authors are shown in Table I.

The Positions of the hydrogen atoms were not determined but it was suggested (9) that their positions might be similar to those in CaH_2 (1o).

Table I

Lattice constants of orthorhombic Ytterbium dihydride at atmospheric pressure

Sample	Reference	a(Å)	b(Å)	c(Å)
YbD_2	6	5.871	3.561	6.763
YbH_2	7*	5.9o5	3.57o	6.792
$YbH_{1.78}$	8*	5.895	3.574	6.8o1
YbH_2	this work	5.898	3.576	6.765

*) For reasons of comparison the lattice constants were interchanged.

The basic results of our high pressure measurements are presented in Table II and in Fig. 1 showing characteristic examples of diffraction spectra at atmospheric pressure, 14.3, 17.o, and 28.2 GPa. As can be seen, at pressures up to 11.5 GPa all diffraction peaks (except one discussed below) can be indexed in an orthorhombic unit cell. At pressures from 19.2 GPa all peaks (except two discussed below) can be indexed in a hexagonal close packed cell. At 14.3 GPa most of the peaks belong to the orthorhombic structure, however some already indicate the presence of the h.c.p. structure. At 17.o GPa the situation is reversed. By decreasing pressure the h.c.p. structure turns back to the initial orthorhombic and thus the transition is reversible.

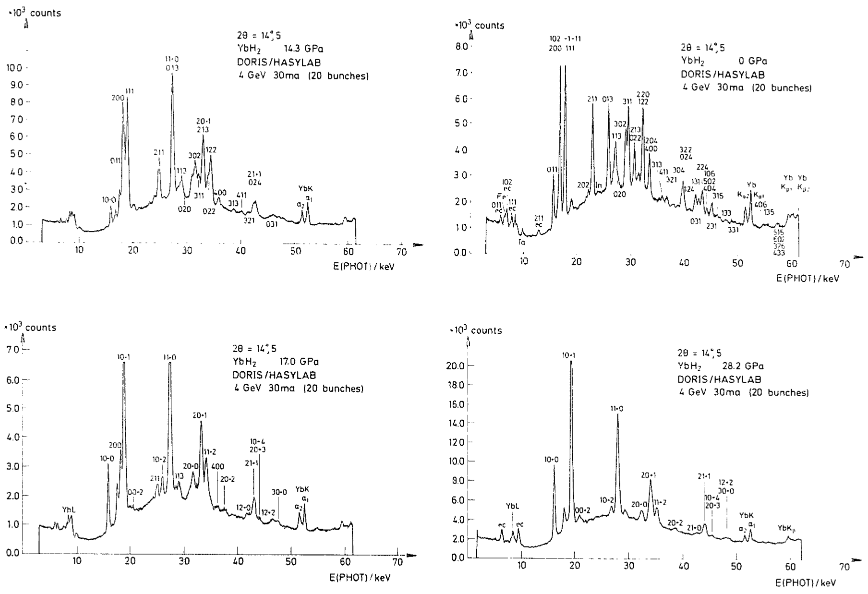

Fig. 1. X-ray energy-dispersive diffraction patterns of YbH_2 at serveral pressures.

Table II

Lattice constants of YbH_2 as function of pressure. $\bar{\Delta}$ is the mean difference (in channel numbers) between the observed and calculated peak positions for the 7 strongest lines in each spectrum.

Pressure	Orthorhombic phase				h.c.p. phase		
GPa	a	b	c	$\bar{\Delta}$	a	c	$\bar{\Delta}$
0.0	5.898	3.576	6.765	0.9			
9.3	5.521	3.410	6.482	0.9			
11.53	5.465	3.385	6.448	1.4			
14.3	5.335	3.405	6.382	1.4	3.614	4.848	1.6
17.0	5.183	3.450	6.317	1.5	3.595	4.802	0.6
19.2					3.574	4.753	0.6
21.9					3.560	4.718	0.9
24.5					3.542	4.674	0.7
25.8					3.533	4.652	0.4
27.5					3.521	4.622	0.7
28.0					3.517	4.614	1.0
28.2					3.516	4.610	0.6
17.95					3.584	4.787	1.1
15.4					3.606	4.830	1.3
4.9	5.710	3.470	6.607	2.7			
1.2	5.830	3.550	6.696	0.7			

One small peak at about 19 keV in the orthorhombic phase cannot be indexed (it might be explained partly as an escape peak), and two small peaks at about 19 keV and 29 keV in the hexagonal phase cannot be indexed either. They have most probaly another origin than YbH_2.

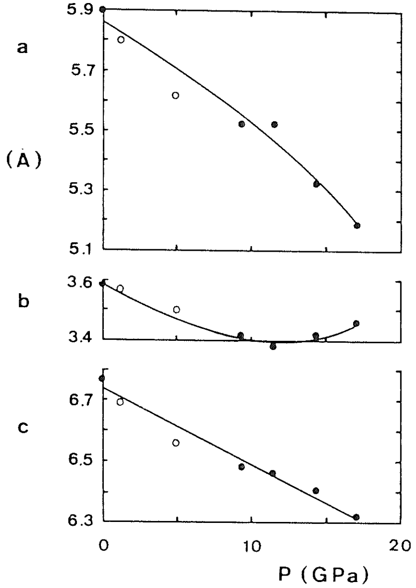

Fig. 2. Pressure dependence of the YbH_2 orthorhombic unit cell dimensions.

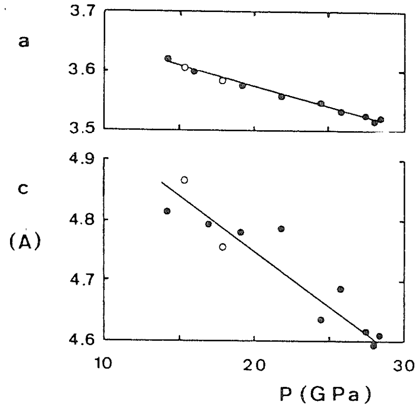

Fig. 3. Pressure dependence of the YbH_2 h.c.p. unit cell dimensions.

Fig. 2 presents the pressure dependence of the unit cell dimensions of the orthorhombic phase, and Fig. 3 of the h.c.p. phase. The indicated points (full circles for increasing pressure and open circles for decreasing pressure) represent a first approximation based on the position of three lines in the spectra. A subsequent refinement using the seven strongest lines results in lattice parameters indicated by the curve drawn through the points. These refined parameters are given in Table II.

Fig. 4 shows the pressure dependence of the unit cell volume divided by the number of Yb atoms in the respective unit cell (4 in the orthorhombic and 6 in the large h.c.p. unit cell).

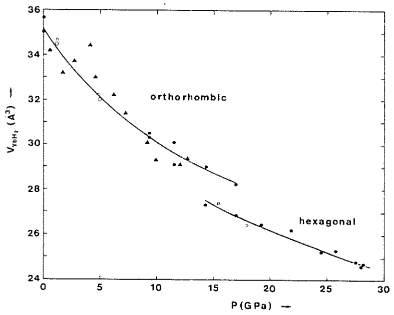

Fig. 4. Pressure dependence of the unic cell volume of YbH_2 divided by the number of Yb atoms in the respective unit cell (4 in the orthorhombic and 6 in the large h.c.p. unit cell).

On the basis of the above results we conclude that YbH_2 undergoes at about 14 GPa a pressure induces first order transition. The transition is accompanied by a 5.4% decrease in volume and a change in structure from an orthorhombic to a close packed hexagonal.

4. DISCUSSION

The high pressure phase of YbH_2 is thus not an f.c.c. as one could expect a priori on the basis of the analogy presented in the introduction.

Knowing, however, that the high pressure phase is a h.c.p. We may try a posteriori to find some good reasons for it. Such an attempt is discussed below.

We translate the origin of the orthorhombic unit cell to the position of one Yb atom and rename the basic vectors of the unit cell. At 14.3 GPa we have a_o = 3.4o5 Å, b_o = 6.382 Å and c_o = 5.335 Å (the index "o" stands for orthorhombic), and the Yb atoms positions are: (O;O;O), (o.5o; o.78; o.52) (o.5o; o.o2) and (o; o.28; o.5o), if we use the values for X and Z quoted earlier from ref. (7). Fig. 5 shows the positions of the Yb atoms in the $(\vec{a}_o,\vec{b}_o)$ plane of the orthorhombic unit cell and the projections on it of the other atoms present in this unit cell (underlined marking). In the same figure the basal plane of the h.c.p. large unit cell of the high pressure phase of YbH_2 is drawn with the Yb atoms in this plane and the projection on it of the other atoms in this unit cell (not underlined marking). The drawing is made in scale for the lattice constants at 14.3 GPa where both phases are present:

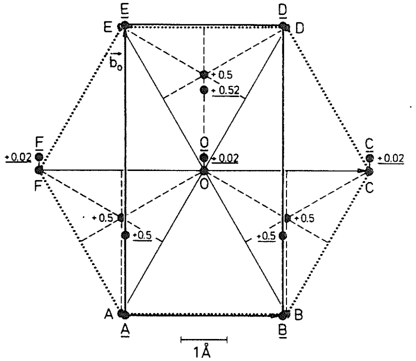

Fig. 5. The projections of the Yb atoms in the orthorhombic unit cell on the $(\vec{a}_o,\vec{b}_o)$ plane (underlined marking) and the Yb atoms in the h.c.p. large unit cell on the basal plane (not underlined marking). The drawing is in scale for the 14.3 GPa lattice constants. For details see text.

$\underline{AB} = a_o$ = 3.4o5 Å $\underline{AE} = b_o$ = 6.382 Å

$AB = a_h$ = 3.614 Å $AE = a_h\sqrt{3}$ = 6.26o

It is striking to notice that all Yb atoms in the basal plane of the hexagonal structure are very close to atoms lying in the $(\vec{a}_o,\vec{b}_o)$ plane or a bit above it (all marked by letters). Not much movement is thus needed for atoms lying in the $(\vec{a}_o,\vec{b}_o)$ plane or close to it in order to bring them in the hexagonal positions. As concerns the 3 Yb atoms with relative coordinates o.5o and in the $\vec{c}_o$ direction a similar statement could be made if c_o = 5.335 Å would be equal to c_h = 4.848 Å. It follows, however, from this discussion that the arrangement of the Yb atoms in the orthorhombic phase at 14.3 GPa is a slightly distored hexagonal packing with c/a $\approx$ 5.335 Å: 3.4o5 Å $\approx$ 1.57. This statement is similar to that made in ref. (1o) concerning the structure of CaH_2.

In view of that the discussed phase transformation in YbH_2 can be interpreted as a transition from a distored hexagonal lattice with c/a $\approx$ 1.57 to a collapsed hexagonal lattice with c/a = 4.848 Å: 3.614 Å = 1.34. The collapse is most probably due to the change of the valence state from $4f^{14}(5d6a)^2$ to $4f^{13}(5d6s)^3$.

As already mentioned the results and the discussion presented here are of a preliminary nature. A comprehensive paper will be published later.

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