

## Neutron Diffraction Studies of Ytterbium Dihydride: The Crystal Structure at 300 K

BY B. LEBECH

*Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark*

N. HESSEL ANDERSEN

*Physics Department and Metallurgy Department, Risø National Laboratory, DK-4000 Roskilde, Denmark*

S. STEENSTRUP

*Physics Laboratory II, University of Copenhagen, DK-1168 Copenhagen, Denmark*

AND A. SCHRØDER PEDERSEN

*Metallurgy Department, Risø National Laboratory, DK-4000 Roskilde, Denmark*

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**Abstract.** The crystal structures of  $\text{YbD}_2$  and  $\text{YbH}_2$  have been studied by elastic neutron scattering on powdered samples at room temperature and atmospheric pressure. The neutron diffraction data have been analysed by means of the *EDINP* profile structure refinement program. The analyses confirmed the assumption that both compounds are isostructural with the hydrides of the alkaline-earth metals at room temperature and atmospheric pressure. All atoms are found to occupy the 4(c) position in the orthorhombic space group  $D_{2h}^{16}$  (*Pnma*). The atomic positions were found to be:  $x(\text{Yb}) = 0.243$ ,  $z(\text{Yb}) = 0.111$ ;  $x(\text{D}') = 0.358$ ,  $z(\text{D}') = 0.433$ ; and  $x(\text{D}'') = -0.021$ ,  $z(\text{D}'') = 0.675$ . By inference from these atomic positions, it is suggested that the room-temperature high-pressure ( $p > 15$  GPa) hexagonal structure of  $\text{YbH}_2$  is  $D_{6h}^4$  ( $P6_3/mmc$ ) with the metal atoms in 2(c) positions and the hydrogen atoms in 2(a) and 2(d) positions.

**Introduction.** The structures of ytterbium dihydride have been extensively studied by X-ray diffraction, at room temperature and above, in both the deuterated (Korst & Warf, 1956) and the hydrogenated (Warf & Hardcastle, 1966; Messer & Gianoukos, 1968) forms. Therefore it is well established that the stable structures of  $\text{YbD}_2$  and  $\text{YbH}_2$  are orthorhombic  $D_{2h}^{16}$  (*Pnma*) at ambient temperature, although several cubic phases, formed at elevated temperatures, have been reported to persist down to room temperature (Warf & Hardcastle, 1966; Messer & Gianoukos, 1968). Naturally, the X-ray studies did not allow a determination of the hydrogen positions, but because of the similarities between the infrared absorption spectra of  $\text{YbH}_2$ ,  $\text{YbD}_2$  and  $\text{CaH}_2$ , it was suggested (Warf & Hardcastle, 1966) that the hydrogen positions in  $\text{YbH}_2$  and  $\text{YbD}_2$  are the same as those found in  $\text{CaH}_2$ . The latter substance was

studied in powdered form by neutron diffraction by Bergsma & Loopstra (1962), who suggested from geometrical considerations that the metal and hydrogen atoms are in the same plane [4(c) positions] of the  $D_{2h}^{16}$  (*Pnma*) orthorhombic structure. They found this arrangement in agreement with the observed neutron intensities for  $\text{CaD}_2$ .

Recently,  $\text{YbH}_2$  was studied by X-ray scattering (Staub Olsen *et al.*, 1981) at room temperature and high pressure. Staub Olsen *et al.* (1981) found that at  $\sim 15$  GPa the orthorhombic structure of  $\text{YbH}_2$  transforms *via* a first-order transition to a hexagonal structure. In order to achieve a better understanding of this transformation and to suggest a possible high-pressure structure, we found it necessary to establish the hydrogen positions more firmly than by inference from the hydrogen positions suggested for  $\text{CaH}_2$ . The present neutron diffraction study of powdered  $\text{YbD}_2$  and  $\text{YbH}_2$  was made with this aim. As neutron diffraction measurements at 15 GPa are not possible in the foreseeable future, the measurements had to be restricted to atmospheric pressure and ambient temperature.

**Experimental.** Below we describe the sample preparation and other experimental details.

The Yb powder used in the sample preparation was of purity 99.9% and approximate grain size 0.5 mm, supplied by Rare Earth Products Ltd, England. The powder, which was stable in air, was hydrogenated in a high-pressure microbalance capable of accurately determining the amount of gas intake. The sample was heated at  $5 \text{ K min}^{-1}$  in hydrogen at a pressure of 0.2 MPa. At 450 K, a reaction could be observed. This reaction became vigorous at 525–550 K. The heat evolution was substantial, and immediately caused the

sample temperature to rise above 800 K. The reaction was completed within a few seconds, and the composition could be calculated to be  $\text{YbH}_{1.92}$  (see also Korst & Warf, 1956). The calculation incorporated the buoyancy effect due to the specific volume difference between Yb and  $\text{YbH}_2$ , which is approximately 15% based on the X-ray density of  $\text{YbH}_2$  (Korst & Warf, 1966). Despite their slight hydrogen or deuterium deficiency, the samples will be referred to as  $\text{YbH}_2$  and  $\text{YbD}_2$  for the sake of simplicity. On the basis of this test preparation, the samples for the neutron diffraction measurements (approximately 10 g) were prepared in a volumetric/manometric equipment under conditions identical to the test conditions, *i.e.* heating at a rate of  $5 \text{ K min}^{-1}$  to 575 K in 0.2 MPa hydrogen or deuterium atmosphere. The  $\text{YbH}_{1.92}$  and  $\text{YbD}_{1.92}$  formed were black, graphite-like materials in which the original grains could still be identified. The materials were found to be stable in air and to lose only undetectably small amounts of hydrogen or deuterium when left in the atmosphere for a period of one week. Both materials were crushed to a fine powder in porcelain mortars before use in the diffraction experiments to be described below.

Neutron powder diffraction patterns\* were measured using a triple-axis spectrometer at one of the thermal beams at the DR3 steady-state reactor at Risø National Laboratory. The spectrometer was operating in the elastic mode with pyrolytic-graphite monochromator and analyser. The neutron wavelengths were 2.44 and 1.43 Å. At 2.44 Å, a pyrolytic-graphite filter was used to reduce the higher-order contamination of the incident beam. At 1.43 Å the higher-order contamination was found to be negligible. The collimator angles before and after the monochromator and before and after the analyser were 56, 20, 23 and 66°. The diffraction patterns were recorded for scattering angles  $2\theta$  from 10 to 100° in steps of 0.1°, counting for about 5 min per scan point. The  $\text{YbD}_2$  sample ( $\sim 2 \text{ cm}^3$ ) was contained in a 13 mm diameter thin-walled Al cylinder giving relatively weak diffraction peaks. Those regions of  $2\theta$  coinciding with the strongest container peaks were excluded from the data when refining the structure.

#### Discussion. Analysis of the diffraction data

Examples of the data obtained using incident neutrons of wavelengths 2.44 and 1.43 Å are shown in Figs. 1 and 2. The data were analysed using the profile-refinement program *EDINP* (Pawley, 1980).

1. *Reliability of the profile analysis.* In order to indicate the reliability of a structure refinement, one usually quotes the reliability factor  $R$  defined as

\* Lists of numerical data corresponding to the diffraction profiles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38903 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$R = 100(\sum |y_{\text{obs}} - y_{\text{calc}}| / \sum y_{\text{obs}})\%$ , where  $y_{\text{obs}}$  and  $y_{\text{calc}}$  are the observed and calculated profile intensities.

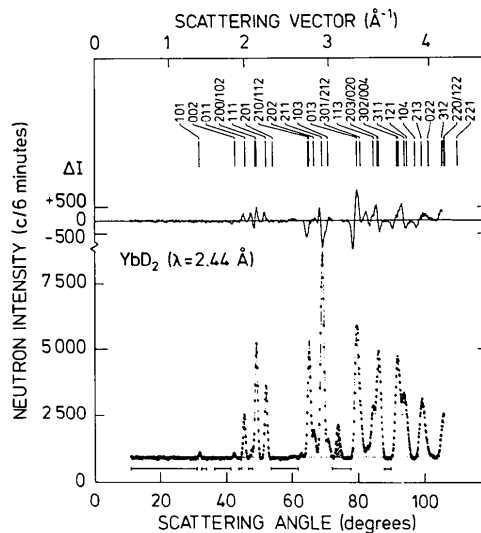


Fig. 1. Observed and calculated diffraction pattern of  $\text{YbD}_2$  at ambient temperature and pressure for incident neutrons of wavelength 2.44 Å. The solid line in the lower part is calculated using the parameters listed for  $\text{YbD}_2$  in Table 1. The upper curve shows the difference between the observed and calculated patterns. The vertical lines show the positions of all non-zero reflections. The corresponding Miller indices are also given. The dotted line is the background estimate, which was kept constant in the refinement. The hatched peak is a sample-container peak. — indicates regions excluded when calculating  $R_s$  (Table 1).

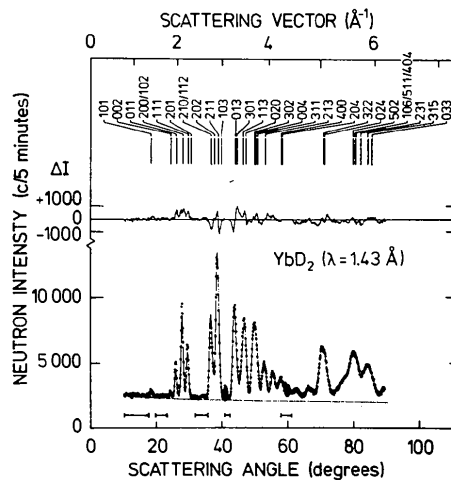


Fig. 2. Observed and calculated diffraction pattern of  $\text{YbD}_2$  at ambient temperature and pressure for incident neutrons of wavelength 1.43 Å. The vertical lines show, for scattering angles less than 30°, the positions of all nonzero reflections and, for scattering angles larger than 30°, the positions of reflections having intensities larger than 10% of the 020 reflection. The corresponding Miller indices are also given. Other details have the same meaning as in Fig. 1.

In the *EDINP* refinement program the summations include all data points except those excluded for experimental reasons. In this respect *EDINP* deviates from the Rietveld method where regions without diffraction peaks are excluded. Pawley (1980, and references therein) has discussed the differences in *R* factors obtained from these two refinement methods and more generally the problems involved in establishing a unique measure of the reliability by which a crystal structure is determined from powder diffraction data. He argues that the *R* factor of a full profile refinement should be calculated from all data points. The regions without diffraction peaks should be included since they contribute to establish the background profile data which are subtracted in order to obtain the diffraction spectra. However, if considered as a reliability factor for the crystal structure only, the *R* factor might become unrealistic if the background contributions dominate the full powder pattern. Pawley has also discussed the situation of high incoherent scattering contributions which, for example, is encountered in the present study of  $\text{YbH}_2$ . Although our  $\text{YbH}_2$  data and the corresponding fit were clearly less reliable than the corresponding results on  $\text{YbD}_2$ , the *R* factors based on all data points are of the same order of magnitude. The opposite, more or less hypothetical, situation of unrealistically high *R* factors might occur if only a few strong peaks, which are well described by the fit, are present on a background of negligible intensity.

Therefore, we invoke the following scheme of refinement and data treatment which may be generally used in order to establish an *R* factor which gives a more-nearly unique measure of reliability for comparison between various structural results without neglecting or being confused by the information contained in the background data:

(1) A full powder pattern refinement analysis should be performed excluding only regions where the diffraction pattern is known to be contaminated by, for instance, sample-container peaks, cryostat peaks, etc.

(2) A background profile pattern should thereby be established preferentially by a fit to the data, alternatively by interpolation between evaluated background points.

(3) The *R* factor should then be calculated on the basis of the diffraction spectra which have been cleaned up by subtraction of the background profile pattern and by exclusion of regions without reflections allowed by the space group in question.

2. *Profile analysis of the room-temperature data for  $\text{YbD}_2$  and  $\text{YbH}_2$ .* Following the refinement procedure outlined in § 1 and using the data shown in Figs. 1 and 2, we refined the structure of  $\text{YbD}_2$ . Details of the refinement are given below. The resulting *R* factors and the positional parameters for the Yb and deuterium atoms are quoted in Table 1. In all cases, unit weights were used in the minimization procedure.

Table 1. *Crystallographic data of orthorhombic  $\text{YbD}_2$  and  $\text{YbH}_2$  at ambient temperature and pressure*

Lattice constants are determined by the X-ray Guinier technique. Fractional coordinates of  $\text{YbD}_2$  are obtained from profile analysis by *EDINP*; the space group is *Pnma* ( $D_{2h}^{16}$ ) and all atoms occupy the 4(*c*) positions. *R* factors calculated for  $\text{YbD}_2$  and  $\text{YbH}_2$  by the *EDINP* program.  $R_S$  refers to *R* factors calculated after exclusion of the background and empty regions of scattering angles [see (3) in § 1 of the *Discussion*].  $R_B$  refers to *R* factors calculated for the full diffraction pattern [see (1) in § 1 of the *Discussion*].

	$\text{YbD}_2$ $\lambda = 1.43 \text{ \AA}$	$\text{YbD}_2$ $\lambda = 2.44 \text{ \AA}$	$\text{YbH}_2$ $\lambda = 1.43 \text{ \AA}$
$a_o$ (Å)	$5.875 \pm 0.002$		$5.900 \pm 0.002$
$b_o$ (Å)	$3.565 \pm 0.002$		$3.576 \pm 0.002$
$c_o$ (Å)	$6.781 \pm 0.002$		$6.776 \pm 0.002$
<i>x</i> (Yb)	$0.243 \pm 0.009$		
<i>y</i> (Yb)	$\frac{1}{4}$		
<i>z</i> (Yb)	$0.111 \pm 0.002$		
<i>x</i> (D')	$0.358 \pm 0.003$		
<i>y</i> (D')	$\frac{1}{4}$		
<i>z</i> (D')	$0.433 \pm 0.011$		
<i>x</i> (D'')	$-0.021 \pm 0.015$		
<i>y</i> (D'')	$\frac{1}{4}$		
<i>z</i> (D'')	$0.675 \pm 0.003$		
$R_S$ (%)	11.9	16.3	33
$R_B$ (%)	6	11	4

The large incoherent scattering from hydrogen caused a background and profile intensity variation in the  $\text{YbH}_2$  data which could not be corrected for in a reliable way. A structure refinement of the positional parameters of  $\text{YbH}_2$  was therefore not attempted and the data were only used to establish the consistency between the  $\text{YbH}_2$  and  $\text{YbD}_2$  structures with satisfactory confidence. The *R* factors from the  $\text{YbH}_2$  data obtained by use of the positional and thermal parameters inferred from the  $\text{YbD}_2$  refinements are quoted in Table 1.

The space group *Pnma* ( $D_{2h}^{16}$ ) has eight general positions [8(*d*)] which reduce to the four special positions [4(*c*)] in the proposed  $\text{CaH}_2$  structure because  $y = \frac{1}{4}$  for all atoms. The data were refined using the nuclear scattering amplitudes given by Koester (1977) [ $b(\text{Yb}) = 12.62$ ,  $b(\text{D}) = 6.67$ , and  $b(\text{H}) = -3.74$  fm] and isotropic temperature factors for all atoms. The lattice parameters (Table 1) were determined independently by X-ray Guinier techniques using thin layers of powder taken from the same batches of samples as used for the neutron diffraction measurements. These lattice parameters agree with the X-ray results of Korst & Warf (1956) and the X-ray analysis revealed that small amounts of cubic phase ( $a \sim 5.218 \text{ \AA}$ ) were present in both  $\text{YbD}_2$  and  $\text{YbH}_2$ . However, no trace of cubic-phase diffraction peaks was detectable in the neutron diffraction patterns. The incident neutron wavelengths were known with limited accuracy and were therefore adjusted to the values

(1.427 and 2.439 Å) that made the lattice parameters of  $\text{YbD}_2$ , determined from the neutron diffraction data equal to the X-ray lattice parameters.

In the refinement of  $\text{YbD}_2$ , we used the X-ray lattice parameters listed in Table 1 and, as starting values in the structure refinement, the positional parameters for  $\text{CaH}_2$  (Bergsma & Loopstra, 1962). Both sets of room-temperature data ( $\lambda = 1.43$  or  $2.44$  Å) for  $\text{YbD}_2$  converged within ten iterations to a stable set of positional parameters. In the refinements, the lattice parameters and the positional parameters  $y$  ( $=\frac{1}{4}$ ) were fixed, while the scale factor, the half-width parameters, the zero-point error, and the positional parameters  $x$  and  $z$  were allowed to vary. At first, the individual temperature factors were allowed to vary and they converged to  $B(\text{Yb}) = 0.44 \pm 0.02 \text{ \AA}^2$  and  $B(\text{D}) = 1.5 \pm 0.5 \text{ \AA}^2$ . Within the accuracy of the data, the latter value agrees with the value of  $B(\text{D}) = 1.14 \text{ \AA}^2$  inferred from the root-mean-square displacement  $\sqrt{\langle u^2 \rangle} = 0.17 \text{ \AA}$  of hydrogen in  $\text{CaH}_2$  deduced from the inelastic neutron scattering study of Bergsma & Goedkoop (1961). A test refinement using  $B(\text{D}) = 1.14 \text{ \AA}^2$  had insignificant effect on  $B(\text{Yb})$  and the positional parameters. Therefore, as we consider powder diffraction an unreliable tool for determining individual temperature factors, we fixed the individual  $B$  values at  $B(\text{Yb}) = 0.44$ ,  $B(\text{D}) = 1.5$  and  $B(\text{H}) = 3.0 \text{ \AA}^2$ . An estimated background, shown as the dotted lines in Figs. 1 and 2, was subtracted before the refinement. As a check of the estimated background level and the influence of possible weak absorption, the background level and an overall temperature factor ( $B$ ) were allowed to vary.  $B$  rapidly converged from 0.2 to less than  $0.01 \text{ \AA}^2$  and the background level converged to the estimated value with negligible effect on the other free parameters. Hence, we conclude that the flat background is a reasonable choice and that the absorption, expressed in the terms of the overall  $B$  value, is weak. As a final test of the analysis, the positional parameters  $y$  for all three types of atoms were also allowed to vary. For the  $\text{YbD}_2$  data obtained with incident neutrons of wavelength 1.43 Å,  $y$  remained very close to  $\frac{1}{4}$  for all atoms with negligible effect on the other parameters and on the overall agreement between the observed and calculated diffraction patterns. For the  $\text{YbD}_2$  data obtained with incident neutrons of wavelength 2.44 Å,  $y(\text{Yb})$  remained very close to  $\frac{1}{4}$ , while  $y(\text{D}')$  increased and  $y(\text{D}'')$  decreased steadily with increasing number of iterations. These changes in  $y(\text{D}')$  and  $y(\text{D}'')$  caused only minor changes in the other parameters and did not improve the overall agreement between the observed and calculated spectra. Therefore, these changes are artificial and presumably reflect the fact that the diffraction pattern observed at 2.44 Å only includes reflections having small Miller indices. Hence, we conclude that within the accuracy of our powder diffraction data for  $\text{YbD}_2$ , the

positional parameter  $y = \frac{1}{4}$  is valid for all three types of atoms.

Apart from the  $R$  factors quoted in Table 1, another measure of the reliability of the refinement may be obtained by inspection of Figs. 1 and 2, which show the observed ( $\bullet$ ) and calculated ( $-$ ) profile intensities for  $\text{YbD}_2$ . The upper curves in Figs. 1 and 2 show (on the same scale) the differences between the observed and calculated profile intensities. The solid lines in the lower parts of Figs. 1 and 2 were calculated using the lattice constants and positional parameters listed in Table 1. The positional-parameter values quoted in Table 1 are mean values of the results of profile analyses of the observed data at 1.43 and 2.44 Å for  $\text{YbD}_2$ , using either all measured data points or every second data point. Each analysis was equivalent in the sense that we used the same fit parameters and start values of these parameters and kept the fixed parameters identical. The errors listed in Table 1 are *not* the errors calculated by the *EDINP* refinement program, but reflect the agreement between the fit-parameter values resulting from

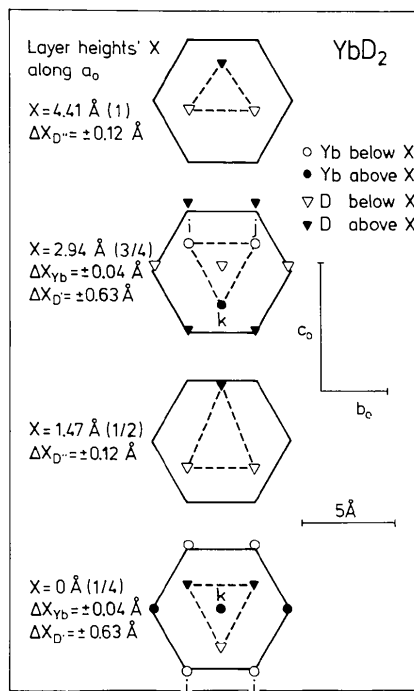


Fig. 3. Projection (all distances in Å) on the YZ plane of the four almost-hexagonal layers of Yb ( $\circ$ ,  $\bullet$ ) and D ( $\triangle$ ,  $\blacktriangle$ ) in orthorhombic  $\text{YbD}_2$  at ambient pressure and temperature. Filled signatures correspond to atoms above the drawing plane, unfilled signatures to atoms below the drawing plane. The regular hexagon shown has the same area as the irregular hexagon defined by the orthorhombic axes  $b_0 = 3.565$  and  $c_0 = 6.781 \text{ \AA}$ . The distances  $X$  refer to the layer heights along the  $X$  axis above the YZ plane, and the distances  $\Delta X_{\text{Yb}}$ ,  $\Delta X_{\text{D}'}$  and  $\Delta X_{\text{D}''}$  to shifts of the individual atoms above and below the corresponding  $X$  layer. The numbers in parentheses refer to relative lattice units along  $a_0$  ( $=5.875 \text{ \AA}$ ). The origin (for  $X$ ) has been shifted  $\frac{1}{4}a_0$  upwards compared to the unit-cell specifications given in Table 1.

the various analyses. The errors calculated by the *EDINP* refinement program are typically five times smaller than the errors listed in Table 1.

3. *The room-temperature structure of YbD<sub>2</sub>*. In YbD<sub>2</sub> all atoms are found to occupy the 4(c) special positions of the space group *Pnma* ( $D_{2h}^{16}$ ) and therefore the structure consists of two layers (see Fig. 4a), one at  $y = \frac{1}{4}$ , and one at  $y = \frac{3}{4}$  along the orthorhombic  $b_o$  axis. However, the structure may also be visualized as a distorted hexagonal structure (Bergsma & Loopstra, 1962), a fact which is essential for the understanding of the high-pressure structure (Staub Olsen *et al.*, 1981; see below). The distorted hexagonal structure is illustrated by Fig. 3, which shows the projections (drawn to scale using the parameters for YbD<sub>2</sub> listed in Table 1) on the *YZ* plane of atoms close to  $x = \frac{1}{4}$ ,  $x = \frac{1}{2}$ ,  $x = \frac{3}{4}$  and  $x = 1$  (0) of the orthorhombic  $a_o$  axis. In the four projections shown in Fig. 3, the filled signatures correspond to atoms above the plane of the drawing and the unfilled signatures to atoms below this plane. The distances  $\Delta X_{Yb}$ ,  $\Delta X_D$ , and  $\Delta X_{D'}$  refer to the shifts of the atoms (in Å) above and below the  $X$  value of a particular projection, where  $X$  (in Å) is measured from the lowest projection shown in Fig. 3 ( $x = \frac{1}{4}$ ). Hence, in the distorted hexagonal picture: the individual atoms wobble below and above the underlying hexagon. Because the wobbling ( $\Delta X_{Yb}$ ) of the Yb atoms at  $X_{Yb} \sim 0$  or  $X_{Yb} \sim \frac{1}{2}a_o$  is quite small, it follows from inspection of Fig. 3 that the Yb lattice is close to h.c.p. packing. However, at ambient temperature and pressure the wobbling of the deuterium atoms is considerable, especially for those closest to the Yb atoms.

#### *The high-pressure phase of YbD<sub>2</sub>*

In a recent experiment using synchrotron X-ray radiation from the electron storage ring DORIS at DESY-HASYLAB in Hamburg, Federal Republic of Germany, and the white-beam energy-dispersive technique (Buras, Gerward, Glazer, Hidaka & Staub Olsen, 1979), it was found (Staub Olsen *et al.*, 1981) that at ambient temperature, YbH<sub>2</sub> undergoes a first-order structural phase transition at  $\sim 15$  GPa from the orthorhombic to a hexagonal structure. The white-beam X-ray energy-dispersive technique allows an accurate unit-cell determination; however, because of possible pressure-induced texture in the sample, a determination of the positions of the Yb atoms based on the Bragg intensities is unreliable. In the pressure region close to the phase transition (14.3–17 GPa), the X-ray patterns of Staub Olsen *et al.* (1981) showed diffraction peaks from both the orthorhombic and the hexagonal structure and, hence, the lattice constants of both phases are known in the transition region. Staub Olsen *et al.* (1981) therefore took advantage of the previously mentioned fact (see Fig. 3) that the orthorhombic Yb lattice can be viewed as a distorted h.c.p.

lattice and were able to show that only slight movements of the Yb atoms are needed to convert the distorted h.c.p. cell of the orthorhombic phase to a h.c.p. cell. This is evident from a calculation of the nearest-neighbour ( $ij$ , Fig. 3) and next-nearest-neighbour ( $ik = jk$ , Fig. 3) Yb distances in the orthorhombic phase. Using the orthorhombic lattice parameters at 17 GPa ( $a_o = 5.183$ ,  $b_o = 3.450$ ,  $c_o = 6.317$  Å) (Staub Olsen *et al.*, 1981) and the Yb positions listed in Table 1,  $ij = 3.45 \pm 0.003$  Å and  $ik = jk = 3.60 \pm 0.003$  Å, which is close to the hexagonal axis ( $a_h = 3.595$  Å) determined from the X-ray data at 17 GPa. Hence, Staub Olsen *et al.* (1981) suggested that in the high-pressure hexagonal phase, the Yb lattice in YbH<sub>2</sub> is h.c.p. Assuming h.c.p. Yb positions in the high-pressure phase, is it then possible to infer the corresponding deuterium positions from those of the low-pressure structure? Let us consider Fig. 4, which shows projections on the *XZ* plane (in orthorhombic coordinates) of the two layers of Yb and D in YbD<sub>2</sub>. The projections are drawn to scale using the lattice constants (at ambient pressure) from Table 1 and those of Staub Olsen *et al.* (1981) at high pressure (17 GPa). To the left in Fig. 4 are shown the projections of the orthorhombic structure ( $D_{2h}^{16}$ ) found at ambient temperature and pressure. To the right are shown the projections of a postulated 'orthorhombic' cell at 17 GPa of dimensions  $a'_o = 4.80$ ,  $b'_o = 3.60$ , and  $c'_o = 6.23$  Å, in which all the nearest-neighbour Yb and nearest-neighbour D distances are equal. This structure is hexagonal  $D_{6h}^4$  ( $P6_3/mmc$ ) with  $c_h \equiv a'_o$  and  $a_h \equiv c'_o/\sqrt{3}$ , and corresponds to one of the four hexagonal supergroups of the space group  $D_{2h}^{16}$ . This structure, which has a d.h.c.p. (double hexagonal) arrangement of the deuterium atoms and an h.c.p. arrangement of Yb atoms, is shown in Fig. 5.

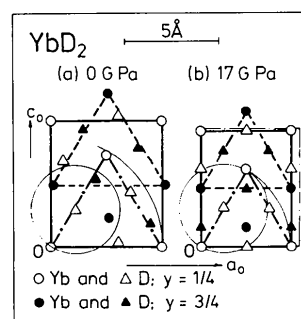


Fig. 4. Projections (all distances in Å) on the *XZ* plane of the two layers of Yb (O, ●) and D (Δ, ▲) in YbD<sub>2</sub>. Unfilled signatures correspond to layers having  $y = \frac{1}{4}$ , filled signatures to atoms having  $y = \frac{3}{4}$ . To the left are shown the projections of the orthorhombic structure  $D_{2h}^{16}$  (*Pnma*) at ambient temperature and pressure as determined by the present neutron diffraction study. To the right are shown the projections of the proposed hexagonal structure  $D_{6h}^4$  ( $P6_3/mmc$ ) at ambient temperature and pressures above 14.3 GPa (see text). The dot-dashed rectangle in the right-hand-side structure indicates the orthorhombic cell size at  $\sim 17$  GPa. The origins of both cells are marked by 0.

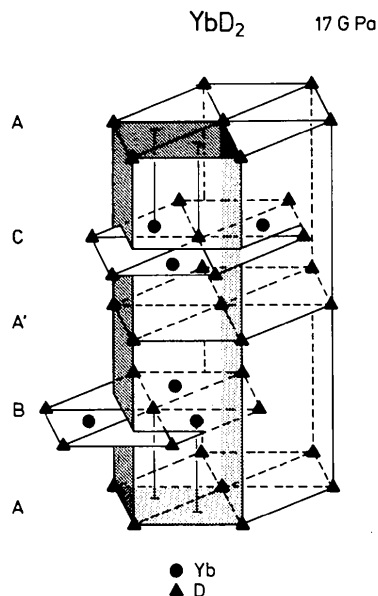


Fig. 5. Illustration of the proposed hexagonal structure ( $D_{6h}^2$ ) of  $\text{YbD}_2$  at ambient temperature and pressures above 14.3 GPa [Yb ( $\bullet$ ) and D ( $\blacktriangle$ )]. The deuterium atoms are arranged in a d.h.c.p. lattice [ $2(a)$  and  $2(d)$  positions] with stacking sequence  $ABA'C$ , and the Yb atoms in an h.c.p. lattice [ $2(c)$  positions] in the  $B$  and  $C$  layers of the deuterium lattice. Note that the drawing has been expanded along  $c$  for illustrative purposes; the  $c/a$  ratio of  $\text{YbD}_2$  equals 1.34 at 17 GPa and ambient temperature. When comparing Figs. 3 and 5,  $x = (\frac{1}{2})$  and  $(\frac{2}{3})$  correspond to  $B$  and  $C$  layers,  $x = (\frac{1}{3})$  and  $(0)$  or  $(1)$  correspond to  $A'$  and  $A$  layers.

### Conclusions

This neutron powder diffraction study of  $\text{YbD}_2$  and  $\text{YbH}_2$  has confirmed the previous assumption that at ambient temperature and pressure the crystal structure is  $D_{2h}^{16}$  ( $Pnma$ ) with all atoms in the  $4(c)$  positions. The lattice constants of both compounds are in agreement with those previously determined by X-ray experiments (Korst & Warf, 1956; Warf & Hardcastle, 1966; Staun Olsen *et al.*, 1981). The

positional parameters of the Yb atoms were found to agree with those reported for  $\text{CaD}_2$  (Bergsma & Loopstra, 1962). The deuterium positions in  $\text{YbD}_2$  (and  $\text{YbH}_2$ ) determined by powder profile analysis of our data are more accurate but in reasonable agreement with those estimated for  $\text{CaD}_2$  (Bergsma & Loopstra, 1962) giving nearest-in-plane ( $y = \frac{1}{4}$  or  $\frac{3}{4}$ ) Yb–D distances of 2.21, 2.31 and 2.37 Å, and nearest-out-of-plane distances of 2.25, 2.52 and 2.57 Å.

By inference from the structure of  $\text{YbD}_2$  at ambient temperature and pressure, we suggest that the room-temperature hexagonal structure observed in  $\text{YbH}_2$  at pressures above  $\sim 14.3$  GPa (Staun Olsen *et al.*, 1981) is  $D_{6h}^4$  ( $P6_3/mmc$ ) with the metal atoms in  $2(c)$  positions and the hydrogen atoms in  $2(a)$  and  $2(d)$  positions.

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## Tetrasodium Divanadate, $\text{Na}_4[\text{V}_2\text{O}_7]$

BY KATSUO KATO AND ELI TAKAYAMA

National Institute for Research in Inorganic Materials, 1–1 Namiki, Sakura-mura, Niihari-gun, Ibaraki-ken 305, Japan

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**Abstract.**  $M_r = 305.84$ , monoclinic,  $C2/c$ ,  $a = 15.376$  (2),  $b = 5.7573$  (5),  $c = 32.564$  (2) Å,  $\beta = 95.08$  (1)°,  $V = 2871.3$  (4) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 2.830$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70930$  Å,  $\mu = 2.68$  mm<sup>-1</sup>,  $F(000) = 2336$ ,  $T = 298$  K. Final  $R = 0.050$  for 6949 unique observed reflections. One of the two independent  $\text{V}_2\text{O}_7$  groups has a nearly eclipsed conformation with a V–O–V angle of 149.4 (1)°.

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