THE SYMMETRY OF THE HYDROGEN SUBLATTICE IN YTTRIUM TRIHYDRIDE

Fedotov V.K.*, **Antonov V.E.**, **Bashkin I.O.**, **Hansen T.** (1), **I. Natkaniec I.** (2), **Zavaritskaya V.A.**
Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia
(1) Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France
(2) Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow District, Russia
* *Факс: 7 096 524 9701, E-mail: fedotov@issp.ac.ru*

Introduction

Powder neutron diffraction studies showed [1–3] that trihydride of yttrium is isostructural with HoH_3. The unit cell of HoH_3, space group $P\bar{3}c1$, is a $(\sqrt{3}\times\sqrt{3})R30°$ expansion of the hcp unit cell in the basal plane [4]. Two thirds of the H atoms occupy distorted tetrahedral *t* sites. The remaining one third of the H atoms occupy trigonal-like sites in or near the metal basal planes, referred to as *m* sites. The *m* sites can be considered as resulting from the vertical displacement of octahedral sites toward the metal-defined basal planes.

However, recent *ab initio* calculations demonstrated that significant features of the electronic band structure [5] and the vibrational spectrum [6,7] of YH_3 cannot be explained if its structural symmetry is $P\bar{3}c1$. Instead, two other structures, $P6_3cm$ and $P6_3$, were proposed [6,7]. These new "broken symmetry" structures allow a better explanation of the results of INS [8,9] and also of NMR [10,11], Raman and IR [12,13] studies of YH_3. All three structures proposed for yttrium trihydride are characterised by correlated placements of H_t and H_m atoms leading to the 3-fold increase in the parent hcp unit cell.

Calculations [6,7] renewed the discussion on the crystal structure of YH_3. The present paper reports on the results of a neutron diffraction (ND) and inelastic neutron scattering (INS) investigation of YH_3 and YD_3 aimed at answering two questions:

- To what extent can the method of powder neutron diffraction discern the new "broken symmetry" structures $P6_3cm$ and $P6_3$ from the HoH_3-type $P\bar{3}c1$ structure;
- Is there a way to reconcile the results of ND studies with the requirements to the symmetry of the YH_3 structure following from the data of INS, NMR and some other experiments.

Results and discussion

Powdered samples of YH_3 and YD_3 were studied at 95 K by neutron diffraction with good statistics using the high-luminosity D20 diffractometer at ILL, Grenoble. The YH_3 sample was also investigated by INS at 20 K in the range of neutron energy transfers 4–300 meV using the NERA-PR time-of-flight neutron spectrometer at JINR, Dubna.

Fig. 1 shows the neutron diffraction pattern of YD_3 (dots) superimposed on its profile fit for the $P6_3$ structure (solid curve) and also three thin solid curves representing differences between the experimental spectrum and profile fits calculated with the structure parameters listed in Table 1.

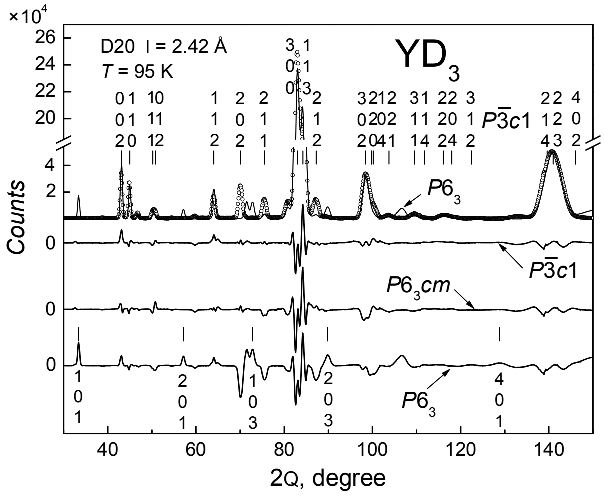

Fig. 1. The powder ND pattern of YD_3 (dots) and results of its Rietveld analysis (solid lines). The refined values of structural parameters are listed in Table 1. The Miller indices of reflections of the $P\bar{3}c1$ structure are shown in the upper part of the figure; those of additional reflections of the $P6_3$ structure in its bottom part.

As one can see from Fig. 1, the $P6_3$ structure is qualitatively inapplicable to modelling the ND pattern since it gives a series of rather intense additional lines (101), (201), (103), etc., missing in experiment. Modelling with the $P6_3cm$ structure does not contradict the experimental data, but the resulting fit is noticeably worse than in the case of the $P\bar{3}c1$ structure. Thus, in agreement with Refs. 1–3, our investigation shows that neutron diffraction only allows for the HoH_3 type structure of YH_3.Table 1. Refined positions (*xyz*) of atoms in YH_3 modelled with the $P\bar{3}c1$, $P6_3$ and $P6_3cm$ structure, and displacements (Δ_{xyz}) of these positions in the $P6_3$ and $P6_3cm$ structures relative to those in the $P\bar{3}c1$ structure.

	$P\bar{3}c1$	$P6_3$		$P6_3cm$	
	“0”	*xyz*	Δ_{xyz}	*xyz*	Δ_{xyz}
Y		6*c*		6*c*	
x	6*f*	0.667	–	0.669	–
y	0.663	–0.003	–		–
z		0.250	–	0.250	–
$H_1(t)$		6*c*		6*c*	
x		0.345	0.003	0.306	0.042
y	12*g*	–0.015	0.040		0.025
z	0.348	0.093	–	0.091	–
$H_1(t)$	0.025	6*c*		6*c*	
x	0.093	–0.308	0.040	–0.354	
y		–0.042	–0.017		–0.006 0.025
z		–0.093	–	–0.092	
$H_1(m)$		2*a*		2*a*	
x	2*a*		–		–
y			–		–
z		–0.316	0.066	0.324	0.074
$H_2(m)$		2*b*			
x			–		
y	4*d*		–	4*b*	
z		0.184	0.003		–
$H_3(m)$		2b			–
x	0.181		–	0.200	0.019
y			–		
z		–0.216	0.035		

On the other hand, *ab initio* calculations [6,7] show that YH_3 with the HoH_3 structure must be unstable and the “soft mode” moves in-plane H_m atoms out of the Y-defined planes. This is exactly how the broken symmetry structures are formed (see Table 1).

The discrepancy can be eliminated by assuming that the local symmetry of hydrogen arrangements in YH_3 is lower than the long-range $P\bar{3}c1$ symmetry determined by such methods as neutron diffraction. The occurrence of large hydrogen displacements correlated on a short-range scale is consistent with the available neutron diffraction data and explains the enormously large values of the Debye-Waller factors calculated for hydrogen atoms arranged in the $P\bar{3}c1$ structure.

This also explains why the properties of YH_3 measured by NMR [10,11] and INS [8,9], Raman and IR [12,13] spectroscopy are better described with the $P6_3cm$ or $P6_3$ structure [6,7] than with the higher symmetry $P\bar{3}c1$ structure: as a matter of fact, those methods are mostly sensitive to the local environment of the scattering atom.

Moreover, the absence of long-range order in the hydrogen placements suggests that such properties as the hydrogen vibrational spectrum in YH3 should be better described by a certain mixture of the spectra calculated for various “broken symmetry” structures. This is illustrated in Fig. 2 where the average of the calculated P63cm and P63 spectra represent the experimental feature near 57 meV better than the P63 spectrum and the feature near 124 meV better than the P63cm spectrum.

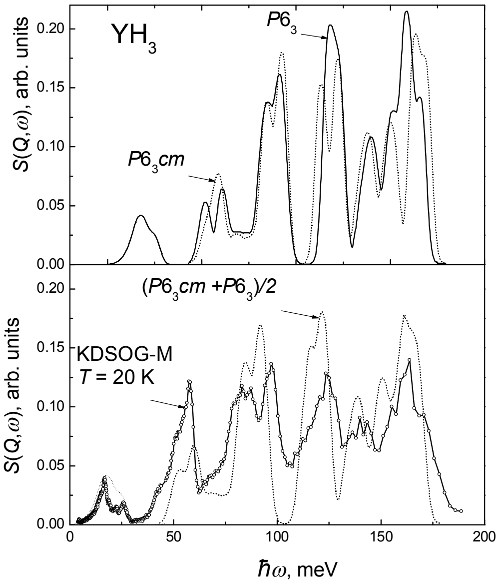

Fig. 2. The dynamical structure factor S(Q,ω) of YH3 powder at T = 20 K as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons (dots) and the total phonon densities of states (dashed lines) calculated [6,7] in the broken symmetry structures P63cm and P63 (upper part of the figure) and their average (bottom part).

References

1 N.F. Miron et al. Sov. Phys. Cryst. 1972;17:342.
2 T.J. Udovic et al. J. Phys. Chem. Sol. 1996;57:423.
3 T.J. Udovic et al. Phys. Rev B 1999;59:1852.
4 M. Mannsmann, W.E. Wallace, J. Phys. (Paris) 1964;25:454.
5 P.J. Kelly et al. Phys. Rev. Lett. 1997;78:1315.
6 P. van Gelderen et al. Phys. Rev. B 2001;63:100301.
7 P. Van Gelderen et al. Phys. Rev B 2003;68:094302.
8 T.J. Udovic et al., in: Hydrogen in Semiconductors and Metals, ed. by N.N. Nickel et al., MRS Symp. Proceed. No. 513 (MRS, Pittsburgh, 1998), p. 197.
9 T.J. Udovic et al. Phys. Rev. B 2000;61:12701.
10 J.J. Balbach et al. Phys. Rev. B 1998;58:14823
11 O.J. Zogal et al. Phys. Rev.B 2001;64:214110.
12 H. Kierey et al. Phys. Rev. B 2001;63:134109.
13 J. Schoenes et al. J. Alloys Comp. 2003; 356-357:211.