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Displacive ordering in the hydrogen sublattice of yttrium trihydride

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Abstract
Powder samples of YH_3 and YD_3 have been studied by neutron diffraction (ND) with a much higher statistical accuracy than obtained previously. The profile analysis of the obtained ND patterns confirmed the high-symmetry HoH_3-type structure of YH_3 and ruled out the 'broken symmetry' structures proposed recently to explain the insulating properties and lattice dynamics of this compound. At the same time, it was demonstrated that the HoH_3-type structure is only the structure of the mean lattice of YH_3. Large static displacements of H atoms from the symmetrical positions in this structure do occur, and ordering of these displacements on a short-range scale can settle the controversies between the crystal structure and physical properties of YH_3.

1. Introduction

Yttrium trihydride has been intensely studied after the discovery [1] of a reversible metal–insulator phase transition between the reflecting dihydride and optically transparent trihydride occurring in the Y–H system on varying the pressure of hydrogen gas. Not only did such a 'switchable mirror' seem promising for applications, but the trihydride offered a challenge to both theorists and experimentalists as its insulating properties and lattice dynamics appeared inconsistent with the crystal structure (see e.g. [2] for discussion and references).

In fact, powder neutron diffraction studies showed [3–5] that yttrium trihydride 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°

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expansion of the hexagonal unit cell of the hcp metal lattice in the basal plane [6]. Two thirds of the H atoms occupy distorted tetrahedral t-sites in the hcp metal lattice. 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.

On the other hand, *ab initio* calculations demonstrated that significant features of the electronic band structure [7–9] and of the vibrational spectrum [10, 2] 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 [10, 2]. With the positional parameters for hydrogen atoms properly chosen (optimized), these new 'broken symmetry' structures have lower total energy than the $P\bar{3}c1$ structure and allow a better explanation of the results of inelastic neutron scattering (INS) measurements [11, 12] and also of NMR [13, 14], Raman and IR [15, 16] studies of YH_3. All three structures proposed for yttrium trihydride are characterized by correlated placements of H_t and H_m atoms leading to a threefold increase in the parent hcp unit cell.

Calculations [10, 2] renewed the discussion of the crystal structure of YH_3. The present paper reports on the results of a neutron diffraction (ND) investigation of YH_3 and YD_3 that was 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 the ND studies with the requirements of the symmetry of the YH_3 structure arising from the data of the INS, NMR and some other experiments?

Compared to earlier ND studies of YH_3 and YD_3, the diffraction patterns were measured with a much higher statistical accuracy in order to get smooth background and to establish the absence or the presence and intensities of weak reflections reliably.

2. Sample preparation and experimental details

Yttrium trihydride and trideuteride were synthesized by gas-phase absorption in a Sieverts-type apparatus using 99.9 wt% Y metal and hydrogen or deuterium produced by thermal decomposition of TiH_2 or TiD_2, respectively. The compositions of the samples thus prepared were determined from the gained weight and proved to be close to YH_3 and YD_3 in agreement with [11]. A room-temperature x-ray diffraction examination (SIEMENS D-500 diffractometer, monochromated Cu $K\alpha_1$ radiation) showed that the samples were single-phase hcp compounds with the lattice parameters $a = 3.6712(5)$ Å, $c = 6.6068(8)$ Å, $c/a = 1.7996(4)$ for YH_3 and $a = 3.6712(5)$ Å, $c = 6.5968(8)$ Å, $c/a = 1.7969(4)$ for YD_3.

Powdered samples of YH_3 and YD_3, each weighing 5 g, were studied at 95 K by neutron diffraction using the high-luminosity D20 diffractometer at ILL, Grenoble. The diffraction patterns were recorded in steps of 0.1° in 2ϑ. The sample was placed in a cylindrical, thin-walled vanadium can. The background was determined in a separate empty-can measurement and subtracted from the measured diffraction patterns. The resulting neutron spectra were analysed using the Rietveld profile refinement technique implemented in the DBWS-9411 computer program [17].

3. Results and discussion

The experimental ND patterns of YH_3 and YD_3 are shown by dots in figure 1. To compare the goodness of the fits achievable while modelling the patterns with the $P\bar{3}c1$, $P6_3cm$ and

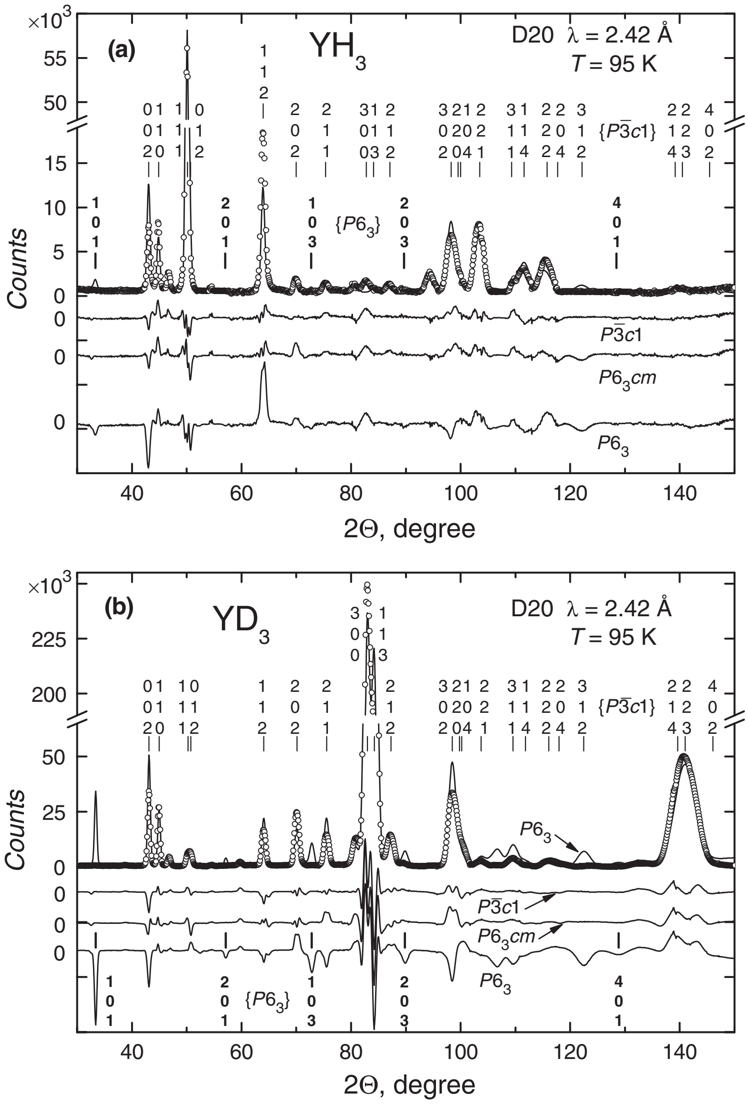

Figure 1. Powder neutron diffraction patterns of YH_3 (a) and YD_3 (b) measured at 95 K with the D20 diffractometer at ILL, Grenoble, using neutrons with a wavelength of $\lambda = 2.42$ Å (dots), and results of their Rietveld analysis (solid lines). A linear fit to the background is subtracted from the experimental spectra for better visualization of small diffraction features. Three lines at the bottom of each figure show the differences between the experimental spectrum and the spectra calculated assuming the indicated crystal structure of the sample. The calculated $P6_3$ spectra are also superimposed on the corresponding experimental spectra. The rows of vertical bars labelled $\{P\bar{3}c1\}$ in the upper part of each figure show the positions of reflections of the $P\bar{3}c1$ structure. The lower rows of bars labelled $\{P6_3\}$ show the positions of additional reflections characteristic of the $P6_3$ structure.

$P6_3$ structure, we used the values of positional parameters optimized in [2] for each of these structures to have the lowest total energy. These values are listed in table 1. The only variable parameters of the fitting procedure were the thermal factors, B_Y and B_H or B_D. Each factor was considered isotropic and independent of the site symmetry. The optimum values of the

Table 1. Optimized [2] positions (xyz) of atoms in the YH_3 unit cell 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.

		$P\bar{3}c1$			$P6_3$			$P6_3cm$		
		x	y	z	x	y	z	x	y	z
	Site		6f			6c			6c	
Y	xyz	0.663	0	1/4	0.667	−0.003	0.250	0.669	0	0.250
	Δ_{xyz}	—	—	—	0.004	−0.003	0	0.006	0	0
	Site		12g			6c			6c	
H_1 (t)	xyz	0.348	0.025	0.093	0.345	−0.015	0.093	0.306	0	0.091
	Δ_{xyz}	—	—	—	0.003	−0.040	0	−0.042	−0.025	−0.002
	Site					6c			6c	
H_2 (t)	xyz				−0.308	−0.042	−0.093	−0.354	0	−0.092
	Δ_{xyz}				0.040	−0.017	0	−0.006	0.025	0.001
	Site		2a			2a			2a	
H_1 (m)	xyz	0	0	1/4	0	0	−0.316	0	0	0.324
	Δ_{xyz}	—	—	—	0	0	−0.066	0	0	0.074
	Site		4d			2b			4b	
H_2 (m)	xyz	1/3	2/3	0.181	1/3	2/3	0.184	1/3	2/3	0.200
	Δ_{xyz}	—	—	—	0	0	0.003	0	0	0.019
	Site					2b				
H_3 (m)	xyz				1/3	2/3	−0.216			
	Δ_{xyz}				0	0	0.035			

Table 2. Thermal factors (B) and expected (R_{ex}) and obtained (R_p) profile factors resulting from the Rietveld analysis of the neutron diffraction data for YH_3 and YD_3 (figure 1) using the positional parameters from table 1.

				R_p (%)		
Phase	B_Y (Å^2)	B_H, B_D (Å^2)	R_{ex} (%)	$P\bar{3}c1$	$P6_3$	$P6_3cm$
YH_3	0.4	1.8	2.6	5.6	7.7	14.5
YD_3	0.4	1.5	1.1	5.8	9.6	22

thermal factors proved to be approximately the same for each of the analysed structures. These optimum B-values are presented in table 2 together with the values of the profile factors.

As one can see from figure 1 and table 2, the $P6_3$ structure is qualitatively inapplicable to modelling the ND patterns of both YH_3 and YD_3. Not only are the resulting R_p factors unreasonably large for both compounds, but a series of rather intense additional lines (101), (201), (103) and (203) appears in the pattern of YD_3, while these lines are obviously missing in the experimental data (see figure 1(b)).

Modelling with the $P6_3cm$ structure does not directly contradict the experimental data, but the resulting fit is noticeably worse than in the case of the $P\bar{3}c1$ structure. This fact is most clearly seen for YD_3, from comparison of the R_p factors equal to 9.6% and 5.8%, respectively (see table 2).

Varying the positional parameters and using different and reasonably anisotropic thermal factors for H or D atoms on different sites in the $P\bar{3}c1$, $P6_3$ and $P6_3cm$ structure did not result in a significant decrease in the R_p values compared to those indicated in table 2. The positional parameters of each structure proposed in [2] appeared optimum for fitting the experimental ND patterns. The analysis of the YH_3 and YD_3 patterns using these parameters therefore shows with certainty that neither of the $P6_3$ and $P6_3cm$ broken symmetry structures is consistent with the ND data. It is the HoH_3-type $P\bar{3}c1$ structure that agrees with the experimental data better than other structures, in accordance with earlier results [3–5].

On the other hand, calculations [2] show that YH_3 with the HoH_3-type structure is dynamically unstable and the 'soft mode' moves in-plane H_m atoms out of the Y-defined planes. This is exactly how the alternative, broken symmetry structures $P6_3cm$ and $P6_3$ are formed (see lines 'Δ_{xyz}' for the H_m atoms in table 1). The discrepancy can be eliminated by assuming that the short-range 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.

In view of the small changes in the powder neutron diffraction pattern caused by any proposed type of long-range ordering in the hydrogen sublattice of YH_3 and YD_3, there is no chance immediately to detect changes in the diffuse scattering resulting from the short-range ordering. Detecting such changes would be a difficult problem even with a good single crystal of YD_3, if it were ever grown. Nevertheless, some other experimental and theoretical findings suggest that a sort of displacive short-range ordering is very likely to occur in yttrium trihydride.

The occurrence of large static hydrogen displacements, either chaotic or correlated on a short-range scale, is consistent with the available neutron diffraction data and explains the enormously large values of the thermal factors calculated for hydrogen atoms in the $P\bar{3}c1$ structure (table 2). The assumption that $P\bar{3}c1$ is only the symmetry of the 'mean' lattice of YH_3 and YD_3 also agrees with the large values of the R_p/R_{ex} ratio reaching as much as $5.8/1.1$ for YD_3 (table 2). The problem of the too large R_p and B_D values concomitant with modelling an ND pattern of YD_3 with the $P\bar{3}c1$ structure was earlier encountered in [4] and it was partly solved by allowing a 'fractional disorder' in the occupancy of the two non-equivalent m-sites by deuterium atoms. Further NMR study of YD_3 showed that D atoms on t-sites also 'sit in a distribution of local environments' [13]. The displacements of both D_m and D_t atoms were considered chaotic [4, 13], but any short-range ordering of those displacements did not contradict the experiment data either.

Meanwhile, the occurrence of a short-range order in the static hydrogen displacements from symmetrical positions in the $P\bar{3}c1$ structure can explain why the properties of YH_3 measured by NMR [13, 14] and INS [11, 12], Raman and IR [15, 16] spectroscopy are better described with the $P6_3cm$ or $P6_3$ structure than with the $P\bar{3}c1$ structure. As a matter of fact, all those methods are mostly sensitive to the local environment of the hydrogen atom, while the $P\bar{3}c1$ structure characterizes the more symmetrical mean lattice.

Moreover, the absence of the periodical structure corresponding to the lower short-range symmetry in the hydrogen placements suggests that such properties of YH_3 as the hydrogen vibrational spectrum should be better described by a certain mixture of the spectra calculated for various 'broken symmetry' periodical structures. This is illustrated in figure 2 where the average of the calculated $P6_3cm$ and $P6_3$ spectra represent the experimental feature near 57 meV better than the $P6_3$ spectrum and the feature near 124 meV better than the $P6_3cm$ spectrum.

Interestingly, calculations [2] showed that subtle changes in the placements of H atoms in the YH_3 structure led to drastic changes in the optical part ($\hbar\omega > 35$ meV) of the vibrational spectrum. At the same time, this part of the spectrum determined in the experiment (figure 2, [18]) is fine-structured and practically coincides with the spectrum of YH_3 from [11] measured at $\hbar\omega > 35$ meV. The occurrence of the well-resolved and well-reproducible fine structure in the H vibrational spectrum of YH_3 therefore implies a rather high degree of order in the hydrogen sublattice of this compound, since the spectrum would be smoothed and smeared if the displacements of H atoms were chaotic.

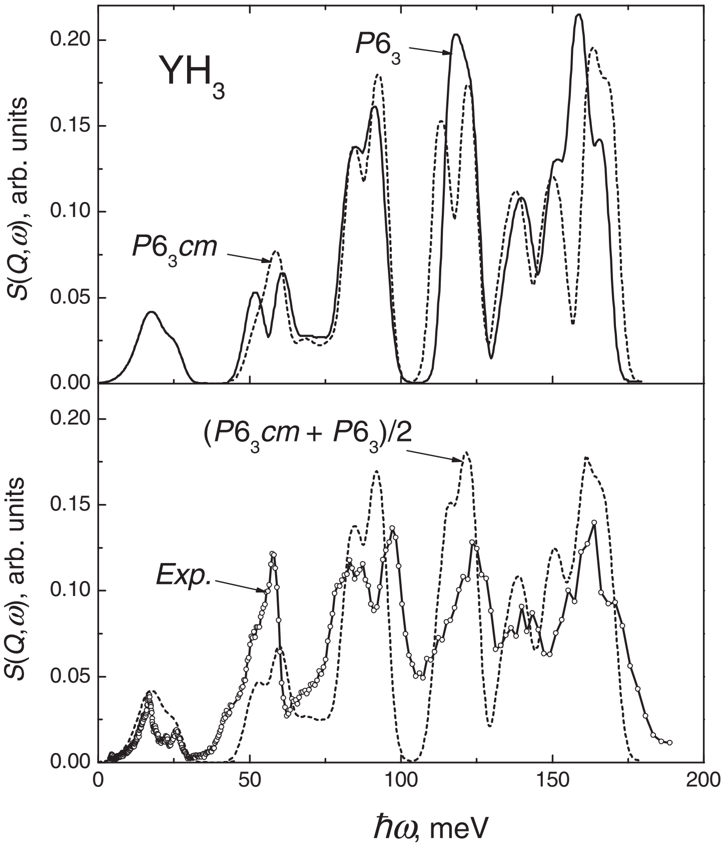

Figure 2. The one-phonon inelastic neutron scattering spectrum $S(Q, \omega)$ of YH$_3$ powder at 20 K [18] (dots, bottom part of the figure) and the total phonon densities of states (lines) calculated in the broken symmetry structures $P6_3cm$ and $P6_3$ [2] (upper part of the figure) and their average (bottom part). The YH$_3$ sample studied by ND in the present paper was the same as in [18].

This also suggests that the calculated $P6_3cm$ and $P6_3$ structures [2] reflect significant features of the short-range ordering in YH$_3$. Note in this connection that calculations [2] were carried out for relatively small supercells containing 192 atoms and therefore gave optimized parameters for the clusters rather than periodic structures.

As seen from table 1, the large displacements of H$_\mathrm{m}$ atoms in the $P6_3cm$ or $P6_3$ structures relative to their positions in the $P\bar{3}c1$ structure are accompanied by large displacements of H$_\mathrm{t}$ atoms. As long as the $P6_3cm$ or $P6_3$ structure represents the arrangement of hydrogen in YH$_3$, the displacements of H$_\mathrm{m}$ and H$_\mathrm{t}$ atoms in this trihydride should therefore be correlated.

A similar short-range ordering of the hydrogen sublattice is likely to be inherent to many other trihydrides as well. Accurate powder neutron diffraction studies showed that trihydrides of heavy rare-earth metals (e.g., Tb, Dy, Ho, Er [11]) had the crystal structure of the HoH$_3$-type. The INS investigation carried out in the same work of [11] demonstrated that the spectra of optical H vibrations in all these trihydrides were very similar to the spectrum of YH$_3$. In the light of results of the present paper, one can speculate that the fine structure in the spectra of those rare-earth trihydrides was also due to the occurrence of large static displacements of H atoms correlated on a short-range scale, while the $P\bar{3}c1$ symmetry only referred to the mean lattice.

Moreover, the optical H spectra of LuH_3 [11] and ScH_3 [18] proved to be similar to that of YH_3, while the neutron diffraction patterns of those trihydrides showed no distinct signs of displacive ordering in the hydrogen sublattice and rather indicated the $P6_3/mmc$ symmetry of the crystal structure [11, 18]. The $P6_3/mmc$ symmetry is higher than $P\bar{3}c1$ and trihydrides of Lu and Sc have the smallest lattice parameters among trihydrides of the group III metals. This suggests an increase in the symmetry of the mean lattice of such trihydrides with decreasing atomic volume, the short-range order of the hydrogen sublattice remaining largely the same.

4. Conclusions

The conflict between the $P\bar{3}c1$ structure of yttrium trihydride and some properties of this compound that are inconsistent with the high symmetry of the $P\bar{3}c1$ structure finds a non-contradictory solution under the assumption that (i) $P\bar{3}c1$ is the symmetry of the mean lattice of YH_3; (ii) the structure of YH_3 is characterized by large static displacements of H atoms from symmetrical m- and t-positions of the $P\bar{3}c1$ structure and these displacements are correlated on a short-range scale. The origin of the conflict was that the method of neutron diffraction used to determine the crystal structure was mostly sensitive to the averaged, long-range symmetry of the YH_3 (or YD_3) samples, while other their properties were measured by such techniques as NMR and INS, optical and IR spectroscopy that were mostly sensitive to the less-symmetrical local environments of hydrogen (or deuterium) atoms.

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