© by Oldenbourg Wissenschaftsverlag, München

The nature of deuterium arrangements in YD₃ and other rare-earth trideuterides

Terrence J. Udovic*, Qingzhen Huang, Antonio Santoro and John J. Rush

NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, MS 6102, Gaithersburg, Maryland 20899-6102, USA

Received June 4, 2008; accepted September 30, 2008

Centrosymmetric structure / Neutron powder diffraction / Neutron vibrational spectroscopy / Noncentrosymmetric structure / Rare-earth deuterides / Twinning

Abstract. The efficacy of different structural models for describing the observed neutron-powder-diffraction (NPD) measurements of bulk polycrystalline YD₃ as well as other hexagonal rare-earth (*i.e.*, Nd, Tb, Dy, Ho, Er, and Tm) trideuteride powders has been investigated via Rietveld refinement. Between the two possible structural configurations, centrosymmetric $P\overline{3}c1$ and noncentrosymmetric $P6_{3}cm$, the latter can be excluded due to very high correlations found between the positions of the D sites. Hence, the true "diffraction-average" structure for YD₃ and all other rare-earth deuterides studied is centrosymmetric (P3c1). This seems to contrast with the prior evidence from first-principles calculations and various spectroscopic probes suggesting that the true local symmetry is not P3c1, but rather, noncentrosymmetric. A possible way to reconcile the apparently conflicting conclusions from NPD and spectroscopic measurements is by assuming that the real structure is a twinned arrangement of nanosized, noncentrosymmetric configurations. For example, we demonstrate that the diffraction-average centrosymmetric P3c1 structure can result from a superposition of individual, noncentrosymmetric P3c1 twins. A comparison of neutron vibrational spectra for YH3 and YD3 confirms that both compounds share similar structural arrangements.

1. Introduction

As a prototypical example of rare-earth-hydride-based, optical-switching materials [1, 2], the yttrium-hydrogen system has been a subject of considerable interest for many years. Indeed, it has been shown [1] that hydrogenation of thin Y films on a variety of substrates leads to the formation of an optically-opaque, metallic β -YH_{2+z} cubic phase followed by the reversible transformation to an opticallytransparent, insulating γ -YH_{3- δ} hexagonal phase, a novel phenomenon with potential technological applications. The relationship between the insulating YH₃ structure and optical transparency has been the focus of numerous theoretical studies [3-14]. Such studies greatly benefit from the crystallographic details provided by experiment, which are key to a detailed understanding of the physics of these interesting materials.

The basic YH₃ structure is comprised of a hexagonalclose-packed yttrium metal lattice elongated in the *c* direction to accommodate the three H atoms per Y atom. Twothirds of the H atoms occupy distorted interstitial tetrahedral (t) sites and are identified as H_t atoms. The remaining one-third of the H atoms are displaced along the *c* axis from regular octahedral sites, instead occupying so-called metal (m) sites in the vicinity of the yttrium *ab* planes, and are identified as H_m atoms. The differences between the various proposed structures and their overall symmetries involve subtle differences in the correlated *c*-axis displacements of H_m atoms together with accommodating, mostly lateral (*ab*-planar) displacements of the surrounding H_t and Y atoms.

Previous neutron-powder-diffraction (NPD) studies of YD₃ [15–18] and most other hexagonal rare-earth trideuterides [19-23] suggested structures possessing P3c1 symmetry. Later, a related structure with P6₃cm symmetry was also reported to be in agreement with the diffraction data [22, 24], although no refinement details were provided. A more recent study [18] concluded that, although the P63cm structure did not directly contradict NPD data for YD₃ and YH₃, the resulting fit was noticeably worse than for the P3c1 structure. An alternative broken-symmetry structure was proposed for YH₃ films by Kelly et al. [6]. Such a structure was found by density functional calculations to be of slightly lower energy than the $P\overline{3}c1$ and $P6_{3}cm$ structures [25]. Neutron diffraction measurements of YD₃, for both bulk powders [16-18] and epitaxial films [24, 26], were found to be inconsistent with this lower-symmetry structure, since no diffraction peaks were observed corresponding to the expected additional reflections. Debye-Waller factor calculations [25] seemed to discount the possibility that these additional reflections in NPD experiments would be masked (i.e., drastically attenuated) by the large zero-point motions of the H_m atoms. Hence, for any possible agreement with neutron diffraction

^{*} Correspondence author (e-mail: udovic@nist.gov)

data, one must assume that an average higher symmetry exists by either an appropriate nanotwinning [17] or a quantum mechanical superposition of degenerate broken-symmetry structures [6, 7].

It was hoped that crystallographic studies of epitaxial thin-film samples [24] would shed some further light on the structural symmetry of bulk-powder samples, despite speculation [7] that strain effects in epitaxial films might stabilize a different structural symmetry compared with bulk YH₃. Unfortunately, epitaxial YD₃ and YH₃ films on crystalline substrates were not monocrystalline, but rather, were comprised of incoherent arrangements of azimuthally-aligned, (twinned or untwinned) submicron crystalline domains with the c axis also aligned perpendicular to the substrate surface [24, 27, 28]. These domains were separated by a network of [110]-oriented crystalline ridges. Thus, individual domains in such films behaved as aligned yet isolated crystallites with respect to a diffracting neutron beam, and the collective Bragg scattering from all crystallites equaled the sum of the Bragg scattering from each individual crystallite. The net effect was a diffraction pattern identical to that from a conventionally twinned hydride film with individual crystallite c axes directed either up or down with equal probability. Because of this peculiar morphology, the potential advantages of using single-crystal neutron diffraction to distinguish between the closely related $P6_3cm$ and $P\overline{3}c1$ symmetries disappeared, and both symmetries were found to be consistent with the domain-averaged diffraction data [24].

For the structurally analogous LaF₃ and PrF₃ systems [29–31], diffraction powder patterns were also in agreement with both $P\bar{3}c1$ and $P6_3cm$ symmetries. Yet, unlike YH₃, LaF₃ and PrF₃ were both available as twinned single crystals with unequal twin-domain volumes. From these types of samples, X-ray and neutron diffraction measurements were able to confirm that $P\bar{3}c1$, not $P6_3cm$, was the true structural symmetry [30, 31]. The authors concluded that there was a tendency toward twinning for the entire class of tysonite-like compounds. Although it should be acknowledged that the nature of interatomic bonding in YD₃ (and other rare-earth trideuterides) may not be completely analogous to that in LaF₃ and PrF₃, the similarities in structural details have suggested that twinning could also be an integral part of the YH₃ structure.

Different spectroscopic probes such as neutron vibrational spectroscopy (NVS) [18, 21, 22, 32-34], Raman spectroscopy [35, 36], infrared (IR) spectroscopy [35-37], and nuclear magnetic resonance (NMR) [38-40] have provided further clues concerning the local structural symmetry. Initial scrutiny of NV spectra for YH₃ and related hexagonal rare-earth trihydrides [19, 22, 32] led to the suggestion that the hydrogen vibrational lineshapes best reflected a local P3c1 symmetry, although a more rigorous modeling of the data was needed to confirm this. Later, van Gelderen et al. [25, 41] performed phonon density of states (DOS) calculations for YH₃ and concluded that the YH₃ NV spectrum is actually in better agreement with the lower-symmetry $P6_3cm$ and $P6_3$ structures than with the $P\bar{3}c1$ -symmetric structure. Due to the assumptions accompanying the theory, the comparison between calculation and experiment was fair at best for any particular structure.

In fact, the authors mentioned that the assumption of harmonic motion is expected to be the most severe approximation in these calculations, in particular when dealing with the H_m atoms in these structures with their large zeropoint motions. They implied that a more rigorous calculation would involve an *ab initio* molecular-dynamics simulation that incorporates the quantum character of the hydrogen atoms (albeit an overly demanding computation).

Polarization-resolved Raman measurements of YH₃ and YD₃ epitaxial films on CaF₂ substrates were made by Kierey *et al.* [35, 36] in conjunction with factor group analyses and the calculation of angular-dependent intensity patterns for all suggested crystal structures. Neither the number of observed A_1 modes nor the measured angular intensity pattern was compatible with $P\bar{3}c1$ symmetry. Rather, the coincidence of certain lines in Raman and IR spectra as well as the appearance of new Raman lines at different inclination angles were suggestive of a noncentrosymmetric symmetry such as $P6_3cm$ or $P6_3$.

Deuterium NMR data [38] for YD₃ suggested that the approximate 1:1:1 intensity ratio found for different localsymmetry D sites in the structure was more in accord with $P6_3cm$ symmetry, which possesses two inequivalent D_t sites of equal population, in contrast to the reported P3c1 structural model [16], which possesses only one D_t site. If the different types of D_m atoms are assumed to be indistinguishable with respect to their NMR patterns (a hypothesis that has been suggested by van Gelderen et al. [25] based on D_m quantum averaging), then $P6_3cm$ (or even $P6_3$) symmetry could indeed result in a 1:1:1 intensity ratio. A modified $P\bar{3}c1$ structure with a splitting of its single D_t site into two inequivalent sites would be required to be consistent with the NMR data. Subsequently, first-principles calculations by Zogał et al. [40] of the deuterium electric-field gradients (EFG's) associated with P3c1 and P63cm symmetries indicated much better agreement for $P6_3cm$ than for P3c1 between calculated EFG values and those obtained experimentally by NMR. Wolf and Herzig [13, 14] extended this EFG analysis to include P63 symmetry and concluded that agreement was still better for $P6_3cm$, although the results were found to be quite sensitive to the small crystallographic differences between the experimentally reported structures and total-energy optimized structures. Additional comparison [13] of calculated yttrium EFG's with data from ¹⁸¹Tadoped YH₃ in perturbed angular correlation measurements [42] indicated better agreement for both $P6_3cm$ and $P6_3$ structures than for the P3c1 structure.

Hence, the spectroscopic results from a variety of techniques point to a noncentrosymmetric symmetry such as $P6_{3}cm$ or $P6_{3}$, and not $P\overline{3}c1$, as the true local symmetry for YD₃ (and YH₃). With this in mind, in the present paper, we examine in detail the relative merits of the various models based on $P\overline{3}c1$, $P6_{3}cm$, and lower-symmetry nanotwinned structures for describing the observed diffraction data for YD₃ and other rare-earth trideuterides. We attempt to reconcile the average structural symmetry determined by NPD (which requires coherence lengths larger than tens of nanometers) with the local structural symmetry suggested by the various spectroscopic probes (which are sensitive to atomic arrangements on a more localized, subnanometer length scale). A comparison of YH₃ and YD₃ NV spectra suggests similar structural details for both isotopically labeled compounds.

2. Experimental details

Syntheses of the finely powdered RD₃ samples (R = Y, Nd, Tb, Dy, Ho, Er, and Tm) used in the NPD measurements have already been described elsewhere [16, 19, 21]. Neodymium was somewhat exceptional since it could only be deuterided to a stoichiometry of NdD_{2.96}. An additional YH₃ sample was synthesized in a similar fashion from Y (99.99 at.% metal purity, Johnson Matthey¹) and H₂ (Research Grade, 99.9995% purity, Matheson¹). Anhydrous LaF₃ (99.99% metal purity, Alfa Aesar¹) was obtained for structural comparisons. All sample masses were within the range of 5 g to 12 g. The samples were loaded in cylindrical V containers for NPD measurements. YH₃ was reloaded in a thin flat-plate Al container and YD₃ was kept in a V container for NVS measurements.

All neutron scattering measurements were performed at the NIST Center for Neutron Research. Powder patterns were collected using the BT-1 high-resolution powder diffractometer [43] with the Cu(311) monochromator at wavelengths ranging from 1.5391(1) Å to 1.5401(1) Å. The wavelength was calibrated for the various measurements using a NIST Si or Al₂O₃ standard reference material. The horizontal divergences were 15', 20', and 7' of arc for the inpile, monochromatic-beam, and diffracted-beam collimators, respectively. Data were collected every 0.05° over a 2θ angular range of 3 to 160°, although no Bragg features were evident below 20°. All refinements were carried out with the Rietveld method [44] using the program GSAS [45]. Neutron-scattering amplitudes used in the refinements were 7.75, 7.69, 7.38, 16.9, 8.01, 7.79, 7.07, 6.67, and -3.74 fm for Y, Nd, Tb, Dy, Ho, Er, Tm, D, and H, respectively [45]. Wavelength errors were not included in the standard deviations of the unit cells, *i.e.*, the precisions reported in this paper for the structural parameters reflect the quality of the data and the corresponding Rietveld refinement model, assuming a fixed neutron wavelength. NV spectra for YD₃ at 10 K and YH₃ at 295 K were measured with the BT-4 Filter Analyzer Neutron Spectrometer [46] using horizontal 20' collimations before and after the Cu(220) monochromator. Except for the YD₃ diffraction pattern and NV spectrum taken at 10 K (using a temperature-controlled, closed-cycle He refrigerator), all NPD patterns in the current paper were taken near room temperature.

3. Results and discussion

3.1 Conventional refinements

NPD patterns were measured for YD₃, YH₃, LaF₃, and RD₃ ($\mathbf{R} = \mathbf{Y}$, Nd, Tb, Dy, Ho, Er, and Tm). None of the patterns could be ascribed to a lower-symmetry *P*3 or *P*6₃ structural

model because the additional Bragg reflections expected from a lack of c-glide symmetry [17, 18] were typically not observed. Table 1 compares the structural parameters for YD₃ and LaF₃ refined from NPD data using both highersymmetry $P\bar{3}c1$ and $P\bar{6}_3cm$ structural models. For the $P\bar{3}c1$ structural model, which was identical to model II in Ref. 16, atomic positions were the following: R at 6*f* (*x*, 0, $\frac{1}{4}$), D(t) at 12g (x, y, z), D(m1) at 2a (0, 0, $\frac{1}{4}$), and D(m2) at 4d ($\frac{1}{3}$, $\frac{2}{3}$, z). For the P6₃cm structural model, atomic positions were the following: R at 6*c* (*x*, 0, *z*) with *z* fixed at $\frac{1}{4}$, D(t1) at 6c(x, 0, z), D(t2) at 6c(x, 0, z), D(m1) at 2a(0, 0, z), and D(m2) at 4b (1/3, 2/3, z). For both models, all occupancies were fixed at unity with an isotropic temperature factor assumed for R atoms and anisotropic temperature factors for D atoms (and F atoms for LaF₃). Anisotropic temperature factors were used as an indicator of the extent and direction of D (and F) positional disorder.

It should be noted that the relatively high incoherent scattering background for H compared to D meant that NPD data for YH₃ were not very definitive for establishing a favored structure, and results are not shown. Nonetheless, the NV spectra at 10 K for YH₃ (from Ref. 22) and YD₃ in Fig. 1 are more informative. The spectra display strong similarities, indicating that the two isotopically-labeled compounds share similar structural details. Moreover the YH₃ spectrum at 295 K shows no obvious sign of significant change in the phonon density of states upon temperature increase besides the expected peak attenuations due to increased Debye-Waller factors and the emergence of multiphonon downscattering sidebands [47].



Fig. 1. A comparison of NV spectra for YH₃ at 10 K (from Ref. [22]) and 295 K and YD₃ at 10 K. The instrumental energy resolutions (full width at half maximum, FWHM) are depicted by horizontal bars beneath the spectra. Vertical error bars represent \pm one standard deviation in intensity. Lines through the spectra are intended only as guides to the eye. The ratio of energy-loss scales for YH₃ and YD₃ is set to the harmonic value of $\sqrt{2}$ to compensate for the D/H mass ratio.

¹ Manufacturers are identified in order to provide complete identification of experimental conditions and such identification is not intended as a recommendation or endorsement by NIST.

Table 1. Comparison of structural parameters of YD₃ and LaF₃ refined from NPD data using different structural models: $P\bar{3}c1$ (*No.* 165) [atomic positions: R: 6*f* (*x*, 0, $\frac{1}{4}$); X(t): 12*g* (*x*, *y*, *z*); X(m1): 2*a* (0, 0, $\frac{1}{4}$); X(m2): 4*d* ($\frac{1}{3}$, $\frac{2}{3}$, *z*)] and P6₃*cm* (No. 185) [atomic positions: R: 6*c* (*x*, 0, *z*), with *z* fixed at ¹/4; X(t1): 6*c* (*x*, 0, *z*); X(m1): 2*a* (0, 0, *z*); X(m2): 4*b* ($\frac{1}{3}$, $\frac{2}{3}$, *z*)]. N.B.: depending on the compound, R represents Y or La atoms; X represents D or F atoms.

Atom	Parameter	YD ₃ (295 K)		YD ₃ (10 K)		LaF ₃ (295 K)	
		$P\bar{3}c1$	$P6_3 cm^a$	$P\bar{3}c1$	$P6_3cm^a$	$P\bar{3}c1$	$P6_3 cm^b$
	a(Å)	6.3440(2)	6.3441(2)	6.3316(1)	6.3301(1)	7.1907(1)	7.1907(1)
	$c(\text{\AA})$	6.5997(3)	6.5998(2)	6.5905(1)	6.5889(1)	7.3531(1)	7.3531(1)
	$V(Å^3)$	230.03(2)	230.04(2)	228.81(1)	228.64(1)	329.26(1)	329.27(1)
R	x	0.6636(7)	0.6717(8)	0.6626(6)	0.6715(7)	0.6596(2)	0.6742(2)
	$B(Å^2)$	0.34(2)	0.34(2)	0.02(2)	0.02(2)	0.60(1)	0.62(1)
X(t), <i>X</i> (t1)	x	0.3520(5)	0.3055(8)	0.3534(4)	0.3015(6)	0.3655(2)	0.2839(4)
	у	0.0321(3)		0.0326(2)		0.0537(1)	
	z	0.0903(2)	0.090(1)	0.0905(2)	0.0879(9)	0.0813(1)	0.0811(5)
	B(Å ²)						
	$B_{11}(\text{\AA}^2)$	1.9(1)	1.6(2)	1.27(7)	1.0(1)	2.08(5)	1.29(5)
	$B_{22}(Å^2)$	1.9(1)	0.4(1)	1.35(7)	0.9(1)	1.40(4)	1.23(9)
	$B_{33}(\text{\AA}^2)$	1.12(4)	1.4(2)	0.83(4)	1.1(1)	0.87(2)	1.05(9)
	$B_{12}(\text{\AA}^2)$	1.4(1)	0.21(7)	0.83(7)	0.43(6)	1.17(4)	0.62(4)
	$B_{13}(Å^2)$	0.1(1)	0.1(1)	0.3(1)	-0.1(1)	-0.24(5)	0.40(6)
	$B_{23}(\text{\AA}^2)$	-0.06(5)	0	0.04(4)	0	-0.20(2)	0
X(t2)	x		0.3601(7)		0.3571(6)		0.3746(4)
	z $\mathbf{D}(\overset{\wedge}{\lambda}^2)$		0.409(1)		0.4068(7)		0.4187(5)
	$\mathbf{B}(\mathbf{A})$ $\mathbf{B}_{\rm ev}(\mathbf{A}^2)$		1.0(1)		1 32(0)		1 58(4)
	$\mathbf{B}_{11}(\mathbf{A})$ $\mathbf{B}_{11}(\mathbf{A}^2)$		1.9(1)		1.52(9)		2.5(1)
	$\mathbf{B}_{22}(\mathbf{A}^2)$		2.7(2)		1.0(2)		0.67(8)
	$\mathbf{D}_{33}(\mathbf{A})$ $\mathbf{B}_{12}(\mathbf{A}^2)$		1.3(1)		0.3(1)		1.76(6)
	$B_{12}(A^2)$		0.2(1)		0.31(3)		-0.12(7)
	$B_{13}(A^2)$		0.2(1)		0.2(1)		0.12(7)
$\mathbf{V}(\mathbf{m}1)$	D ₂₃ (11)		0.317(2)		0.317(1)		0 3216(8)
A(IIII)	د B(Å ²)		0.317(2)		0.517(1)		0.3210(8)
	$B_{11}(Å^2)$	0.4(1)	1.3(2)	0.5(1)	0.7(1)	1.05(9)	0.64(7)
	$B_{22}(Å^2)$	0.4(1)	1.3(2)	0.5(1)	0.7(1)	1.05(9)	0.64(7)
	$B_{33}(\text{\AA}^2)$	6.6(4)	2.2(3)	6.9(4)	1.5(2)	4.0(2)	0.4(1)
	$B_{12}(\text{\AA}^2)$	0.22(7)	0.67(8)	0.26(7)	0.34(6)	0.53(4)	0.32(4)
X(m2)	z	0.1881(6)	0.207(1)	0.1877(5)	0.2034(8)	0.1873(3)	0.2167(6)
	$B(Å^2)$						
	$B_{11}(Å^2)$	0.84(8)	0.60(8)	0.60(6)	0.60(7)	0.78(4)	0.86(5)
	$B_{22}(\text{\AA}^2)$	0.84(8)	0.60(8)	0.60(6)	0.60(7)	0.78(4)	0.86(5)
	$B_{33}(\text{\AA}^2)$	2.73(9)	3.8(3)	1.35(6)	2.1(2)	1.78(7)	4.2(2)
	$B_{12}({\rm \AA}^2)$	0.42(4)	0.30(4)	0.30(3)	0.30(4)	0.39(2)	0.43(3)
	$R_p(\%)$	4.66	4.49	4.37	4.21	3.85	4.13
	$R_{wp}(\%)$	6.14	6.05	5.69	5.56	5.00	5.26
	χ^2	1.042	1.013	1.328	1.268	1.105	1.224

Constraints: All occupancies were fixed at unity.

a: Correlations are 91% between z[D(t1)] and z[D(t2)] and 84% between z[D(m1)] and z[D(m2)] at 295 K and 10 K.

b: Correlations are 74% between x[F(t1)] and x[F(t2)], 86% between z[F(t1)] and z[F(t2)], and 61% between z[F(m1)] and z[F(m2)].

Although the agreement parameters $(R_p, R_{wp}, \text{ and } \chi^2)$ for the $P\bar{3}c1$ and $P6_3cm$ structural models were comparable for all compounds studied (and previously led us to believe that both were viable descriptions of the YD₃ structure [22, 24]), a closer look at the refinement results for the latter model universally revealed the presence of very high correlations (in some cases >90%; *e.g.*, see YD₃ results in Table 1) between crystallographic site positions for D, both between D(t1) and D(t2) and between D(m1) and D(m2). This indicates that the true diffraction-average structure for all trideuterides studied is indeed centrosymmetric ($P\bar{3}c1$) rather than noncentrosymmetric

Atom	Position	Parameter	YD ₃ (295 K)	NdD ₃ ^{<i>a</i>} (300 K)	TbD ₃ (300 K)	DyD ₃ (295 K)	HoD ₃ (300 K)	ErD ₃ (295 K)	TmD ₃ (295 K)
		a(Å)	6.3440(2)	6.6426(5)	6.3928(2)	6.3442(2)	6.2991(2)	6.2577(2)	6.2169(2)
		c(Å)	6.5997(2)	6.8814(6)	6.6412(2)	6.5984(3)	6.5538(2)	6.5146(2)	6.4770(2)
		$V(Å^3)$	230.03(2)	262.96(5)	235.05(2)	230.00(2)	225.21(1)	220.92(2)	216.80(2)
R	6f(x, 0, 1/4)	X	0.6636(7)	0.662(1)	0.6650(7)	0.6683(7)	0.6630(7)	0.6671(9)	0.6630(8)
		$B(Å^2)$	0.34(2)	0.45(4)	0.32(1)	0.26(2)	0.29(2)	0.34(2)	0.46(2)
D(t)	12g(x, y, z)	x	0.3520(5)	0.347(1)	0.3539(4)	0.346(1)	0.3516(6)	0.3577(5)	0.3552(5)
		у	0.0321(3)	0.0236(6)	0.0296(2)	0.0329(9)	0.0317(3)	0.0307(4)	0.0320(3)
		z	0.0903(2)	0.0903(6)	0.0908(2)	0.0898(5)	0.0907(2)	0.0903(3)	0.0903(2)
		$B_{11}(\text{\AA}^2)$	1.9(1)	1.2(2)	1.65(8)	1.5(2)	2.10(9)	1.1(1)	2.05(9)
		$B_{22}(\text{\AA}^2)$	1.9(1)	1.3(3)	1.54(8)	3.2(3)	2.1(1)	1.5(1)	1.56(9)
		$B_{33}(\text{\AA}^2)$	1.12(4)	3.0(1)	2.00(3)	2.0(1)	1.34(4)	1.28(4)	1.48(4)
		$B_{12}(\text{\AA}^2)$	1.4(1)	0.7(2)	0.84(6)	1.8(2)	1.4(1)	0.38(6)	0.98(8)
		$B_{13}(Å^2)$	0.1(1)	-1.6(3)	0.3(1)	2.1(2)	-0.3(2)	-0.2(1)	-0.2(2)
		$B_{23}({\rm \AA}^2)$	-0.06(5)	-1.6(2)	-0.05(4)	0.5(2)	0.02(6)	0.0(1)	0.02(5)
D(m1)	$2a (0, 0, \frac{1}{4})$	$B_{11}(\text{\AA}^2)$	0.4(1)	0.0(2)	0.3(1)	0.0(4)	0.7(2)	0.7(2)	0.8(2)
		$B_{22}(Å^2)$	0.4(1)	0.0(2)	0.3(1)	0.0(4)	0.7(2)	0.7(2)	0.8(2)
		$B_{33}(\text{\AA}^2)$	6.6(4)	7.1	9.6(5)	17(3)	9.3(9)	7.2(5)	8.6(5)
		$B_{12}({\rm \AA}^2)$	0.22(7)	0.3(1)	0.16(6)	-0.1(2)	0.4(1)	0.34(8)	0.38(8)
D(m2)	4d (1/3, 2/3, z)	z	0.1881(6)	0.183(1)	0.1876(6)	0.195(2)	0.1893(8)	0.1886(7)	0.1900(7)
		$B_{11}(\text{\AA}^2)$	0.84(8)	1.2(2)	0.64(6)	1.0(2)	0.85(7)	0.39(7)	0.80(8)
		$B_{22}(Å^2)$	0.84(8)	1.2(2)	0.64(6)	1.0(2)	0.85(7)	0.39(7)	0.80(8)
		$B_{33}(\text{\AA}^2)$	2.73(9)	3.1	3.63(8)	2.9(4)	3.0(1)	2.9(1)	3.2(1)
		$\mathbf{B}_{12}(\mathrm{\AA}^2)$	0.42(4)	-0.2(1)	0.32(1)	0.5(1)	0.38(4)	0.20(3)	0.41(4)
		$R_p(\%)$	4.66	4.30	2.38	4.09	3.18	2.96	3.04
		$R_{wp}(\%)$	6.14	5.54	2.99	4.83	4.04	3.86	3.97
		χ^2	1.042	1.857	1.880	1.064	0.885	1.401	1.650

Table 2. The $P\bar{3}c1$ refinement results for different rare-earth trideuterides near room temperature.

Constraints: All occupancies were fixed at unity.

a: NdD₃ parameters were refined from a 43 mol% cubic NdD_{2.87}/57 mol% hexagonal NdD₃ mixed-phase sample.

Also, the magnitudes of B_{33} for D(m1) and D(m2) were fixed at reasonable values in order to attain convergence.

($P6_3cm$). This conclusion is consistent with the $P\overline{3}c1$ symmetry previously determined for the structurally analogous LaF₃ [30, 31], which also displayed high positional correlations between F sites in the $P6_3cm$ model refinement.

Table 2 extends the comparison of $P\bar{3}c1$ refinement results for YD₃ to those for the other trideuterides. (N.B.: For Nd, the resulting NdD_{2.96} sample contained a small amount of a cubic NdD_{2.87} phase, and NdD₃ structural parameters were determined from a cubic NdD_{2.87}/hexagonal NdD₃ mixed-phase refinement.) As for YD₃, $P\bar{3}c1$ model fits for RD₃ typically resulted in significant anisotropies in the temperature factors for all D atoms. The D_m atoms generally exhibited overly large components along the *c* direction. D_{m1} atoms generally possessed larger B₃₃ values than D_{m2} atoms (*e.g.*, for TbD₃ at 300 K, B₃₃ = 9.6(5) Å² and 3.63(8) Å² for D_{m1} and D_{m2} atoms, respectively).

3.2 Twinning model

The magnitude and anisotropy of the D temperature factors suggest a diffraction-average, D positional disorder, especially significant for the D_m atoms along the *c* direction. On a more local scale, this anisotropy is conceivably a manifestation of the twinning of lower-symmetry, nanosized crystallites to form the higher-symmetry $P\bar{3}c1$ diffraction-average structure. A similar behavior in the F temperature factors for LaF₃ suggests that a nanotwinning of lower-symmetry structures may also be occurring in this compound. If twinning of such nanocrystallites in all these related compounds does indeed occur, it is important to consider what lower-symmetry structures are capable of producing, via nanotwinning, the higher-symmetry $P\bar{3}c1$ structure observed by NPD.

The twin model discussed here focuses on the NPD data for YD_3 and is based on the following considerations:

The structure of YD₃ (as well as that of YH₃) is derived from the one refined in space group $P\bar{3}c1$ (shown in Table 1) by slightly shifting the D atoms as indicated (without perturbing the metal sublattice), as an example, in Fig. 2. As a consequence of these changes, the new structure becomes noncentrosymmetric, although the inversion center and the two-fold axes perpendicular to the three-fold axis at 1/4along *c* remain as elements of pseudo-symmetry.





Fig. 2. The positions of the D atoms (filled circles) in the $P\bar{3}c1$ structure refined using NPD data. Numbers reflect the approximate *c*-axis positions above the basal plane. Arrows indicate possible shifts of the atoms that would break the centrosymmetric configuration. The lengths of the arrows are exaggerated for clarity. (**a**) View showing D_t atoms only, with small vertical shifts omitted. (**b**) View showing D_m atoms only.

The space group of the structure must be a subgroup of $P\bar{3}c1$.

The structure is twinned so that the superposition of two individual twins results in an average configuration that is identical to the one refined from the NPD data.

The simplest model that satisfies the above conditions is a structure that has the symmetry of space group P3c1. (Although it seems that the closest to the model proposed by Kelly *et al.* [6] would be P321, this space group must be excluded from further consideration because it allows reflections of type $h\bar{h}0l$ with l = 2n + 1 (n = integer), which should appear in the NPD pattern but are not observed [17].)

Starting with the P3c1 model, we assume as a twin element one of the two-fold axes normal to the principal axis. Since our twinning is by merohedry, these axes are exactly parallel to the vectors defining the unit cell, and we may select the one along the *a*-axis. With this choice, the atomic sites of the twinned individual will have coordinates generated by the transformation:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{T} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{O}$$
(1)

where the subscripts T and O indicate the atomic coordinates generated by twinning and those of the original individual, respectively. Since the twin element is located at

Fig. 3. Superposition of D atom positions from the P3c1 model structure (filled circles) from Table 1 and its twin (open circles). Numbers reflect the approximate *c*-axis positions above the basal plane. (a) View showing D_t atoms only. Crosses indicate the atomic positions of the P3c1 structure. (b) View showing D_m atoms only.

1/4 above the zero level, 1/2 must be added to the *z*-coordinates obtained with the above transformation.

As mentioned previously, the initial coordinates of the atoms in space group P3c1 are selected by shifting the atoms from their P3c1 positions. The magnitude and direction of such shifts are related to the magnitude and direction indicated by that part of the thermal parameters that can be reasonably attributed to splittings of the atomic sites in the P3c1 structure described in Table 1. The twin operation, coupled with the superposition of two twinned individuals, introduces a two-fold element of symmetry whose effect is, in the final analysis, to split the atomic positions in any desired way, and in a direction and magnitude such that the average of their coordinates correspond to the location of the atomic sites listed in Table 1. The configuration of the D_t sites with the general position 6d 1 of space group P3c1 is illustrated in Fig. 3(a), where, for the sake of clarity, the size of the shifts is greatly exaggerated, and their vertical components are omitted. Figure 3(b) illustrates the configuration of the D_m sites with the positions 2a 3, 2b 3, and 2c 3. The superimposed positions from twinning of the P3c1 model in Figs. 3(a) and (b) mirror the magnitudes of the anisotropic temperature factors found for the refined $P\bar{3}c1$ model. A model of the P3c1 structure that satisfies all the requirements discussed previously is given in Table 3.

The assumption of a nanotwinned, noncentrosymmetric structure such as P3c1 reconciles the results from NPD with the more local spectroscopic probes. Raman spectro-

Table 3. Atomic coordinates of the proposed P3c1 structure for YD₃.

Atom	Position	Coordinates ^a
Y	6 <i>d</i> 1	x = 0.66 y = 0.00 z = 0.25
D(t1)	6 <i>d</i> 1	x1 = 0.33 y1 = 0.03 z1 = 0.08
D(t2)	6 <i>d</i> 1	$x2 = 2^{*}(Qx - Qy) - x1 + y1$ $y2 = y1 - 2^{*}Qy$ $z2 = 0.5 - 2^{*}Qz + z1$
D(m1)	2a 3	$ \begin{aligned} x &= 0 \\ y &= 0 \\ z &= 0.28 \end{aligned} $
D(m21)	2b 3	$x = \frac{1}{3}$ $y = \frac{2}{3}$ z = 0.18
D(m22)	2c 3	$x = \frac{2}{3}$ $y = \frac{1}{3}$ z = 0.30

a: All occupancies are unity. Qx, Qy, and Qz are the coordinates of the D_t atoms obtained in the 295 K refinement for YD₃ in Table 1.

scopy results [35, 36] are potentially in agreement with such a local symmetry, but a more detailed analysis is required to confirm this. Moreover, the presence of two inequivalent D_t sites in the P3c1 structure are in agreement with 1:1:1 D intensity ratios determined from the YD₃ NMR data [38].

It is important to say at this point that there is no direct evidence for the presence of twinning in the hexagonal rare-earth trihydrides. Therefore, our model represents only a possible explanation for the contradictory structural and spectroscopic results. We feel justified, however, in considering this model since the presence of twinning has already been demonstrated in the structurally similar LaF₃ and PrF₃ compounds. In LaF₃, for example, the incorrect $P6_{3}cm$ symmetry reported in Ref. 29 was attributed to the presence of a two-fold twin element coincident with the *c*-axis of the correct $P\overline{3}c1$ space group of the structure [30, 31]. Similar results were found for PrF₃ [30].

Although it can be adjusted appropriately to fit the observed NPD patterns for all samples, the nanotwinned P3c1 model is by no means unique. It may well be possible for other broken-symmetry D arrangements from other subgroups of P3c1 such as P3 to be appropriately nanotwinned to match the observed patterns. Despite the fact that previous attempts to consider a nanotwinned P3 model based on the theoretical low-energy structure of Kelly *et al.* [6] were less than successful [17], this does not necessarily mean that a different nanotwinned P3 model cannot be found to accurately describe the NPD data. Moreover, we cannot rule out the presence of minor fractions of other local configurations such as higher-symmetry $P6_3cm$ and P3c1 structures, as well as nanotwinned P6₃ composite structures (contrary to previous comments [17]) possessing pseudo- $P6_3cm$ symmetry. Such contributions, if indeed minor, would not greatly perturb the overall pseudo- $P\bar{3}c1$ symmetry observed by NPD. Indeed, for YH₃, the $P6_3$ (and P3) broken-symmetry structures were calculated to be more stable than $P6_3cm$ and $P\bar{3}c1$ structures but only by an amount on the order of tens of meV/Y₆H₁₈ unit cell. Since this is comparable to the zero-point energy of about 30 meV for the *c*-axis modes associated with the H_m atoms, van Gelderen *et al.* [41] speculated that the H_m atoms can sample a large part of configuration space, leading at times to the other higher-symmetry structures. The resulting "mixed" structure would most likely have a large band gap (as experimentally observed), since the more recent band-structure calculations [10–12] predict large gaps for both high- and low-symmetry configurations.

In order to judge the merits of such a mixed structure, it is important to revisit the results of van Gelderen et al. [25] concerning the calculated phonon DOS for YH₃ resulting from each of the three local symmetries considered: $P\bar{3}c1$, $P6_3cm$, and $P6_3$. The authors concluded that the calculated phonon DOS for $P6_3$ yields the best overall agreement with the observed NV spectrum for YH3 (shown in Fig. 1) above 100 meV, whereas it appears that the agreement with $P6_3cm$ is better below 100 meV. They observed that the overall agreement with P3c1 is much poorer. Despite the potential shortcomings of the calculations alluded to earlier in the Introduction, and after considering the effects of two-phonon processes, which can significantly affect the neutron spectral landscape [34, 48], Fedetov et al. [18] recently suggested that the observed NV spectrum for YH₃ is better described by a combination of the calculated phonon DOS spectra by van Gelderen et al. [25, 41] for the optimized P63cm- and P63-symmetric structures, implying that a mixture of these local configurations may indeed be present despite the observed, diffraction-average, $P\bar{3}c1$ -symmetric structure. In short, it is clear that the phonon calculations of van Gelderen et al. for any one structure do not satisfactorily reproduce the observed YH₃ NV spectrum, which suggests that a different set of local structural configurations and/or a more sophisticated computation is required. It would be of particular interest to calculate the relative stability and corresponding NV spectrum for the proposed P3c1 structure to see whether it would yield better agreement with experiment.

4. Conclusion

In summary, NPD data for bulk YD₃ and a variety of other hexagonal rare-earth trideuterides RD₃ (R = Nd, Tb, Dy, Ho, Er, and Tm) reasonably fit only a $P\bar{3}c1$ -symmetric structural model. Previous neutron diffraction data on epitaxial YD₃ films are also consistent with these NPD results. Yet, the combined results from the more local spectroscopic probes such as NVS, Raman and IR spectroscopies, and NMR are not consistent with a single local centrosymmetric $P\bar{3}c1$ structure. Instead, these results favor a local noncentrosymmetric structure. Since the neutron diffraction technique depends on a coherence length larger than tens of nanometers, it is possible to reconcile

the NPD and spectroscopic data by assuming that these rare-earth trideuterides are comprised of nanotwinned, noncentrosymmetric crystallites smaller than this length scale, yielding a "diffraction-average" $P\bar{3}c1$ symmetry. We have demonstrated that a twin-derived superposition of P3c1-symmetric nanostructures is one reasonable configuration leading to the observed $P\bar{3}c1$ pseudo-symmetry.

References

- Huiberts, J. N.; Griessen, R.; Rector, J. H.; Wijngaarden, R. J.; Dekker, J. P.; de Groot, D. G.; Koeman, N. J.: Yttrium and lanthanum hydride films with switchable optical properties. Nature **380** (1996) 231–234.
- [2] Griessen, R.; Huiberts, J. N.; Kremers, M.; van Gogh, A. T. M.; Koeman, N. J.; Dekker, J. P.; Notten, P. H. L.: Yttrium and lanthanum hydride films with switchable optical properties. J. Alloys Comp. 253/254 (1997) 44–50.
- [3] Wang, Y.; Chou, M. Y.: <u>Peierls distortion in hexagonal YH</u>₃. Phys. Rev. Lett. **71** (1993) 1226–1229.
- [4] Dekker, J. P.; van Ek, J.; Lodder, A.; Huiberts, J. N.: The gap in YH₃ and its lattice structure. J. Phys.: Condens. Matter 5 (1993) 4805–4816.
- [5] Wang, Y.; Chou, M. Y.: Structural and electronic properties of hexagonal yttrium trihydride. Phys. Rev. B51 (1995) 7500–7507.
- [6] Kelly, P. J.; Dekker, J. P.; Stumpf, R.: <u>Theoretical prediction of the structure of insulating YH</u>₃. Phys. Rev. Lett. **78** (1997) 1315-1318.
- [7] Kelly, P. J.; Dekker, J. P.; Stumpf, R.: Reply to Comment on "Theoretical prediction of the structure of insulating YH₃." Phys. Rev. Lett. **79** (1997) 2921-2921.
- [8] Eder, R.; Pen, H. F.; Sawatzky, G. A.: Kondo-lattice-like effects of hydrogen in transition metals. Phys. Rev. B56 (1997) 10115-10120.
- [9] Ng, K. K.; Zhang, F. C.; Anisimov, V. I.; Rice, T. M.: Theory for metal hydrides with switchable optical properties. Phys. Rev. B59 (1999) 5398–5413.
- [10] Miyake, T.; Aryasetiawan, F.; Kino, H.; Terakura, K.: GW quasiparticle band structure of YH₃. Phys. Rev. B61 (2000) 16491– 16496.
- [11] van Gelderen, P.; Bobbert, P. A.; Kelly, P. J.; Brocks, G.: <u>Para-meter-free quasiparticle calculations for YH</u>₃. Phys. Rev. Lett. 85 (2000) 2989–2992.
- [12] van Gelderen, P.; Bobbert, P. A.; Kelly, P. J.; Brocks, G.; Tolboom, R.: Parameter-free calculation of single-particle electronic excitations in YH₃. Phys. Rev. B66 (2002) 075104 (1–13).
- [13] Wolf, W.; Herzig, P.: First-principles investigations for YH₃ (YD₃): Energetics, electric-field gradients, and optical properties. Phys. Rev. B66 (2002) 224112 (1–9).
- [14] Wolf, W.; Herzig, P.: Energetics, electric-field gradients and optical properties of YH₃ (YD₃) by first-principles calculations. J. Alloys Comp. **356/357** (2003) 73–79.
- [15] Miron, N. F.; Shcherbak, V. I.; Bykov, V. N.; Levdik, V. A.: Neutron-diffraction study of yttrium trihydride. Sov. Phys. Crystallog. 17 (1972) 342–344. [Krystallografiya 17 (1972) 404–406].
- [16] Udovic, T. J.; Huang, Q.; Rush, J. J.: Characterization of the structure of YD₃ by neutron powder diffraction. J. Phys. Chem. Solids 57 (1996) 423–435.
- [17] Udovic, T. J.; Huang, Q.; Rush, J. J.: Comment on "Theoretical prediction of the structure of insulating YH₃." Phys. Rev. Lett. 79 (1997) 2920–2920.
- [18] Fedotov, V. K.; Antonov, V. E.; Bashkin, I. O.; Hansen, T.; Natkaniec, I.: Displacive ordering in the hydrogen sublattice of yttrium trihydride. J. Phys.: Condens. Matter 18 (2006) 1593–1599.
- [19] Udovic, T. J.; Huang, Q.; Rush, J. J.: A neutron-powder-diffraction study of the rare-earth deuteride two-phase region. J. Alloys Comp. 356/357 (2003) 41–44.
- [20] Renaudin, G.; Fischer, P.; Yvon, K.: Neodymium trihydride, NdH₃, with tysonite type structure. J. Alloys Comp. **313** (2000) L10-L14.
- [21] Udovic, T. J.; Huang, Q.; Lynn, J. W.; Erwin, R. W.; Rush, J. J.: Neutron-scattering study of the nuclear and magnetic struc-

ture of DyD_3 and associated vibrational and magnetic excitations. Phys. Rev. B **59** (1999) 11852–11858.

- [22] Udovic, T. J.; Huang, Q.; Rush, J. J: Neutron scattering studies of the structures and vibrational dynamics of the hcp rare-earth trihydrides. In: *Hydrogen in Semiconductors and Metals*, Mat. Res. Soc. Symp. Proc., Vol. **513** (Eds. N. N. Nickel, W. B. Jackson, R. C. Bowman, R. G. Leisure), p. 197-201. Materials Research Society 1998.
- [23] Mansmann, M.; Wallace, W. E.: The structure of HoD₃. J. Phys. (Paris) 25 (1964) 454–459.
- [24] Udovic, T. J.; Huang, Q.; Erwin, R. W.; Hjörvarsson, B.; Ward, R. C. C.: Structural symmetry of YD₃ epitaxial thin films. Phys. Rev. B 61 (2000) 12701–12704.
- [25] van Gelderen, P.; Kelly, P. J.; Brocks, G.: Structural and dynamical properties of YH₃. Phys. Rev. B68 (2003) 094302 (1–13).
- [26] Remhof, A.; Song, G.; Sutter, C.; Schreyer, A.; Siebrecht, R.; Zabel, H.; Güthoff, F.; Windgasse, J.: Hydrogen and deuterium in epitaxial Y(0001) films: Structural properties and isotope exchange. Phys. Rev. B59 (1999) 6689–6699.
- [27] Nagengast, D. G.; Kerssemakers, J. W. J.; van Gogh, A. T. M.; Dam, B.; Griessen, R.: Epitaxial switchable yttrium-hydride mirrors. Appl. Phys. Lett. **75** (1999) 1724–1726.
- [28] Kerssemakers, J. W. J.; van der Molen, S. J.; Koeman, N. J.; Günther, R.; Griessen, R.: Pixel switching of epitaxial Pd/YH_x/ CaF₂ switchable mirrors. Nature **406** (2000) 489–491.
- [29] Gregson, D.; Catlow, C. R. A.; Chadwick, A. V.; Lander, G. H.; Cormack, A. N.; Fender, B. E. F.: The structure of LaF₃ A single-crystal neutron-diffraction study at room-temperature. Acta Cryst. B**39** (1983) 687–691.
- [30] Maximov B.; Schulz, H.: Space group, crystal-structure and twinning of lanthanum trifluoride. Acta Cryst. B41 (1985) 88– 91.
- [31] Zalkin A.; Templeton, D. H.: Refinement of the trigonal crystalstructure of lanthanum trifluoride with neutron-diffraction data. Acta Cryst. B41 (1985) 91–93.
- [32] Rush, J. J.; Flotow, H. E.; Connor, D. W.; Thaper, C. L.: <u>Vibra-tional spectra of yttrium and uranium hydrides by the inelastic scattering of cold neutrons</u>. J. Chem. Phys. 45 (1966) 3817–3825.
- [33] Udovic, T. J.; Rush, J. J.; Huang, Q.; Anderson, I. S.: Neutron scattering studies of the structure and dynamics of rare-earth hydrides and deuterides. J. Alloys Comp. 253/254 (1997) 241–247.
- [34] Antonov, V. E.; Bashkin, I. O.; Fedetov, V. K.; Khasanov, S. S.; Hansen, T.; Ivanov, A. S.; Kolesnikov, A. I.; Natkaniec, I.: Crystal structure and lattice dynamics of high-pressure scandium trihydride. Phys. Rev. B73 (2006) 054107 (1–6).
- [35] Kierey, H.; Rode, M.; Jacob, A.; Borgschulte, A.; Schoenes, J.: Raman effect and structure of YH₃ and YD₃ thin epitaxial films. Phys. Rev. B63 (2001) 134109 (1–11).
- [36] Schoenes, J.; Borgschulte, A.; Carsteanu, A.M.; Kiery, H.; Rode, M.: Structure and bonding in YH_x as derived from elastic and inelastic light scattering. J. Alloys Comp. **356/357** (2003) 211-217.
- [37] Lee, M. W.; Shin, W. P.: Optical properties of the γ -phase yttrium trihydride YH_{3- δ}. J. Appl. Phys. **86** (1999) 6798-6802.
- [38] Balbach, J. J.; Conradi, M. S.; Hoffmann, M. M.; Udovic, T. J.; Adolphi, N. L.: Nuclear magnetic resonance evidence of disorder and motion in yttrium trideuteride. Phys. Rev. B58 (1998) 14823–14832.
- [39] Herzig, P.; Wolf, W.; Żogał, O. J.: Electric-field gradients in the yttrium deuterides YD_{2.25} and YD₃. Phys. Rev. B62 (2000) 7098-7102.
- [40] Żogał, O. J.; Wolf, W.; Herzig, P.; Vuorimäki, A. H.; Ylinen, E. E.; Vajda, P.: Probing the YD₃ structure by ²H NMR electric-field gradients: A comparison with first-principles calculations. Phys. Rev. B64 (2001) 214110 (1–7).
- [41] van Gelderen, P.; Kelly, P. J.; Brocks, G.: Phonon spectrum of YH₃: Evidence for a broken symmetry structure. Phys. Rev. B63 (2001) 100301(R) (1–4).
- [42] Forker, M.; Hütten, U.; Lieder, M.: Investigation of the electricfield gradient at the Y site in YH₃. Phys. Rev. B49 (1994) 8556–8560.
- [43] http://www.ncnr.nist.gov/instruments/bt1/
- [44] Rietveld, H. M.: A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 2 (1969) 65–71.

- [45] Larson, A. C.; Von Dreele, R. B.: General Structure Analysis System, University of California, 1985.
- [46] Udovic, T. J.; Neumann, D. A.; Leão, J.; Brown C. M.: Origin and removal of spurious background peaks in vibrational spectra measured by filter-analyzer neutron spectrometers. Nucl. Instr. and Meth. A 517 (2004) 189–201.
- [47] Udovic, T. J.; Rush, J. J.; Anderson, I. S.; Barnes, R. G.: Hydrogen vibrational modes and anisotropic potential in α-ScH_x. Phys. Rev. B41 (1990) 3460–3465.
- [48] Íñiguez, J.; Yildirim, T.; Udovic, T. J.; Sulic, M.; Jensen, C. M.: Multi-phonon scattering and Ti induced hydrogen dynamics in sodium alanate. Phys. Rev. B70 (2004) 060101(R) (1–4).