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Structural symmetry of YD_3 epitaxial thin films

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A thin-film laminated structure comprised of Pd(5 nm)/Nb(5 nm)/Y(500 nm)/Nb(5 nm) on α-$Al_2O_3(110)$ was synthesized by molecular beam epitaxy to yield a crystalline Y layer with the *c* axis oriented perpendicular to the growth plane. Neutron diffraction and topographical measurements of the epitaxial YD_3 layer formed after deuteriding the Y metal layer were consistent with a twinlike structure possessing $P6_3cm$ and/or $P\bar{3}c1$ symmetry.

It has been reported[1,2] that the hydrides of the rare-earth metals exhibit interesting optical properties with potentially important technological applications. In the original work of Huiberts *et al.*,[1] polycrystalline Y films were deposited under ultrahigh vacuum conditions onto Al_2O_3 substrates and capped with Pd overlayers. Hydrogenation of the Y films led first to the formation of an opaque, metallic β-YH_{2+z} cubic phase followed by the transformation to a transparent, insulating γ-$YH_{3-\delta}$ hexagonal phase. Transformations between the two phases and the concomitant optical switching were reversible, accomplished by the mere addition or removal of hydrogen gas. Besides Y, this optical switching behavior turned out to be fairly typical for all the lanthanide metals.[2,3] Although the YH_x films were markedly textured, they remained polycrystalline like the precursor metal film.

It has since been shown that epitaxial YH_x films can be synthesized via the hydriding of a monocrystalline Y film grown by molecular beam epitaxy on a sapphire substrate with a Nb-buffer layer[4,5] and more recently on $CaF_2(111)$.[6] Such epitaxial films allow for a more detailed characterization of the prevalent crystallographic structure, which may be important for understanding the physics behind the novel optical switching phenomenon. Moreover, it is of interest to compare the structural symmetry of epitaxial thin films with that of bulk powder samples. For example, there was some speculation by Kelly, Dekker, and Stumpf[7] that strain effects might stabilize a different structural symmetry for thin-film YH_3 compared to that for the bulk material. Previous neutron powder diffraction (NPD) studies of YD_3 (Refs. 8–10) and the majority of other hcp rare-earth trideuterides[11–13] have indicated a structure possessing $P\bar{3}c1$ symmetry with a $(\sqrt{3}\times\sqrt{3})R30°$ expanded unit cell in the basal plane. Two D atoms per Y atom occupy distorted tetrahedral sites and the remaining one D atom per Y atom occupies trigonal-like sites in or near the metal basal planes, referred to as *m* sites. Figure 1(a) depicts the wavelike arrangement (with respect to the metal planes) of the D_m atoms in the $P\bar{3}c1$ structure. This differs from the lower-symmetry $P3$ structure [see Fig. 1(c)] for YH_3 films proposed by Kelly, Dekker, and Stumpf,[14] which was determined by density functional calculations to be a lower-energy configuration compared to the

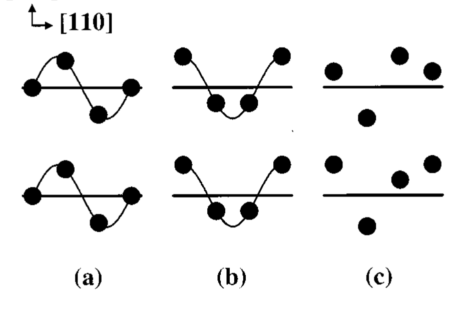

FIG. 1. The wavelike arrangements of the D_m atoms for YD_3 structures with (a) $P\bar{3}c1$, (b) $P6_3cm$, and (c) $P3$ symmetries. The metal planes are designated by the horizontal lines. The higher-symmetry D_m arrangements of the first two structures are more clearly delineated by the sinusoidal lines.

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$P\bar{3}c1$ structure. Subsequent neutron diffraction measurements of epitaxial YD_3 films by Remhof *et al.*[5] were found to be inconsistent with the $P\bar{3}$ structure, instead indicating general agreement with the $P\bar{3}c1$ structure found for powder samples.

Recently, we came to the realization, after investigating the possible structural symmetries associated with the analogous tysonitelike systems LaF_3 and PrF_3,[15–17] that our original NPD data[9] for YD_3 could be fit equally well assuming another structure possessing $P6_3cm$ rather than $P\bar{3}c1$ symmetry.[12] The $P6_3cm$ structure is similar to the $P\bar{3}c1$ structure, mainly differing by the subtle arrangements of the D atoms in the *m* sites [see Fig. 1(b)]. It cannot be easily distinguished from the $P\bar{3}c1$ structure by NPD measurements, since both structures yield similar powder patterns. Confusion between $P\bar{3}c1$ and $P6_3cm$ symmetries proved also to be the case for the analogous LaF_3 and PrF_3 systems.[15–17] X-ray and neutron diffraction measurements of twinned single crystals of LaF_3 and PrF_3 having unequal twin-domain volumes confirmed that $P\bar{3}c1$, not $P6_3cm$, was the true structural symmetry.[16,17] The authors concluded that the possibility of twinning is inherent in the whole class of tysonitelike compounds.

Following the rationale behind the trifluoride measurements, the present neutron diffraction measurements on an epitaxial YD_3 film were undertaken in a similar attempt to distinguish between the possible $P\bar{3}c1$ and $P6_3cm$ structures, a topic that was not addressed in the previous noteworthy work of Remhof *et al.*[5] In particular, we measured a variety of paired single-crystal reflections that are separated in **Q** space yet occur at the same Bragg scattering angle and contribute to the same powder peak for bulk YD_3. If one assumes that the YD_3 film is an untwinned monocrystalline sample, the relative structure factors of these related reflections will differ for $P\bar{3}c1$ and $P6_3cm$ structures and can therefore be used to corroborate a particular symmetry.

A monocrystalline Y metal film was synthesized by molecular beam epitaxy techniques described in detail previously,[18] similar to Remhof *et al.*[4] A 5-nm-thick bcc Nb(110) buffer layer was deposited onto a 20×22-mm hcp α-$Al_2O_3(110)$ substrate, followed by a 500-nm-thick hcp Y(001) layer. The Y layer was covered with an additional 5-nm-thick Nb(110) overlayer followed by a 5-nm fcc Pd(111) capping layer. The Nb overlayer enhances Pd layer growth, while the Pd capping layer facilitates D_2 dissociation during the deuteriding process. Moreover, both the Nb and the Pd layers protect the underlying Y layer from oxidation. X-ray diffraction confirmed that the Y layer was monocrystalline with the *c* axis perpendicular to the plane of the film and the $Y[1\bar{1}0]$ azimuthal axis parallel to the $Nb[\bar{1}10]$ axis, in agreement with earlier work.[5]

The initial deuteriding of the Y metal film was performed in ≈ 0.1MPa D_2 at 473 K and resulted in the formation of first the YD_{2+z} cubic phase and then the $YD_{3-\delta}$ hexagonal phase as evidenced by the transformation from optical opacity to optical transparency. Removal of gas-phase D_2 led to the transformation back to the stoichiometric (i.e., $z=0$) YD_2 cubic phase, since any excess D atoms above the dideuteride stoichiometry (i.e., $0<z\leqslant 0.08$) (Ref. 19) reside in the octahedral interstices and are only stabilized by a small yet nonzero D_2 vapor pressure at room temperature. Like the previous YH_x experiments,[1,4,5] such deuteride phase changes concomitant with the addition or removal of gas-phase D_2 were found to be reversible. For the YD_3 neutron diffraction experiments, the deuterided film was mounted in a thin-walled, vacuum-tight, tubular Al container equipped with a valve for both evacuation and D_2 gas treatment. The YD_3 film was stabilized in ≈ 0.1 MPa D_2 during the measurements.

TABLE I. Comparison of theoretical and measured squared-structure-factor (F^2) ratios for various related YD_3 reflections. Measured values are based on the assumption that the positive *c*-axis vector was perpendicular to and directed out of the surface of the film.

			Measured ratios	
F^2 ratios	$P\bar{3}c1$ (theory)	$P6_3$cm (theory)	In-plane	Growth axis
$F^2_{10\bar{2}}/F^2_{102}$	0.174	1	1.1(1)	1.0(1)
$F^2_{20\bar{2}}/F^2_{202}$	1.461	1	0.78(5)	0.79(6)
$F^2_{10\bar{4}}/F^2_{104}$	0.209	1	1.05(5)	0.83(5)
$F^2_{20\bar{4}}/F^2_{204}$	438	1	1.1(2)	

The neutron diffraction measurements were performed using the BT-9 triple-axis spectrometer at the NIST Center for Neutron Research with a pyrolytic graphite (002) monochromator at wavelengths of either 1.709 or 2.359 Å. The horizontal divergences were typically 40′, 24′, 24′, and 600′ of arc for the in-pile, monochromatic-beam, diffracted-beam, and analyzer collimators, respectively. All diffraction measurements were taken at room temperature ($\approx$295 K). In agreement with the x-ray and neutron diffraction data of Remhof *et al.*,[4,5] the present neutron diffraction data confirmed that structural coherence was maintained for the hcp YD_3 film, with the close-packed Y planes [i.e., $YD_3(001)$] remaining parallel to the sapphire substrate plane and the $YD_3[1\bar{1}0]$ azimuthal axis parallel to the $Nb[\bar{1}10]$ axis. Moreover, similar to the earlier results,[4,5] the initial transition from Y to YD_3 was accompanied by increased Bragg-peak widths, indicating some loss in the quality of crystallinity. Yet as previously observed, these widths, corresponding to a film mosaic of around 1°, did not change upon undergoing multiple transitions between YD_2 and YD_3. The *a* and *c* lattice constants for the YD_3 film were found to be 6.349(5) and 6.601(5) Å, respectively, in line with the YD_3 bulk values.[9]

Table I summarizes the diffraction results. Theoretical squared-structure-factor (F^2) ratios for $P\bar{3}c1$ symmetry were calculated from the structural parameters of the preferred disorder model of the NPD data in Ref. 9. In contrast, $P6_3cm$ symmetry requires that all ratios $F^2_{hk\bar{l}}/F^2_{hkl}=1$. The experimental F^2 values were determined from integrated Bragg-peak intensities and known Lorentz-factor corrections under the arbitrary assumption that the positive *c*-axis vector was directed *out of* (as opposed to *into*) the surface of the film. This distinction is important to consider for $P\bar{3}c1$ symmetry since the presence of a positive *c*-axis vector directed

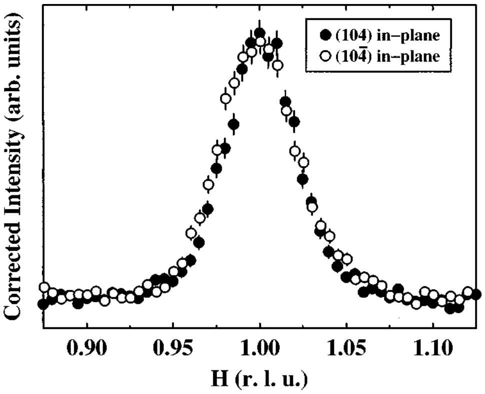

FIG. 2. A comparison of the (104) and (10$\bar{4}$) in-plane Bragg peaks corrected by their respective Lorentz factors. The integrated intensities are proportional to the squared structure factors F^2. The peak widths reflect a YD_3 film mosaic of ≈1°.

into the film would necessitate comparing the reciprocals of the measured F^2 ratios with the theoretical F^2 ratios. Having said this, it is obvious, nonetheless, that all related reflections measured (e.g., see Fig. 2) possess similar structure factors, which favors $P6_3cm$ over $P\bar{3}c1$ symmetry assuming the presence of an untwinned sample. Unfortunately, a lack of twinning in YD_3 films has not been firmly established. Rather, the twinned rare-earth trifluoride data give credence to the suggestion that a similar twinning may indeed be occurring in the structurally analogous YD_3 films. Moreover, topographical images obtained by scanning probe microscopy of similar yttrium-hydride films epitaxially grown on $CaF_2(111)$ substrates[6] have provided enlightening details of the surface microstructure. In particular, the surface of the YH_3 films appears to be comprised of small crystallites (submicron in size) azimuthally aligned with each other atop the $CaF_2(111)$ template and separated by a network of [110]-oriented ridges (≈4 nm in height and ≈100 nm in width). The ridges were interpreted as being due to material that was squeezed out of the surface as a result of in-plane thermal expansion differences of the substrate and film and in-plane expansion of the Y lattice during hydriding. We have observed similar topographical behavior for our samples using optical microscopy. Additional optical measurements for these and other epitaxial rare-earth hydride films on a variety of other substrates indicate that this topographical behavior is typical and not strongly dependent on the substrate. These results suggest that the individual crystallites in such films, although azimuthally aligned, are *incoherently* separated from each other by the ridges, and as such, will behave as aligned yet isolated crystallites with respect to the diffracting neutron beam. Thus, even if each individual crystallite were untwinned (which is also not at all obvious in light of the bulk YD_3 and rare-earth trifluoride data), the collective Bragg scattering resulting from all crystallites would equal the sum of the Bragg scattering from each individual crystallite. The net effect would be a diffraction pattern that is identical to that from a conventionally twinned single-crystal YD_3 film. Hence, the present data alone cannot confirm the intrinsic structural symmetry of an individual YD_3 crystallite. For an appropriately ''twinned'' (i.e., twinlike) sample (with the crystallite *c* axes pointing either up or down with equal probability), both $P6_3cm$ and $P\bar{3}c1$ symmetries would be consistent with the diffraction data, since such twinlike behavior would lead to unity F^2 ratios for all related reflections in Table I.

It should be noted that data from different spectroscopic techniques such as neutron vibrational spectroscopy (NVS) and nuclear magnetic resonance (NMR) (which are considered more localized probes) currently provide no consistent answer to the symmetry question. In particular, the H_m vibrational bands in YH_3 and related hcp rare-earth trihydrides as measured by NVS are believed to be most in agreement with a local $P\bar{3}c1$ symmetry,[12,20] although a more rigorous modeling of the data is needed to corroborate this assertion. In contrast, the deuterium NMR data[21] for YD_3 suggest that there are two inequivalent tetrahedral D sites, which is more in accord with $P6_3cm$ symmetry, although splitting the tetrahedral sites within the currently accepted $P\bar{3}c1$ structure into two distinct groups would yield a modified $P\bar{3}c1$ structure also in accord with the NMR data.

In agreement with the results of Remhof *et al.*[5] and the earlier powder diffraction studies,[8,9] no diffraction peaks were observed corresponding to the additional reflections expected for the P3 structure such as (203), (20$\bar{3}$), (303), and (30$\bar{3}$). [N.B., the absence of the (103) and (10$\bar{3}$) peaks could not be verified due to overlap with other unrelated scattering features.] Hence, for any possible agreement with the present thin-film data, one must assume that an average $P\bar{3}c1$ or $P6_3cm$ symmetry exists *for each crystallite* via appropriate microtwinning of the P3 structure. So far, similar microtwinned model fits of the earlier powder diffraction data have been found to be less than satisfactory.[8] Nonetheless, we are at present still attempting to reconcile the differences between experiment and theory by considering more detailed structural fits of the powder data based on the quantum-mechanical superposition of the different P3 broken-symmetry states proposed by Kelly, Dekker, and Stumpf,[7] which in theory could result in a ''quantum-averaged,'' $P\bar{3}c1$-symmetric structure.

In conclusion, taken alone, the neutron diffraction data for the epitaxial YD_3 film are consistent with either an untwinned structure with $P6_3cm$ symmetry or a twinned structure comprised of $P6_3cm$ and/or $P\bar{3}c1$ symmetry. Additional topographical data suggest that these types of films are actually comprised of azimuthally aligned YD_3 crystallites and that the neutron diffraction data is, in effect, a summation of the diffraction intensities from each crystallite. Hence, the diffraction data most likely represent a ''twinlike'' topographical structure with the individual crystallite *c* axes pointing either up or down with equal probability. This topographical arrangement precludes a definitive determination by this diffraction technique of the intrinsic YD_3 structure of an individual crystallite. Based on these results and those of Remhof *et al.*,[4,5] it is probable that the individual epitaxial-film and bulk YD_3 crystallites possess the same intrinsic structure. Yet, the results from bulk techniques have still not provided an unequivocal answer concerning YD_3 symmetry. Diffraction data on structurally analogous rare-earth trifluorides as well as neutron vibrational spectra of bulk YD_3 favor an intrinsic $P\bar{3}c1$ structure, whereas NMR data favor a structure with two inequivalent tetrahedral D sites, which is characteristic of a $P6_3cm$-symmetric structure. It is clear that more detailed analyzes of the diffraction and spectroscopic data are necessary to help resolve this discrepancy. As for LaF_3,[16] it might be enlightening for YD_3, in addition to these types of measurements, to search for a piezoelectric effect and/or second harmonic generation, two properties associated with a noncentrosymmetric structure such as $P6_3cm$ yet absent for a centrosymmetric structure such as $P\overline{3}c1$.

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