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A neutron-powder-diffraction study of the rare-earth deuteride two-phase region

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Abstract

Neutron-powder-diffraction measurements of bulk, polycrystalline, rare-earth deuterides (RD_y, $2<y<3$, R=Y, Nd, Tb, Dy, Ho, Er, Tm, and Lu) have been made in the β-RD_{2+x}/γ-RD_{3-z} two-phase region at room temperature. The phase-boundary lattice parameters and x and z values for the superstoichiometric f.c.c. dideuteride and substoichiometric h.c.p. trideuteride phases, respectively, have been determined by Rietveld refinement.

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1. Introduction

For Y and most lanthanide rare-earth metals heavier than Pr (with the exception of mixed-valent Yb and Eu), the rare-earth–hydrogen phase diagram possesses a two-phase region of superstoichiometric f.c.c. dihydride (β-RH_{2+x}) and substoichiometric h.c.p. trihydride (γ-RH_{3-z}). For β-RH_{2+x}, there are two interstitial tetrahedral (*t*) sites and one interstitial octahedral (*o*) site per f.c.c. R atom. The *t* sites are completely filled with hydrogen, with the *o* sites accommodating the remaining x hydrogens. Similarly for γ-RH_{3-z}, there are two distorted *t* sites and one highly displaced *o* site (more appropriately called a metal-plane or *m* site) per h.c.p. R atom. The distorted *t* sites are completely filled with hydrogen, with the *m* sites accommodating the remaining $1-z$ hydrogens. Hence, z is a measure of the fraction of *m*-site vacancies. The β-RH_{2+x}/γ-RH_{3-z} phase-boundary value of x (x_{max}) is extremely element-dependent, varying widely from nearly 1 to nearly 0 as one goes from the lighter to the heavier rare-earth metals. Values for x_{max} have been estimated by various techniques for the different rare-earth–hydrogen systems, although exact magnitudes have been found to depend somewhat on starting metal purity [1] (i.e. metal purities of 99.9% atomic fraction typically yielding deceptive results). Moreover, there is some confusion over the phase-boundary values of z (z_{max}). Although there are indications that z_{max} is only at the percent level for bulk γ-RH_{3-z} systems [2,3,4], epitaxial thin-film materials have been reported to have vacancy fractions up to 0.15 [5]. For this to be possible, substrate clamping effects must result in nonbulk-like behavior that enables much larger vacancy fractions than observed for bulk materials. It is not clear yet whether or not this is the case.

Neutron powder diffraction (NPD) is known to be a particularly powerful technique for determining the hydrogen location and content in metal hydrides. Typically one uses deuterium instead of hydrogen in order to avoid the much larger hydrogen incoherent scattering background. Thus, in the present study, we performed systematic room-temperature NPD measurements of the β-RD_{2+x}/γ-RD_{3-z} two-phase region for a series of eight rare-earth–deuterium binary alloys (where R=Y, Nd, Tb, Dy, Ho, Er, Tm, and Lu). Subsequent data analyses via Rietveld refinement yielded the phase-boundary lattice parameters as well as the magnitudes of both x_{max} and z_{max}.

2. Experimental

Rare-earth deuterides of Y, Nd, Tb, Dy, Ho, Er, Tm, and

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Lu were synthesized as discussed elsewhere [6]. (Sm and Gd were avoided because of their strong neutron absorption cross sections). Typically, the pure dideuterides were prepared first, followed by the calibrated addition of excess D to yield alloys in the two-phase region or single-phase trideuterides. Rare-earth metal purities were 99.99%. Deuterium isotope enrichment was 99.9%. All samples were finely pulverized to avoid preferential orientation and sealed inside cylindrical vanadium cans. All NPD measurements were taken at the NIST Center for Neutron Research on the high-resolution, 32-counter BT-1 diffractometer [7]. The Cu(311) monochromator was used at a wavelength of 1.5396(1) Å. The wavelength was calibrated using a NIST Si standard reference material. The horizontal divergences were 15′, 20′, and 7′ of arc for the in-pile, monochromatic-beam, and diffracted-beam collimators, respectively. Data were collected every 0.05° over a 2θ angular range of 3 to 168°. All refinements were carried out with the Rietveld method [8] using the program GSAS [9]. 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.

3. Results and discussion

Room-temperature NPD patterns were measured for the following rare-earth deuterides in the two-phase region: $YD_{2.35}$, $NdD_{2.96}$, $TbD_{2.35}$, $DyD_{2.35}$, $HoD_{2.35}$, $ErD_{2.35}$, $TmD_{2.35}$, and $LuD_{2.10}$. Moreover, room-temperature patterns were measured for the corresponding single-phase rare-earth trideuterides, except for γ-NdD_3. In general, the data were satisfactorily refined assuming that the room-temperature f.c.c. β-RD_{2+x} and h.c.p. γ-RD_{3-z} phases had $Fm3m$ and $P\bar{3}c1$ symmetries, respectively [4,10,11]. Although it is known that the superstoichiometric β-RD_{2+x} alloys can undergo transitions marked by ordering within the D *o*-site sublattice with a concomitant tetragonal lattice distortion [12,13], these tend to occur at lower temperatures for the alloys in question. One exception is $TbD_{2+x_{max}}$, where the room-temperature symmetry is indeed tetragonal ($I4/mmm$) because a long-range D_o-ordering transition was found to commence at a higher temperature of ≈330 K [14]. As for the γ-RD_{3-z} phases, there are some indications that the true local symmetry may very well be $P6_3cm$ or $P6_3$ [4,15–19]. (In the latter case, a diffraction-average $P\bar{3}c1$ symmetry presumably results from a microtwinning or quantum superposition of degenerate $P6_3$ configurations). In any case, refinements of the present data using either $P\bar{3}c1$ or $P6_3cm$ symmetry typically yielded the same result. The only exception was the γ-LuD_{3-z} phase, which possessed a more complex NPD pattern, indicative of a lower unknown symmetry. This was also apparent from the more complex hydrogen vibrational density of states found for γ-LuH_3 compared to the other rare-earth trihydrides [4]. Preliminary analyses of the single-phase γ-LuD_3 NPD pattern indicated that the main peaks could be satisfactorily modeled using $P6_3/mmc$ symmetry with a reduced unit cell, although there were numerous minor diffraction features that could not be indexed [4]. For the sake of refinement of the minor γ-LuD_{3-z} phase present in $LuD_{2.10}$, $P6_3/mmc$ symmetry was assumed.

Table 1 summarizes the refined room-temperature x_{max} values and lattice parameters for the β and γ phases within the two-phase region. The z_{max} values were estimated to be of the order of 0.01 or less for all rare-earth metals measured and could not be more precisely determined by refinement. In order to obtain such an estimate, we routinely determined the goodness of fit χ^2 for a range of discrete z values near zero, each time holding z fixed during the refinement. Fig. 1 illustrates the behavior of χ^2, typical of all rare-earth deuterides measured, as exemplified for single-phase γ-YD_3 and the two-phase alloy $YD_{2.92}$. The latter was synthesized from the single-phase sample by removing the equivalent of 0.08 D/Y followed by reequilibration. It is clear that χ^2 is sensitive to small changes in z and is minimized near $z \approx 0$ for the pure γ phase, consistent with the stoichiometry determined by D_2 uptake. Moreover, the position of the minimum does not change significantly (i.e. $\Delta z < 0.01$) for the case of γ-YD_{3-z} in the two-phase region. This behavior was checked further for the Y–D system by removing the equivalent of only 0.01 D/Y from single-phase γ-YD_3 and reequilibrating the resulting $YD_{2.99}$ sample. The subsequent room-temperature refinement established that a two-phase alloy had already formed with approximately 0.9(1) mole % β phase present. A simple D mass balance indicated that the change in trideuteride vacancy fraction from YD_3 to $YD_{2.99}$ was $\Delta z \approx 0.001(1)$.

In order to ensure good x_{max} values, we routinely determined χ^2 and x_{max} for a range of discrete D_o thermal factors U_{D_o}, each time holding U_{D_o} fixed during the refinement. The value of x_{max} was chosen for that value of U_{D_o} corresponding to a minimum in χ^2. In general, the refined x_{max} values and corresponding β/γ-phase mole % ratios lead to calculated overall RD_y stoichiometries that are reasonably consistent with those determined by D_2 uptake during the alloy syntheses. $LuD_{2.10}$ refinements yielded the largest percentage discrepancy above the dideuteride with a calculated stoichiometry of $LuD_{2.06}$. This most likely was due to the inadequacy of the assumed γ-phase $P6_3/mmc$ symmetry mentioned above, which ignores the extra minor LuD_{3-z} peaks that are present.

The refined β-phase lattice parameters a_c and x_{max} values are plotted against atomic number in Fig. 2, illustrating the general trend of decreasing *o*-site occupation and unit-cell size with increasing atomic number.

Table 1
Room-temperature lattice parameters and x_{max} values for various two-phase rare-earth deuterides and single-phase rare-earth trideuterides as determined by Rietveld refinement of NPD data

R	Atomic No.	For RD_y, y (exp.)[a] y (calc.)[b]	x_{max}	Reported values for RH_y (x_{max}), Ref.	β-RD_{2+x}/γ-RD_{3-z} mole % ratio (refined)	Two-phase β phase [$Fm\bar{3}m$][c] (a_c, Å)	Two-phase γ phase [$P\bar{3}c1$][d] a (Å) c (Å)	Single-phase γ-RD_3 [$P\bar{3}c1$][d] a (Å) c (Å), Ref.
Y	39	2.20 2.20	0.077(4)	0.10 [24]	87.2/12.8	5.1954(1)	6.3517(4) 6.6009(5)	6.3440(2) 6.5997(3) [2]
Nd	60	2.96 2.94	0.87(2)	0.65 [25]	43/57	5.4187(4)	6.6423(5) 6.8811(6)	not measured
Tb	65	2.35 2.32	0.218(8)	0.25 [1]	87.3/12.7	$a_t = 5.2247(2)$, $c_t = 10.4676(4)$[c]	6.3949(5) 6.6400(7)	6.3933(2) 6.6416(2) this work
Dy	66	2.35 2.31	0.182(5)	0.23 [24]	84.2/15.8	5.1884(1)	6.3482(3) 6.5967(4)	6.3442(2) 6.5984(3) [3]
Ho	67	2.35 2.33	0.120(3)	0.15 [1]	76.1/23.9	5.15051(8)	6.3008(2) 6.5531(3)	6.2992(2) 6.5538(2) this work
Er	68	2.35 2.35	0.096(7)	0.1 [26]	71.7/28.3	5.1140(1)	6.2569(3) 6.5112(4)	6.2576(2) 6.5145(3) this work
Tm	69	2.35 2.36	0.058(6)	–	67.7/32.3	5.08077(5)	6.2178(4) 6.4768(5)	6.2168(2) 6.4770(2) this work
Lu	71	2.10 2.06	0.010(3)	0.03 [1]	94.5/5.5	5.02176(8)	3.5529(3)[d] 6.4124(8)	3.5542(2)[d] 6.4146(3) this work

[a] Experimental RD_y stoichiometry from synthesis.

[b] Calculated RD_y stoichiometry from refinement.

[c] The β-TbD_{2+x} phase was refined in space group $I4/mmm$, and a_t and c_t are tetragonal lattice parameters.

[d] The γ-LuD_{3-z} phase was refined in space group $P6_3/mmc$ with a reduced unit cell.

From the observed behavior of the nonlanthanide Y with respect to the lanthanides, it is obvious that the magnitude of x_{max} depends on more than simply unit-cell size. The somewhat larger x_{max} values reported for the corresponding R–H alloys and also summarized in Table 1 are an isotope effect consistent with the slightly larger β-phase lattice parameters that result from replacing D with H [11,24]. One discrepancy with the literature is the refined x_{max} value of 0.87(2) for $NdD_{2.96}$. Significantly smaller x_{max} values of 0.61 and ≈0.65 were reported for Nd deuteride [11] and hydride [25], respectively. (The deuteride value is included in Fig. 2). This is somewhat

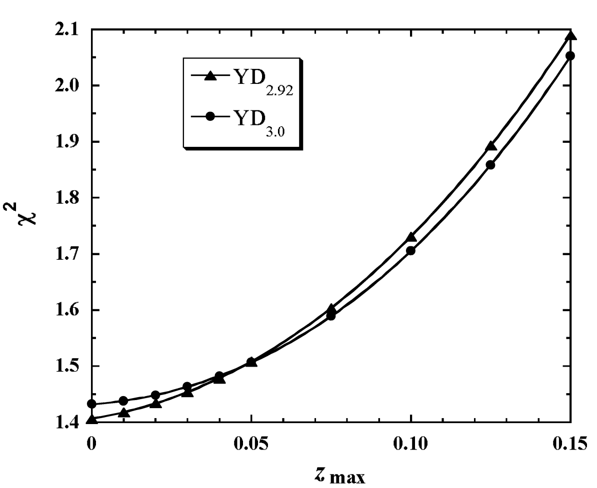

Fig. 1. Plot of χ^2 versus z_{max} for single-phase γ-YD_3 and the $YD_{2.92}$ two-phase alloy.

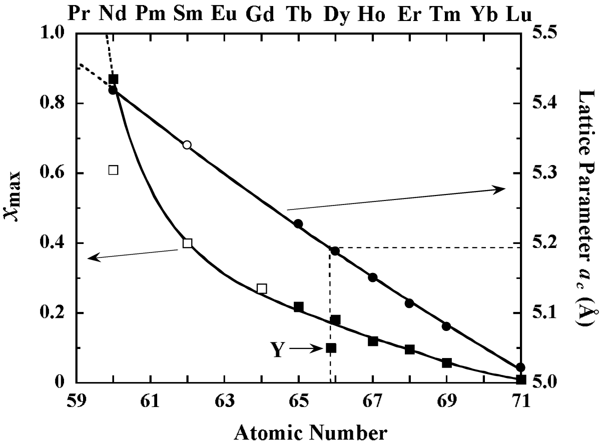

Fig. 2. The refined β-$RD_{2+x_{max}}$ lattice parameters a_c and x_{max} values plotted against atomic number of the lanthanides. For tetragonal β-$TbD_{2.218}$, an average cubic lattice parameter $a_c = (2a_t + c_t/2)/3$ is plotted instead. As indicated by the dashed lines, the lattice parameter vs. atomic number curve was used to determine the 'effective' atomic number position to plot the Y x_{max} value for comparison. Open symbols for Nd [11], Sm [20], and Gd [21] refer to values determined from the literature, as explained in the text.

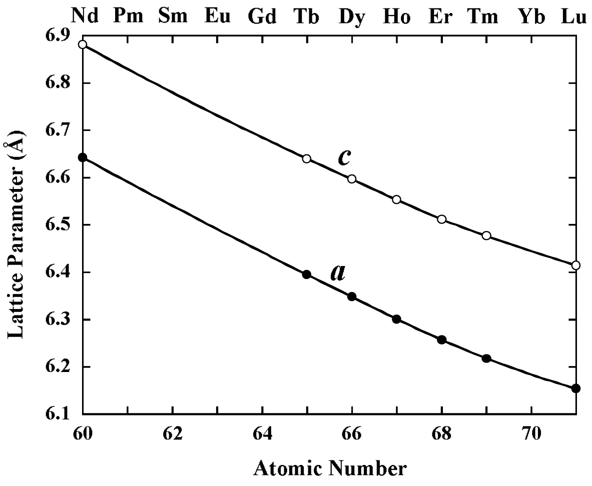

Fig. 3. The refined γ-$RD_{3-z_{max}}$ lattice parameters *a* and *c* plotted against atomic number of the lanthanides. For γ-LuD_{3-z}, the lattice parameter *a* of the $P6_3/mmc$ reduced unit cell was scaled by a factor of $\sqrt{3}$ for comparison with the other *a* values.

confusing since the refined overall stoichiometry of $NdD_{2.94}$ in the present paper is in good agreement with what was determined from the measured D_2 uptake. Literature values estimated for Sm [20] and Gd [21] are also included in Fig. 2. For Sm, x_{max} was equated to the reported Δx range that defined the onset and end of change in the β-phase deuteride lattice parameter (i.e. $x_{max} = \Delta x \approx 0.40$). For Gd, x_{max} for the β-phase deuteride was estimated to be about 0.27, 90 % of the value reported for the β-phase hydride, in general agreement with the isotope effect mentioned above.

The refined γ-phase lattice parameters *a* and *c* are plotted against atomic number in Fig. 3 (excluding the nonlanthanide Y), indicating a decreasing unit-cell size with increasing atomic number. A comparison of γ-phase lattice parameters between single-phase and two-phase alloys in Table 1 suggests subtle differences, which probably stem from slight differences in stoichiometry (i.e. $z_{max} > 0$) as well as lattice-strain effects in the two-phase region due to shared β/γ-phase domain interfaces. As expected, the γ-phase deuterides display slightly smaller lattice parameters than their hydride analogues [11,22].

4. Conclusions

A systematic NPD study of bulk polycrystalline rare-earth deuterides in the β-RD_{2+x}/γ-RD_{3-z} two-phase region was undertaken. Retvield refinements indicated that the β- and γ-phase lattice parameters and x_{max} (the β-phase D_o/R molar ratio) all decreased with increasing lanthanide atomic number. The value of x_{max} varied widely from 0.87 for $NdD_{2.96}$ to ≈ 0.01 for $LuD_{2.10}$. The trend in x_{max} is consistent with the suggestion [23] that, as the β-phase lattice parameter decreases (i.e. as the atomic number increases), energy losses from repulsive D–D interactions increasingly offset energy gains due to R–D bond shortening or the addition of new R–D bonds, leading to a decrease in the β-RD_{2+x} homogeneity range. In contrast to x_{max}, the value of z_{max} (the γ-phase *m*-site vacancy fraction) was found to be very small, on the order of 0.01 or less for all R–D alloys measured. As such, no similar trend for z_{max} with atomic number could be definitively established. It is clear that more neutron diffraction measurements of epitaxial thin-film specimens are needed, in particular, to verify the order-of-magnitude larger values of z_{max} suggested by other methods [5].

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