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Structural study of metal–hydrogen interactions in cubic PrH_{2+x} and rare-earth analogues

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Abstract

Neutron diffraction data on cubic $PrD_{2.92}$ show that the deuterium atoms in the octahedral interstices are displaced by 0.31 Å from the centre towards the faces. This leads to a considerable shortening of the Pr–D bonds (2.57 Å as compared to 2.74 Å for the centre position) and thus to a gain of energy. A comparison with other cubic RD_{2+x} structures (R=La, Ce, Nd) shows that the displacements and the shortening of the R–D bonds decrease as the atomic size of R decreases, whereas the shortest contact distances between the deuterium atoms in octahedral and tetrahedral interstices remain nearly constant (~2.1 Å). These findings suggest that as one goes from light to heavy R elements (or from low to high hydrogen contents) the energy gain due to R–H bond shortening (or the addition of new R–H bonds) is increasingly offset by the energy loss due to repulsive H–H interactions. This trend is consistent with the decreased homogeneity range of the cubic RH_{2+x} phase and the appearance of the trigonal RH_3 phase in R–H systems containing heavy R elements.

Keywords: Hydrogen absorbing materials; Rare earth alloys and compounds; Crystal structure; Neutron diffraction

1. Introduction

Trivalent rare-earths (R) generally form a hydrogen-poor cubic phase of composition RH_{2+x} ($0<x<1$) and a hydrogen-rich trigonal phase of composition RH_3. Early lanthanides such as La, Ce and Pr form the cubic phase only, at least under ordinary conditions, whereas late lanthanides form both the cubic and the trigonal phase. As one goes from light to heavy lanthanides the homogeneity range of the cubic phase decreases and the width of the two-phase region in the R–H phase diagram increases, i.e. the trigonal phase appears at lower overall hydrogen contents [1]. The reason for this behaviour is unknown. From a structural point of view it is interesting to note that the hydrogen atoms in the octahedral interstices of the cubic RH_{2+x} phase ($x>0$) are generally not located at the centre but are displaced along $\langle 111 \rangle$ toward the tetrahedral interstices. In $LaH_{2.96}$, for example, these displacements are 0.37 Å [2]. They lead to a considerable shortening of the La–H bonds (2.60 Å as compared to 2.80 Å for the centre position) and presumably contribute to the structural stability of the cubic phase. Similar displacements also occur in cubic $CeH_{2.90}$ although to a lesser extent (0.34 Å [3]). Still smaller displacements have been observed in hydrogen deficient cubic $NdH_{2.6}$ (0.29 Å [4]) which is in equilibrium with trigonal NdH_3. The data available so far suggest that the displacement amplitudes (i.e. the R–H bond shortening) depend on the atomic size of R and correlate with the range of existence of the cubic RH_{2+x} phase. The aim of the present work was to investigate this hypothesis in more detail. For this purpose neutron diffraction data were collected on cubic praseodymium deuteride. No such data have been reported as yet. From atomic size considerations one would expect that the deuterium atom displacements in this compound are intermediate to those in the Ce and Nd analogues.

2. Experimental

2.1. Sample preparation

Samples were prepared by hydrogenation (deuteration) of praseodymium metal (pieces, 99.99% purity) in an autoclave. The temperature was increased to 823 K at a hydrogen (deuterium) gas pressure of about 100 bar during 1 day. The autoclave was then air-quenched and opened in

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an argon-filled glove box. The powders had a dark grey colour and were sensitive to air and moisture. They consisted of the cubic praseodymium hydride (deuteride) phase, but the X-ray powder diffraction patterns showed broad peaks. Thus the samples were again introduced in the autoclave and annealed during 3 days under a hydrogen (deuterium) pressure of ~100 bar at temperatures varying between 823 and 373 K. The final products were single-phase and well crystallised.

2.2. X-ray diffraction

The samples were characterised by X-ray powder diffraction at room temperature by using a Bruker D8 diffractometer (Bragg–Brentano geometry, Cu Kα_1 radiation) equipped by an air tight sample holder. Corundum (α-Al_2O_3) powder was used as an internal standard ($a=4.7583$ Å, $c=12.9894$ Å). The diffraction patterns were consistent with a cubic close-packed metal atom substructure. Rietveld analysis yielded the cell parameters $a=5.4903(4)$ Å for the hydride and $a=5.4796(1)$ Å for the deuteride.

2.3. Neutron diffraction

The deuterium positions were determined by neutron powder diffraction. The sample (about 4 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and placed on the HRPT [5] powder diffractometer at PSI, Villigen ($\lambda=1.197$ Å; 2θ range 5–165°; step size $2\theta=0.05°$; $T=293$ K). The transmission factor was calculated ($\mu_R=0.13$) and the data corrected accordingly. The structure refinement by FULLPROF [6] included only the PrD_{2+x} phase (space group $Fm\bar{3}m$). No impurity phase was detected and vanadium contributed only marginally to the diffraction pattern. Deuterium atoms were put into tetrahedral (D1) and octahedral interstices (D2) at full occupancy ($x=1$). In a first step those in the octahedral interstices were put at the centre of the octahedra (site 4(b), 1/2, 1/2, 1/2, etc. symmetry $m\bar{3}m$, called $D2_c$), and its occupancy refined while assuming an overall isotropic temperature factor. The value found (occ.=0.919(6)) indicated the overall composition of this phase to be $PrD_{2.92}$. In a second step D2 was allowed to move along ⟨111⟩ to a site of lower symmetry (site 32(f), x,x,x, etc, symmetry $3m$) while its occupancy was fixed to the value found previously (0.92/8) and its isotropic temperature factor was constrained to that of D1. During the last refinement cycles the following 11 parameters were allowed to vary: zero position (one), scale factor (one), profile (four), cell (one), atom position (one), preferred orientation (one) and isotropic temperature factor (two). A refinement of the occupancy factor of D2 on site 32f confirmed the assumed value. The diffraction patterns are shown in Fig. 1 and refinement results are listed in Table 1. Selected bond distances and displacement amplitudes are summarised in Table 2.

3. Results and discussion

The displacements of the deuterium atoms in the octahedral interstices of $PrD_{2.92}$ (0.31 Å along ⟨111⟩) are intermediate to those of $CeD_{2.90}$ (0.34 Å) and $NdD_{2.60}$ (0.29 Å). They lead to a considerable shortening of the

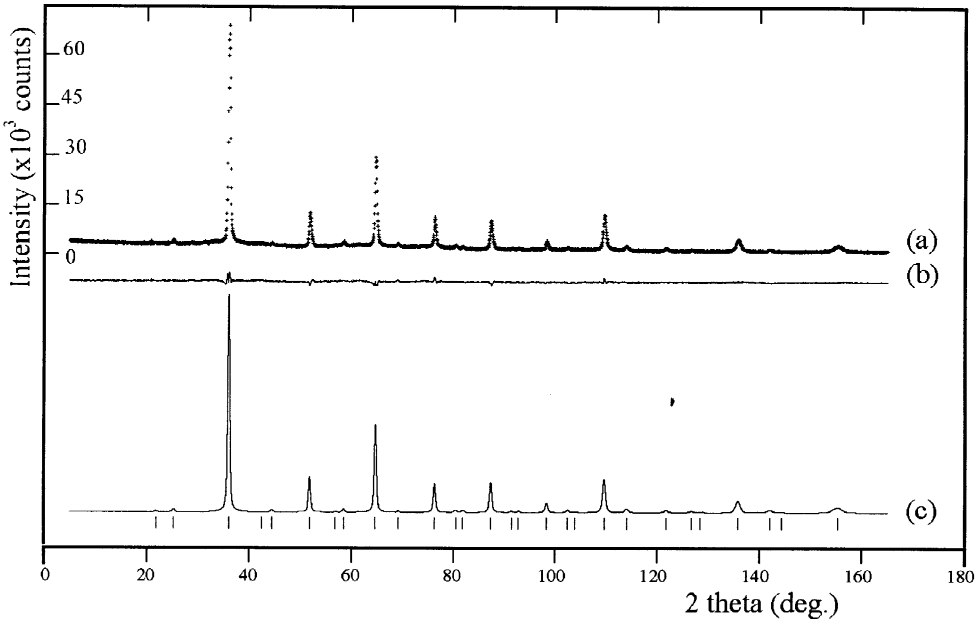

Fig. 1. Observed (a), difference (b) and calculated (c) neutron powder diffraction patterns for $PrD_{2.92}$ ($\lambda=1.197$ Å).

Table 1
Refinement results on neutron powder diffraction data (T=295 K, estimated standard deviations in parentheses)

Phase	Atom	Site	x/a	y/b	z/c	B_{iso} (Å^2)	Occupancy
$PrD_{2.92}$	Pr	4(a)	0	0	0	0.28(2)	1(−)
($Fm\bar{3}m$, $Z=4$)	D1	8(c)	1/4	1/4	1/4	1.41(2)[a]	1(−)
$D_x=5.92$ g/cm^3	D2	32(f)	0.4676(3)	0.4676(3)	0.4676(3)	1.41(−)[a]	0.919(−)/8[b]

[a] Constrained.

[b] Previously refined to 0.919(6) by assuming D2 on site 4(b) and an overall temperature factor.

Table 2
Cell parameters (Å), positional coordinates, distances and displacement amplitudes ε (Å) for $PrD_{2.92}$ and other cubic R deuterides

	a	x(D2)	R–D1	R–D2	R–$D2_c$[a]	D1–D2	D1–$D2_c$[a]	ε=D2–$D2_c$[a]
$LaD_{2.96}$ [2]	5.601(5)	0.4614(6)	2.425(1)	2.602(4)	2.801(3)	2.051(4)	2.425(1)	0.374(3)
$CeD_{2.90}$ [3]	5.5312(9)	0.4645(5)	2.3951(2)	2.584(3)	2.7656(5)	2.055(3)	2.3951(2)	0.340(3)
$PrD_{2.92}$[b]	5.4796(1)	0.4676(3)	2.3727(1)	2.575(2)	2.7398(1)	2.065(2)	2.3727(1)	0.308(2)
$NdD_{2.61}$ [4]	5.4324(2)	0.469(2)	2.3524(1)	2.56(1)	2.7163(1)	2.06(1)	2.3524(1)	0.29(1)

[a] $D2_c$, centre of R octahedron.

[b] This work.

Pr–D bonds (2.57 Å as compared to 2.74 Å for the centre position $D2_c$) and to very close contacts with the deuterium atoms in tetrahedral interstices (D1–D2=2.06 Å). Interestingly, while the displacement amplitudes (see ε=D2–$D2_c$ in Table 2) decrease along the series of light lanthanides La, Ce, Pr and Nd, the deuterium–deuterium contact distances across the triangular metal faces remain practically constant (D1–D2~2.06 Å). This strongly suggests that the displacements of the deuterium atoms in the octahedral interstices are limited by repulsive interactions between deuterium atoms in octahedral and tetrahedral interstices. In order to illustrate this feature the maximum possible displacement of D2 along ⟨111⟩ has been calculated for a fixed D1–D2 contact distance of 2.1 Å (i.e. the value usually found in metal hydride structures [7]) and plotted as a function of the radius of R^{3+} in Fig. 2. Clearly,

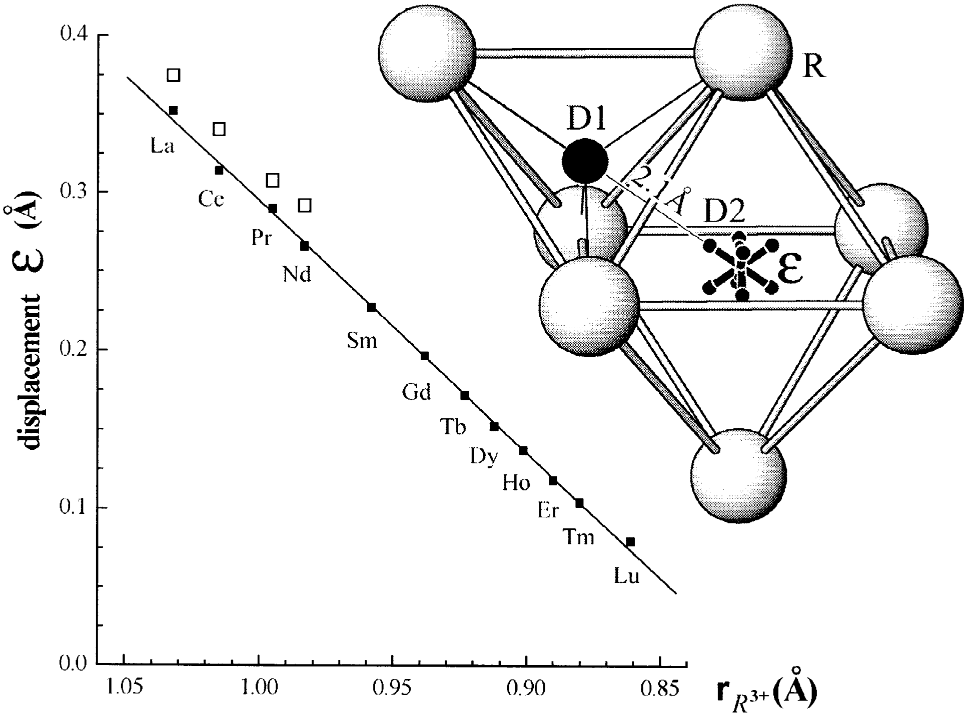

Fig. 2. Measured (open squares) and calculated (filled squares) displacement amplitudes, ϵ, of deuterium atoms in octahedral interstices of cubic RD_{2+x}, plotted as a function of ionic size, R^{3+}. Calculations based on published cell parameters of RH_2 [8] and a fixed D1–D2 contact distance of 2.1 Å (see insert).

the calculated displacements (filled squares) decrease as the lanthanide ions become smaller, and reproduce well the measured displacements for La, Ce, Pr and Nd (open square). As to heavier R elements structure data of sufficient accuracy are not yet available for comparison.

The correlation between the atomic size of R and the displacement amplitudes of hydrogen in the octahedral interstices of the cubic RH_{2+x} structure could be of importance for the understanding of its stability and range of existence. It is conceivable that as one goes from light to heavy R elements (or from small to large hydrogen contents) the energy gain due to the R–H bond shortening (or the addition of new R–H bonds) is increasingly offset by the energy loss due to repulsive H–H interactions. If verified, this trend would be consistent with the observed decrease in homogeneity range of the cubic RH_{2+x} phase and the appearance of the trigonal RH_3 phase in R–H systems containing heavy R. In the trigonal phase the hydrogen atoms occupying octahedral interstices have nearly triangular metal coordinations and their very short R–H bonds are consistent with the absence of strongly repulsive interactions between deuterium atoms in octahedral and tetrahedral interstices [4]. Theoretical band structure calculations and more structure data are needed, in particular for heavier R hydrides, to put this hypothesis on a firmer basis.

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