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Structural properties of RT_3 deuterides synthesized under high pressure of deuterium

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Abstract

Deuterides of $ErNi_3$, $CeCo_3$ and $CeNi_3$ intermetallic compounds are synthesized under deuterium pressures up to 2000 atm and studied by X-ray powder diffraction under ambient conditions. The deuterides are shown to have the same structures of the metal lattice as the initial alloys, the deuteration resulting only in the anisotropic lattice expansion. The deuterides of $ErNi_3$ show weaker anisotropy in the lattice expansion than the deuterides of $CeCo_3$ and $CeNi_3$. The formation of $CeNi_3D_5$ at a pressure of about 2000 atm is accompanied by partial amorphization of the sample. The deuteration induces preferred orientation of the powder particles of each alloy and this orientation is retained after thermodesorption of the deuterium.

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Keywords: Intermetallic compounds (IMC); Hydrides; Deuterides; High and low pressure of deuterium; Thermodesorption

1. Introduction

Intermetallic compounds RT_3 (where R is the rare-earth and T is the transitional element) are able to absorb considerable amounts of hydrogen that makes them promising materials for hydrogen storage. Theoretical study [1] has shown that the maximum hydrogen content of such hydrides is 5–5.6 atoms per formula unit. Hydrogen atoms partly occupy interstitial sites in the lattice of the RT_3 compound that leads to an increase in the metal volume. The occupancy of the interstitial sites can be enhanced using high hydrogen pressure. In the present work, the structure of the metal sublattice of RT_3 deuterides synthesized under high deuterium pressures is studied by X-ray diffraction.

2. Experimental

The initial intermetallic compounds (IMC) were melted from pure components in an electrical furnace under argon atmosphere and then annealed in evacuated quartz ampoules for 240 h. The IMC were loaded with deuterium at pressures up to 2000 atm using the apparatus described in [2]. The obtained high-pressure deuterides were cooled to a liquid nitrogen temperature of 77 K and left at air about 40 min at this temperature for transferring them into inert state. The deuterium content of the inert deuterides was determined by thermodesorption. X-ray powder diffraction patterns of the deuterides and the starting IMC were measured with a "Rigaku" and "Thermo ARL" diffractometer at room temperature using monochromated Cu $K\alpha_1$ radiation. The data were analyzed using the Rietveld profile refinement technique.

3. Results and discussions

The X-ray diffraction patterns of the studied IMC and their deuterides are shown in Figs. 1–3. The quality of the profile refinement is illustrated by the difference spectra placed below the corresponding diffraction patterns. The refined values of the structure parameters are presented in Tables 1 and 2.

All starting IMC were single-phase, and the values of their lattice parameters were in agreement with the results in

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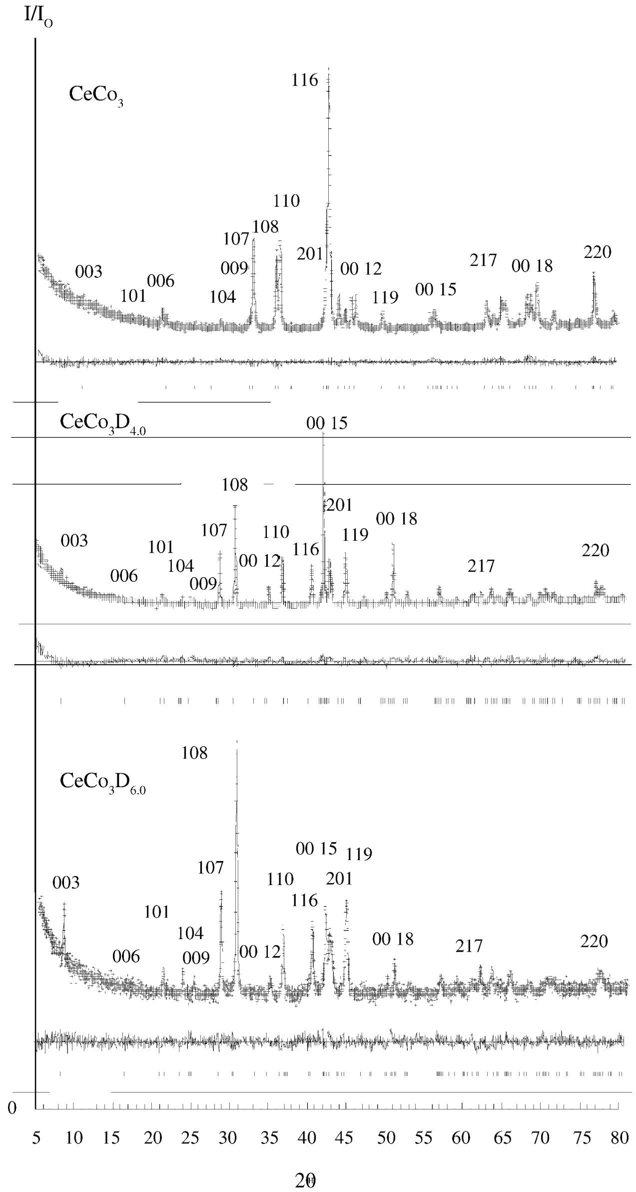

Fig. 1. X-ray powder diffraction patterns of $CeCo_3$, $CeCo_3D_{4.0}$ and $CeCo_3D_{6.0}$ monochromated Cu Kα_1 radiation, room temperature.

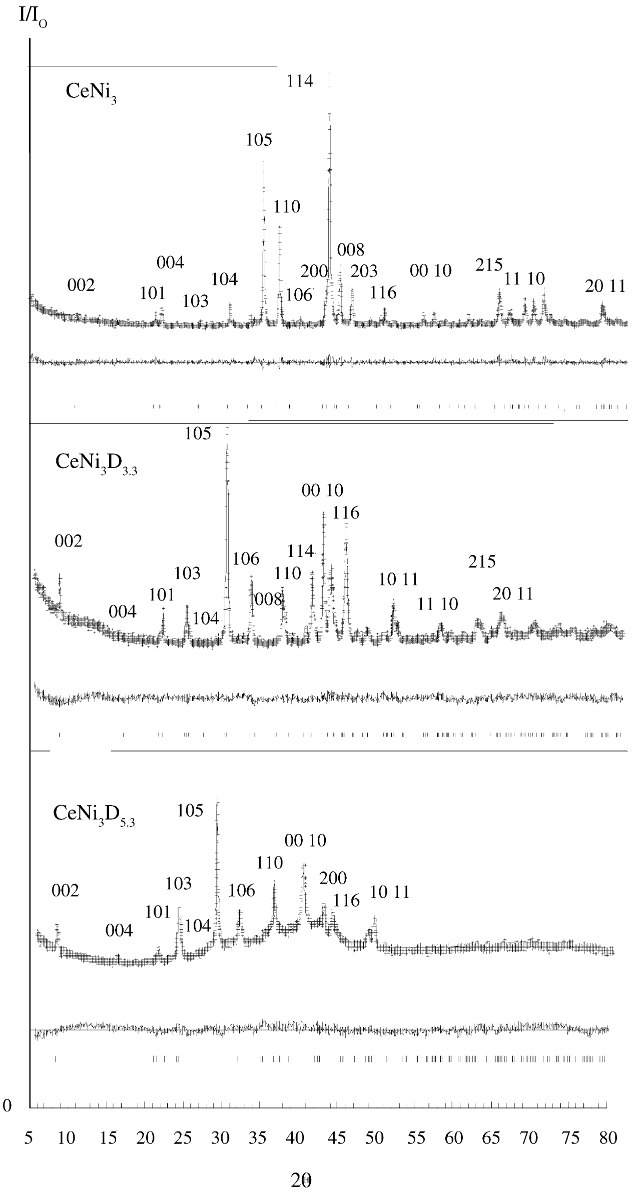

Fig. 2. X-ray diffraction patterns of $CeNi_3$, $CeNi_3D_{3.3}$ and $CeNi_3D_{5.2}$.

Table 1
Results of the X-ray diffraction investigation of IMC and their deuterides at room temperature

Composition	Structure type	Lattice parameters				$\Delta V/x$ (Å^3/atom H)	Conditions of synthesis	
		a (Å)	c (Å)	V (Å^3)	$\Delta V/V$ (%)[a]		P (atm)	T (K)
$CeNi_3$	$CeNi_3$	4.964(2)	16.53(3)	353	–	–	––	–
$CeNi_3D_{3.3}$	$CeNi_3$	4.950(3)	21.79(3)	462	30.9	5.5	5	293
$CeNi_3D_{5.2}$	$CeNi_3$	4.968(3)	22.69(3)	485	37.4	4.2	1990	293
$CeCo_3$	$PuNi_3$	4.990(2)	24.94(3)	538	–	–	––	–
$CeCo_3D_{4.0}$	$PuNi_3$	4.936(3)	32.45(3)	684	27.1	4.1	5	293
$CeCo_3D_{6.0}$	$PuNi_3$	4.980(1)	32.65(2)	701	30.3	3.0	1950	293
$ErNi_3$	$PuNi_3$	4.943(2)	24.28(3)	514	–	–	––	–
$ErNi_3D_{4.0}$	$PuNi_3$	5.332(3)	26.92(2)	661	28.6	4.1	5	223
$ErNi_3D_{5.0}$	$PuNi_3$	5.344(2)	26.95(1)	667	29.8	3.4	1980	293

[a] $\Delta V = V(x) - V(0)$, where x is the H-to-metal atomic ratio.

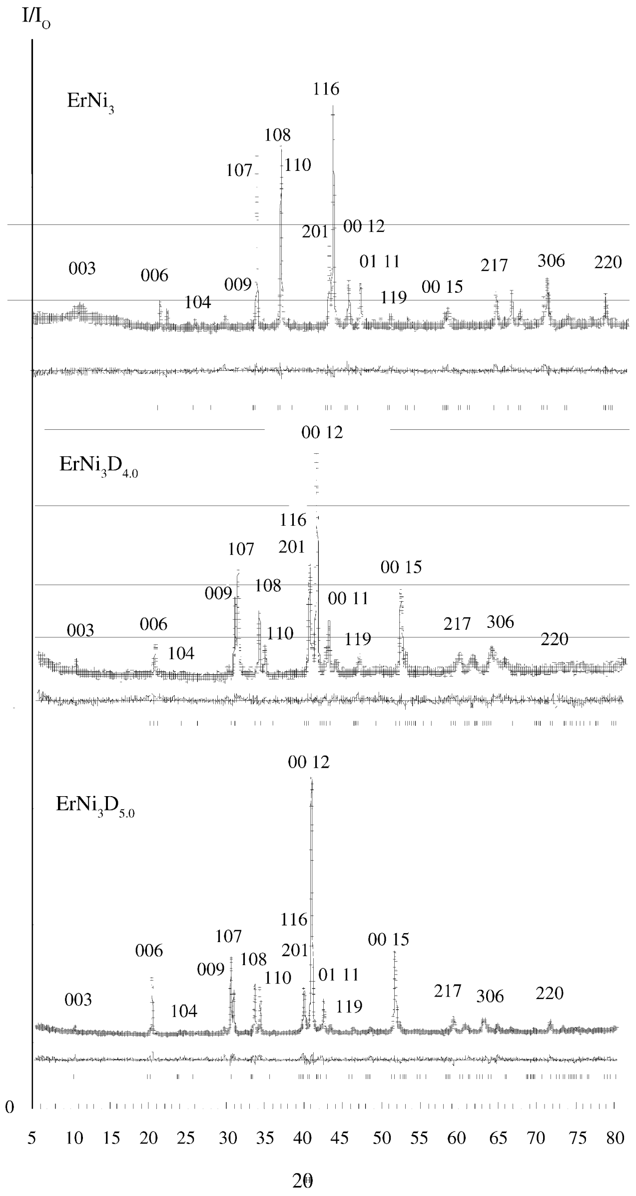

Fig. 3. X-ray diffraction patterns of $ErNi_3$, $ErN_3D_{4.0}$ and $ErN_3D_{5.0}$.

literature [3]. The lattice parameters of the deuterides varied depending on the deuterium concentration that increased with increasing pressure of synthesis.

According to [4,5], the metal lattice of $CeNi_3D_{3.3}$ is anisotropically expanded along the Z axis. The formation of $CeNi_3D_{2.8}$ is accompanied with an orthorhombic distortion of the lattice that lowers its symmetry to the *Pmnc* (62) space group [5]. Deuterium atoms are located within RT_2 units of the metal matrix.

The X-ray pattern of our $CeNi_3D_{3.3}$ sample can be indexed on the basis of a hexagonal $CeNi_3$ type structure with an increased c parameter. A comparison of the X-ray patterns of $CeNi_3D_{3.3}$ and $CeNi_3$ shows differences in the intensity of the peaks due to the rearrangement of atoms in the metal matrix (Table 2). In the X-ray pattern of the $CeNi_3D_{5.2}$ deuteride with a higher deuterium concentration (Fig. 2), there is a halo indicating a partial amorphization of the metal lattice. The intensities of the diffraction peaks of $CeNi_3D_{5.2}$ are changed in comparison with $CeNi_3D_{3.3}$ and the lattice parameters of $CeNi_3D_{5.2}$ are slightly increased (Fig. 4).

Table 2

Results of a profile refinement of the crystal structures of the IMC and deuterides listed in Table 1

Composition	Atom coordinates		
	$Ce_2(z)$		$Ni_4(x,y,z)$
$CeNi_3$	0.041(1)		0.833(1), 0.667(1), 0.127(2)
$CeNi_3D_{3.3}$	0.062(4)		0.829(2), 0.658(2), 0.144(7)
$CeNi_3D_{5.2}$	0.059(5)		0.827(3), 0.654(3), 0.135(8)
Composition	Atom coordinates		
	$Ce_2(z)$	$Co_2(z)$	$Co_3(x,y,z)$
$CeCo_3$	0.143(1)	0.333(2)	0.167(1), −0.167(1), 0.417(2)
$CeCo_3D_{4.0}$	0.124(5)	0.333(6)	0.167(2), −0.167(3), 0.403(5)
$CeCo_3D_{6.0}$	0.125(6)	0.337(7)	0.167(2), −0.167(2), 0.401(6)
Composition	Atom coordinates		
	$Er_2(z)$	$Ni_2(z)$	$Ni_3(x,y,z)$
$ErNi_3$	0.141(1)	0.330(2)	0.167(1), −0.167(1), 0.416(2)
$ErNi_3D_{4.0}$	0.138(3)	0.327(4)	0.167(2), −0.167(2), 0.415(3)
$ErNi_3D_{5.0}$	0.136(4)	0.329(7)	0.167(2), −0.167(2), 0.415(5)

According to [4], the formation of $CeCo_3D_{4.0}$ is accompanied with an anisotropic ($\Delta c > \Delta a$) lattice expansion. Hydrogenation of some RCo_3 compounds [6] led to an isotropic expansion and small orthorhombic distortion of the metal matrix. Our experiments revealed changes in the intensity of X-ray reflections from $CeCo_3D_{4.0}$ caused by the displacements of both Ce and Co atoms along the Z axis (Table 2). The $CeCo_3D_{6.0}$ deuteride synthesized under a higher pressure had an expanded lattice of the initial $CeCo_3$ compound. In comparison with $CeCo_3D_{4.0}$, both a and c lattice parameters of $CeCo_3D_{6.0}$ were slightly increased and the peaks intensities were changed.

The $ErNi_3D_{4.0}$ and $ErNi_3D_{5.0}$ deuterides showed a nearly isotropic expansion of the lattice and smaller changes in the intensity of the diffraction peaks mostly caused by the displacements of Er atoms along the Z axis (Table 2). This indicates that under a high deuterium pressure, $ErNi_3D_{5.0}$ is formed from $ErNi_3D_{4.0}$ as a more concentrated solid solution.

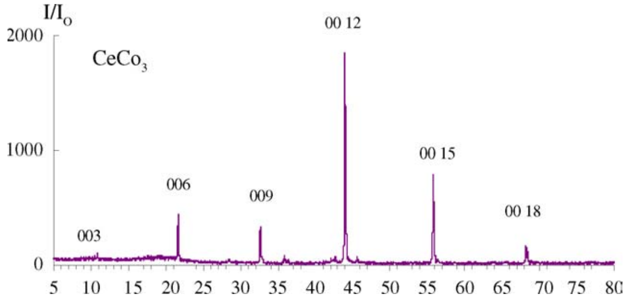

Fig. 4. The X-ray diffraction pattern of a textured $CeCo_3$ sample obtained by thermodesorption of $CeCo_3D_{4.0}$.

The thermodesorption of deuterium brought all high-pressure deuterides except $CeNi_3D_{5.2}$ back into the initial IMC, while the outgassed sample of $CeNi_3D_{5.2}$ remained partly “amorphous” (fine-crystalline). The powder samples of IMC produced by thermodesorption of the deuterides were composed of flat particles that had a strong texture and could be oriented by magnetic field. Peaks of the $(0\,0\,\ell)$ type had maximum intensities in the X-ray patterns of these powders.

4. Conclusions

The synthesized deuterides show different changes in the crystal structure as a function of the deuterium concentration.

The deuterides with low concentrations of deuterium formed in the $CeCo_3$–D_2 and $CeNi_3$–D_2 systems at a pressure of 5 atm demonstrate an anisotropic lattice expansion along the Z axis due to the rearrangement of atoms in the metal matrix.

The transition from $ErNi_3D_{4.0}$ to $ErNi_3D_{5.0}$ occurring in the $ErNi_3$–D_2 system at a higher deuterium pressure is characterized by a smaller anisotropy in the lattice expansion and can be considered as a gradual increase in the concentration of a continuous solid solution. The transition from $CeCo_3D_{4.0}$ to $CeCo_3D_{6.0}$ also proceeds smoothly and is accompanied by an increase in both a and c lattice parameter. A halo observed in the X-ray diffraction pattern of the $CeNi_3D_{5.2}$ deuteride points to its partial amorphization.

The intensity of $(0\,0\,\ell)$ diffraction peaks drastically increases in the X-ray patterns of powder IMC samples formed after thermodesorption of the high-pressure deuterides. The effect can be attributed to the anisotropic lattice expansion and weakening of bonds between the slabs of metal atoms along the Z axis. The texture significantly distorts the diffraction spectra and this fact should be taken into account when the structures of IMC–H_2 phases are analyzed.

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