

Structural properties of two deuterides $\text{LaY}_2\text{Ni}_9\text{D}_{12.8}$ and $\text{CeY}_2\text{Ni}_9\text{D}_{7.7}$ determined by neutron powder diffraction and X-ray absorption spectroscopy

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Abstract

The crystal structure of two deuterides $\text{RY}_2\text{Ni}_9\text{D}_x$ ($R=\text{La}$; $x=12.8$ and $R=\text{Ce}$; $x=7.7$) have been investigated by means of neutron powder diffraction and X-ray absorption spectroscopy. The structures are best described in the space group $R\bar{3}m$. The deuterium location has been determined for both compounds. The nature and the occupancy factors of the different D sites are presented. Comparisons are made between the La-based deuteride and the Ce-one in relation with the crystal structure of the intermetallic compounds. Differences in site occupancies within the RM_2 and RM_5 building units of the PuNi_3 -type structure are discussed and heterogeneous mixed valence state is reported for the cerium compound.

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1. Introduction

Intermetallic compounds RM_n (R =rare earth or transition metal, M =transition metal, $n=1, 2, 3$ or 5) are able to store reversibly large amount of hydrogen and are potential materials for energy storage either by solid-gas [1,2] or electrochemical routes [3,4]. Nowadays, new interests are devoted to RM_3 -type compounds with the recent discovery of new compounds in ternary systems like RM_2Ni_9 (R =rare earth or Ca; M =Mg, Ca, Ti or Y) [5–11]. These compounds crystallize in an ordered variant of the PuNi_3 -type rhombohedral structure ($R\bar{3}m$ space group) [12] and can be described as a stacking of CaCu_5 (Haucke phase) and MgZn_2 (Laves phase) units [13] as shown in Fig. 1. Few hydrides have been investigated from a structural point of view in the RM_3 family. For the RNi_3 system (R =Ho, Er, Y), the PuNi_3 -type structure is generally preserved upon hydrogenation and neither decomposition nor structural

changes are reported. From the neutron diffraction (ND) analysis of $\text{HoNi}_3\text{D}_{1.8}$, Burnasheva et al. [14] found two occupied sites: 71% of the deuterium lies in the interstice $18h_1$ and the remaining atoms are located in the site $6c_1$. However, for CeNi_3H_3 the hydride phase is formed with a huge uniaxial expansion of the cell ($\delta a/a = -0.80\%$, $\delta c/c = 30.76\%$) [15]. Recently, Yartys and coworkers [16,17] found an orthorhombic symmetry lowering into $Pm\bar{c}n$ space group for the deuteride $\text{CeNi}_3\text{D}_{2.7}$ and reported that deuterium was located only within the CeNi_2 units. In the RCO_3 system, two homogeneity domains are reported for YCO_3 . The beta phase YCO_3D_x exists for $1 \leq x \leq 1.9$ and was described in the $R\bar{3}m$ space group by Benham et al. [18] with significant uniaxial volume expansion ($\delta a/a = -0.07\%$, $\delta c/c = 9.72\%$) attributed to the filling of the RM_2 units only. Indeed, all deuterium atoms were found in the tetrahedral site $36i_1$ in agreement with the exclusive hydrogenation of RM_2 units. The gamma phase $\text{YCO}_3\text{D}_{3.8}$ was investigated by Bartashevich [19]. Less anisotropic volume expansion was observed ($\delta a/a = 4.44\%$, $\delta c/c = 8.27\%$) and, in addition to the

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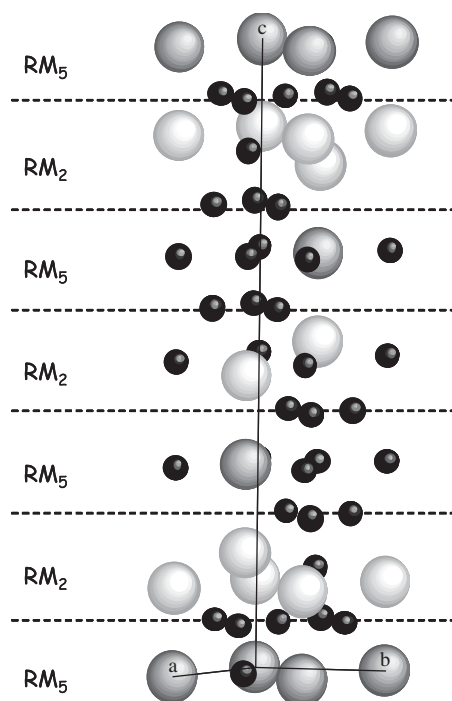


Fig. 1. PuNi_3 -type crystal structure (Space group $R\bar{3}m$; hexagonal axes) showing the stacking of RM_5 and RM_2 units along the c -axis. R atoms lying on sites $3a$ and $6c$ are coloured in grey and light grey, respectively and nickel atoms are represented by small dark circles [21].

site $36i_1$ reported for the beta phase, significant occupations for sites $18h_2$ and $36i_2$ within the RM_5 units were found. A small orthorhombic distortion comparable to that observed in $R\text{Co}_5$ hydrides [20] was also reported. According to these works, it is expected that the beta phase corresponds to the filling of the RM_2 units followed by the filling of the RM_5 units in the gamma phase.

To our knowledge, no structural data have been reported so far on ternary $RM_2\text{Ni}_9$ -type deuterides. In this paper, we will present the structural properties of the two deuterides $\text{LaY}_2\text{Ni}_9\text{D}_{12.8}$ and $\text{CeY}_2\text{Ni}_9\text{D}_{7.7}$ determined by neutron powder diffraction (NPD) and X-ray absorption spectroscopy (XAS). Differences in site occupancies within the RM_2 and RM_5 building units of the PuNi_3 -type structure are also discussed.

2. Experimental

The alloys $RY_2\text{Ni}_9$ ($R = \text{La}, \text{Ce}$) were prepared following the procedure described in [10]. Metallographic examination, powder X-ray diffraction experiments (XRD) (Bruker AXS D8 θ – θ diffractometer, $\text{CuK}\alpha$ radiation, flat plate, Bragg–Brentano geometry, 2θ -range 20 – 120° , step size 0.02° , backscattered rear graphite monochromator) and elemental analysis by electron probe micro-analysis (EPMA) were performed to check the homogeneity of the alloys. Deuterated

samples have been loaded by solid–gas reaction using the Sievert's method allowing accurate determination of the D content. Loading was performed in a cylindrical tight silica cell (inner diameter: 8 mm; height: 70 mm) containing about 6.9 g of powder. When the loading was completed, the tight silica cell was closed under deuterium pressure in order to avoid any desorption effect during ND acquisition. ND patterns were obtained at the Laboratoire Léon Brillouin in Saclay (France) on the 3T2 instrument in the range $6^\circ < 2\theta < 120^\circ$ by step of 0.05° ($\lambda = 1.225 \text{ \AA}$). All patterns were refined with the Rietveld method using program FULLPROF [22]. Background has been linearly interpolated between about 50 points. All diffraction lines were refined assuming a pseudo-Voigt function. Neutron scattering lengths and X-ray form factors were obtained from the program FULLPROF. Since contrast between yttrium and rare earths is better with X-ray data than with neutrons and in order to limit the number of refined parameters the occupancy ratio for sites $3a$ and $6c$ were kept fixed to the values obtained from X-ray analysis of the intermetallic compounds [10]. During the refinement process, reliable calculated pattern for the cerium compound cannot be obtained using simply isotropic thermal B's factor. Thus, all refinements have been performed using anisotropic displacement parameters even for the lanthanum-based deuteride.

XAS has been carried out in LURE (France) at DCI with a beam current in the storage ring of 325 mA (1.8 GeV). Measurements have been performed by transmission mode on the beam line D21 with a Si 311 crystal monochromator. Energy calibration was done with measuring chromium metal. Scan-step was set to 0.30 eV and data were obtained from the sum of two spectra (2 s per point). Data were refined using the software Origin[®] V7.0 [23]. The cerium spectrum was refined by a convolution of lorentzian, gaussian and arctangent functions for each white line according to Ref. [24]. All measurements were done using a special tight cell equipped with 100 μm Mylar windows and allowing in situ hydrogen absorption under controlled gas pressure (see [25] for details). Data have been collected at room temperature on samples made of fine powders sieved below 20 μm and dispersed on a Kapton[™] foil at the Ce– L_{III} edge between 5675 and 5790 eV.

3. Results

The compositions of the alloys obtained by EPMA (see Table 1) are homogeneous and close to the nominal ones. XRD analysis confirms that both samples are single phase and adopt the rhombohedral PuNi_3 -type structure as previously described in [10].

Table 1
Analysis, thermodynamic and crystallographic data for the RY_2Ni_9 compounds in space group $R\bar{3}m$ (hexagonal axes)

Composition (from EPMA)	D/f.u.	P_{eq} (bar) at 25°C (abs.)	a (Å)	c (Å)	V (Å ³)	$\delta a/a$ (%)	$\delta c/c$ (%)	$\delta V/V$ (%)	$\delta V/VRM_5$ (unit %)	$\delta V/VRM_2$ (unit %)
Ce _{1.06(4)} Y _{1.95(4)} Ni _{8.98(2)}	0	—	4.971	24.538	525.12	—	—	—	—	—
	7.7	0.12	4.872	31.312	643.75	−2.0	27.6	22.6	−2.6	47.0
La _{1.04(2)} Y _{2.03(4)} Ni _{9.00(4)}	0	—	5.034	24.507	538.04	—	—	—	—	—
	12.8	0.1	5.396	26.885	677.86	7.2	9.7	26.1	24.7	27.4

Cell parameters are given for the intermetallics and for the deuterides with cell volume expansion. The absorption capacities are given in D atom per formula unit (D/f.u.). In addition, the partial volume expansions of the respective RM_2 - and RM_5 -building units of the $PuNi_3$ -type structure are given.

This structure can be described as an intergrowth between RM_5 unit (Haücke phase) and RM_2 (Laves phase) ones. Among the two available crystallographic sites for R atoms, lanthanum occupies preferentially the site $3a$ leading to an ordered ternary compound. The cerium-based compound does not show symmetry change but leads to a statistical distribution of the cerium atoms over the two sites $3a$ and $6c$. Therefore the compound CeY_2Ni_9 can be seen also described as a pseudo-binary compound with average composition $Ce_{0.33}Y_{0.66}Ni_3$.

Deuterium contents for the two deuterides have been obtained by solid–gas measurements and are given in Table 1 with the measured absorption equilibrium pressures.

ND patterns of both deuterides can be fully indexed in the $PuNi_3$ -type rhombohedral structure (hexagonal axes). Cell parameters are reported in Table 1 and are compared to those of the intermetallics. Interestingly, the cell parameter increase of the lanthanum compounds is almost isotropic whereas the cerium-based deuteride shows strong anisotropy with a reduction of a (−2%) and a huge expansion of c (+27.6%).

According to Burnasheva et al. [14], 13 sites are available for hydrogen in the $PuNi_3$ structure divided into 12 tetrahedrons (T) and one octahedron (O). Depending on the nature of the metal forming polyhedron, the sites can be described with four different environments: $3M_4$, $5RM_3$ and $4R_2M_2$ for the tetrahedrons and one R_2M_4 for the octahedron. Five sites are located within the RM_2 units, six ones belong to the RM_5 unit and the two remaining sites lie on the boundary plane between both units (Table 2). All these different deuterium sites have been tested for the refinement of the crystal structure of the present compounds. Typical refined pattern is shown on Fig. 2 and results are given in Table 3.

The total refined D content for the lanthanum-based deuteride is equal to 12.5(6) D/formula unit (f.u.) and in good agreement with the 12.8 D/f.u. obtained from volumetric measurements. The crystal structure shows significant occupancy factors for eight deuterium sites: $6c_3$, $18h_3$, $18h_6$, $36i_1$, within the RM_2 units, $6c_4$, $18h_5$ and $36i_2$ within the RM_5 ones and the site $18h_2$. The case of this latter site is peculiar since it is expected to lie just on the plane in between the two RM_i ($i = 2$ or 5) units. However, this boundary is defined by the z position of the atom Ni_3 ($z_{Ni_3} = 0.0815(1)$). As the deuterium atom lying in the $18h_2$ site is just above this plane ($z_{18h_2} = 0.091(1)$), it was then assumed that this atom belongs to the RM_2 unit. Accordingly, it was found that 6.4(2) D/f.u. are located within the RM_5 units whereas 3.0(2) D/f.u. are in the RM_2 ones. From the value of z_{Ni_3} , one can also obtain the relative volume expansion of the units RM_5 and RM_2 , respectively. The results are given in Table 1 and a mean volume expansion about ~26% is

Table 2

Available crystallographic sites for hydrogen atoms in the PuNi₃-type structure (space group $R\bar{3}m$) and equivalent positions in the CaCu₅-type (space group $P6/mmm$) or MgZn₂-type (space group $P6_3/mmc$)

Structure blocks	Wyckoff position	Site symmetry	Equivalence in the RM_2/RM_5 systems	
RM_2 units	$6c_1$	T- RM_3	MgZn ₂ -type	$4f$
	$6c_3$	T- M_4		$4e$
	$18h_3$	T- R_2M_2		$12k_1$
	$18h_6$	T- RM_3		$12k_2$
	$36i_1$	T- R_2M_2		$24l$
RM_5 or RM_2 units depending of z_{Ni_3}	$18h_1$	T- R_2M_2	CaCu ₅ - or MgZn ₂ -type	$6m$ or $6h_1$
	$18h_2$	T- R_2M_2		$6m$ or $6h_2$
RM_5 units	$6c_2$	T- M_4	CaCu ₅ -type	$4h$
	$6c_4$	T- M_4		$4h$
	$9e_1$	O- R_2M_4		$3f$
	$18h_4$	T- RM_3		$12o$
	$18h_5$	T- RM_3		$12o$
	$36i_2$	T- RM_3		$12n$

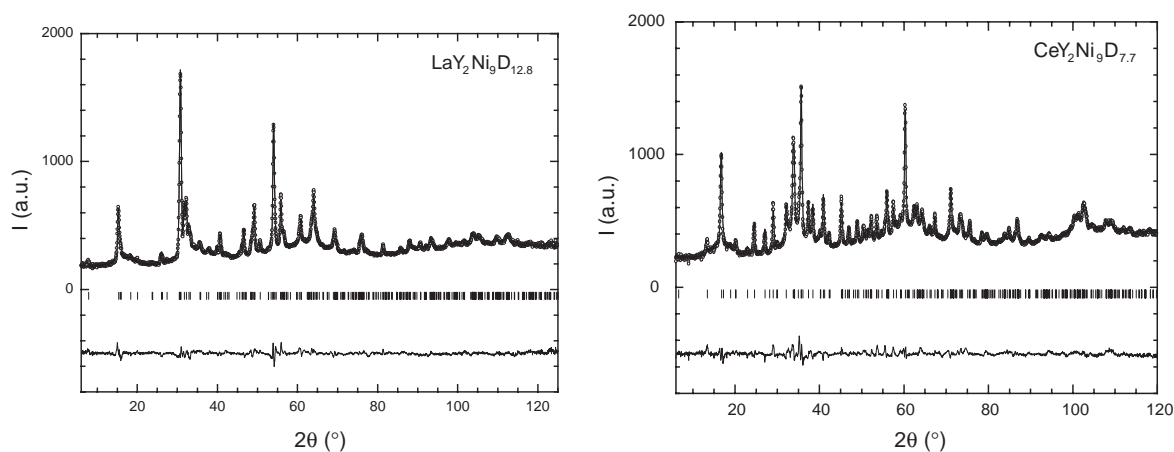


Fig. 2. Refined diffraction patterns of LaY₂Ni₉D_{12.8} (left) and CeY₂Ni₉D_{7.7} (right). Observed (dots), calculated (solid line) and difference curves (below) are shown. Vertical bars correspond to hkl line positions. The wavy background comes from the silica tube container and was linearly interpolated in the refinement.

observed for each unit what is in good agreement with an absorption rate of about 1 D/metal atom.

Significant differences are found between the nature and the occupancy factors of the sites occupied for the cerium compound. As a main feature, no deuterium is found within the RM_5 blocks of the cerium-based deuteride. Within the RM_2 units, four sites are occupied ($6c_1$, $6c_3$, $18h_6$ and $36i_1$). Additionally, few amount of deuterium is found in the site $18h_1$. Again this site is expected to be at the boundary between the two RM_i units but according to its z position ($z_{18h_1} = 0.077(2)$), above the plane defined by the atom Ni₃ ($z_{Ni_3} = 0.0651(1)$), it is accounted as lying within the RM_2 unit. This leads to an overall value of 7.9(5) D/f.u. very close to the value measured by solid-gas process (7.7 D/f.u.). Only 3 sites ($6c_3$, $18h_6$ and $36i_1$) are in common with the lanthanum-based deuteride. As for the La compound, the partial volume expansions for each

RM_i units are reported in Table 1. Beside a small volume contraction observed for the RM_5 unit of CeY₂Ni₉D_{7.7}, a huge volume expansion (up to 47%) is obtained for the RM_2 blocks in agreement with the exclusive hydrogen occupation of the sites within this unit. It is worth to note that during the neutron data refinement, isotropic displacement parameters do not lead to reliable refinement and that significant improvements were achieved by using anisotropic beta factors. This was particularly true for the cerium compound in agreement with the sharply anisotropic cell volume expansion observed upon hydrogenation. Refined values for the beta's parameters are given in Table 4 for both compounds. Moreover, despite the fact that the inter-metallic sublattice is preserved upon deuterium loading, a very large isotropic displacement parameter was first obtained for the atom Ni₁ located in the $3b$ ($0,0,\frac{1}{2}$) position. Improvement could be achieved by refining the

Table 3
Structural parameters for LaY₂Ni₉D_{12.8} and CeY₂Ni₉D_{7.7} (*f* stands for fixed parameter)

Atom	Site	LaY ₂ Ni ₉ D _{12.8}	CeY ₂ Ni ₉ D _{7.7}
R ₁ , Y ₁	3 <i>a</i>	$N_Y = 0.22(f)$	$N_Y = 0.62(f)$
R ₂ , Y ₂		$N_{La} = 0.78(f)$	$N_{Ce} = 0.38(f)$
Ni ₁	6 <i>c</i>	$z = 0.1397(3), N_Y = 0.89(f)$	$z = 0.1265(4), N_Y = 0.69(f)$
Ni ₁ '		$N_{La} = 0.11(f)$	$N_{Ce} = 0.31(f)$
Ni ₂	3 <i>b</i>	$(0, 0, \frac{1}{2}), N = 1$	—
	6 <i>c</i> '	—	$z = 0.5190(2), N = 0.50$
Ni ₃	6 <i>c</i>	$z = 0.3293(2)$	$z = 0.3342(1)$
	18 <i>h</i>	$x = 4958(4), z = 0.0815(1)$	$x = 0.5030(4), z = 0.0651(1)$
<i>RM</i> ₂ units			
D ₁ (<i>RM</i> ₃)	6 <i>c</i> ₁	—	$z = 0.7637(5), N = 0.88(3)$
D ₂ (<i>M</i> ₄)	6 <i>c</i> ₃	$z = 0.565(2), N = 0.24(2)$	$z = 0.563(3), N = 0.30(8)$
D ₃ (<i>R</i> ₂ <i>M</i> ₂)	18 <i>h</i> ₁	—	$x = 0.115(5), z = 0.077(2), N = 0.15(1)$
D ₃ (<i>R</i> ₂ <i>M</i> ₂)	18 <i>h</i> ₂	$x = 0.856(5), z = 0.091(1), N = 0.26(1)$	—
D ₄ (<i>R</i> ₂ <i>M</i> ₂)	18 <i>h</i> ₃	$x = 0.233(8), z = 0.887(1), N = 0.11(1)$	—
D ₅ (<i>RM</i> ₃)	18 <i>h</i> ₆	$x = x_{18h3}, z = -z_{18h3}, N = 0.07(1)$	$x = 0.286(9), z = 0.093(1), N = 0.22(3)$
D ₆ (<i>R</i> ₂ <i>M</i> ₂)	36 <i>i</i> ₁	$x = 0.460(3), y = 0.992(3), z = 0.1404(4), N = 0.240(7)$	$x = 0.464(3), y = -0.005(2), z = 0.1602(4), N = 0.274(8)$
Total <i>RM</i> ₂	D/f.u.	3.02 (18)	3.94 (27)
<i>RM</i> ₅ units			
D ₇ (<i>M</i> ₄)	6 <i>c</i> ₄	$z = 0.615(2), N = 0.33(2)$	—
D ₈ (<i>RM</i> ₃)	18 <i>h</i> ₅	$x = 0.831(3), z = 0.0655(6), N = 0.52(2)$	—
D ₉ (<i>RM</i> ₃)	36 <i>i</i> ₂	$x = 0.478(4), y = 0.002(3), z = 0.0196(5), N = 0.217(6)$	—
Total <i>RM</i> ₅	D/f.u.	6.43 (23)	—
Total D content	D/f.u.	12.5 (6)	7.9 (5)
Cell parameters	<i>a</i> (Å)	5.3957(5)	4.8724(3)
	<i>c</i> (Å)	26.885(3)	31.312(4)
No. of parameters		49	39
No. of reflections		339	331
Space group <i>R</i> $\bar{3}m$	<i>R</i> _p (%)	2.2	2.8
	<i>R</i> _{op} (%)	2.7	3.5
	<i>R</i> _{Bragg} (%)	4.9	8.8
	χ^2	3.7	7.3

Table 4
Anisotropic displacement parameters β_{ij} ($\times 10^{-4}$) for LaY₂Ni₉D_{12.8} and CeY₂Ni₉D_{7.7}

LaY ₂ Ni ₉ D _{12.8}	β_{11}, β_{22}	β_{33}	β_{12}	$\beta_{13}, -\beta_{23}$
La, Y	354(30)	13(1)	177(30)	0
Ni ₁ , Ni ₂	193(16)	3.9(5)	97(16)	0
Ni ₃	175(9)	7.6(4)	107(10)	7(1)
D 6 <i>c</i> ₃ , 6 <i>c</i> ₄	358(145)	12(4)	180(145)	0
D 18 <i>h</i> ₂ , 18 <i>h</i> ₃ , 18 <i>h</i> ₅ , 18 <i>h</i> ₆ , 36 <i>i</i> ₁ , 36 <i>i</i> ₂	208(36)	13(1)	129(52)	1(4)
CeY ₂ Ni ₉ D _{7.7}				
Ce, Y	607(37)	23(2)	304(37)	0
Ni ₁ ', Ni ₂	90(13)	3.3(4)	45(13)	0
Ni ₃	66(6)	12.4(4)	50(7)	-6(1)
D 6 <i>c</i> ₁ , 6 <i>c</i> ₃	221(34)	30(2)	110(34)	0
D 18 <i>h</i> ₁ , 18 <i>h</i> ₆ , 36 <i>i</i> ₁	221(34)	30(2)	110(34)	38(5)

z position of this atom (shifting in 6*c*' position with $z = 0.5194(2)$), but assuming an occupancy factor of 50% to keep constant the overall composition. This

atom split along the *c*-axis into two pseudo-atoms with half occupancy on both sides of the initial 3*b* $(0, 0, \frac{1}{2})$ position.

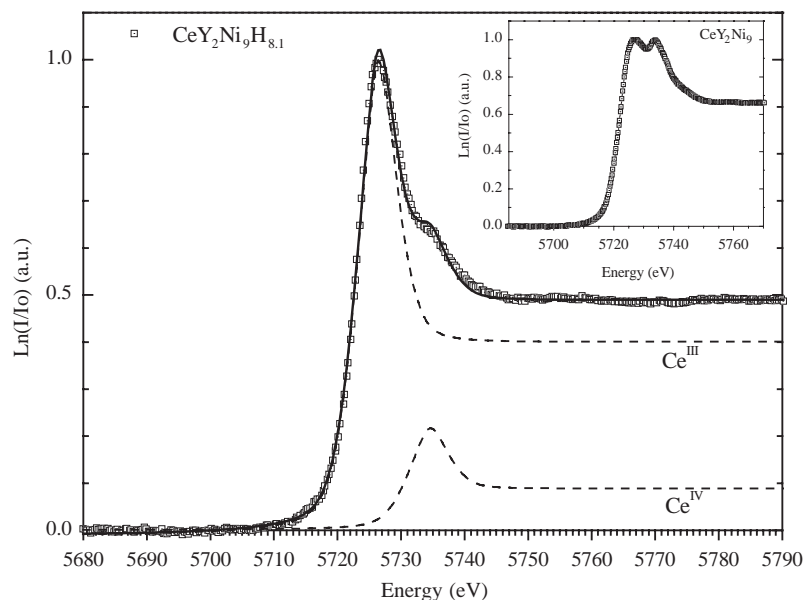


Fig. 3. L_{III} edge of cerium for the deuteride $CeY_2Ni_9D_{8.1}$ for which two different valence states are observed. The full line corresponds to the refinement assuming the two components (Ce^{III} at 5725 eV and Ce^{IV} at 5734 eV) and the intermediate valence is estimated $\nu = 3.19(1)$. The inset shows the L_{III} edge measured earlier for the metallic compounds [10].

Cerium atoms are known to be in intermediate valence state in these intermetallic compounds. Previous XAS measurements [10] leads to a valence $\nu = 3.36(6)$, a value commonly observed in other CeM_5 -type compound [25]. According to the peculiar behaviour observed for the cerium-based deuteride, L_{III} edge of Ce was also measured by XAS for a fully loaded deuteride with a deuterium composition ($CeY_2Ni_9D_{8.1}$) very close to that of the sample measured by NPD (7.8 D/f.u.). The data are shown in Fig. 3. The main component of the spectrum belongs to Ce^{III} at 5725 eV but a significant shouldering is observed at 5734 eV attesting that it exists also as a component in the valence state Ce^{IV} . The refinement assuming these two components leads to an intermediate value estimated equal to $\nu = 3.19(1)$.

4. Discussion

The ternary compound LaY_2Ni_9 absorbs more than 1 D/metal, a value very close to the mean one generally observed in other metallic hydrides. Deuterium is equally distributed within the RM_i units and the cell volume expansion is isotropic. The overall $\delta V/V_s$ (around 26%) are in agreement with value observed in metallic hydrides. If one looks to the nature of the deuterium occupied sites, it is worth to note that they are very similar to those reported for the binary compounds: $4h$, $6m$, $12n$ and $12o$ for the $CaCu_5$ -type (hexagonal space group $P6/mmm$) and $6h_2$, $12k_1$, $12k_2$ and $24l$ for the $MgZn_2$ -type (hexagonal space group $P6_3/mmc$). The only exception is for the site $6c_3$

corresponding to the site $4e$ in the $MgZn_2$ -type structure ($M4$ tetrahedron) which is not expected to be occupied. Similarly, the deuterium contents found in the RM_5 and RM_2 units (6.4 and 3.0 D/f.u., respectively) are in good agreement with the values reported for the compounds $LaNi_5H_{6.7}$ and $Y_{0.95}Ni_2H_{2.6}$. Therefore, as it was postulated in a previous paper, the capacity for H absorption of the ternary compound LaY_2Ni_9 can be well predicted on the basis of the capacities of the building binary RM_i units.

Very different behaviour is obtained for the cerium compound. Deuterium content is much lower and cell volume expansion is strongly anisotropic. All deuterium atoms are located within the RM_2 units. Accordingly the volume of the RM_5 one is almost unchanged whereas that of the RM_2 unit increases for 47%. This is one of the largest value ever observed upon hydrogenation in intermetallic compounds. Most of the deuterium occupied sites are similar to those reported for the $MgZn_2$ -type binary compounds: $6h_1$, $12k_1$, $12k_2$ and $24l$. However, the sites $6c_1$ and $6c_3$ corresponding to the site $4f$ ($T-RM_3$) and $4e$ ($T-M_4$) are also significantly occupied leading to a rather large capacity for the RM_2 unit: 3.9(3) D/f.u.

The peculiar case of the nickel Ni_1 should be mentioned. This atom was affected by a very large displacement parameter and significant improvement in the refinement could be obtained when splitting the $3b$ position into a $6c'$ one with half-occupancy factor in order to keep the overall nickel stoichiometry constant. It is worth to note that Ni_1 lies in the middle plane of the RM_2 unit where all deuterium is located. This atom is therefore strongly affected by deuterium neighbours that

Table 5
First Ni shell surrounding Ce atoms in CeY₂Ni₉ and CeY₂Ni₉D_{7.7}

First Ni shell	CeY ₂ Ni ₉	CeY ₂ Ni ₉ D _{7.7}
Ce ₁ in 3 <i>a</i> (<i>RM</i> ₅ unit)	6 Ni ₂ at 2.87 Å	6 Ni ₂ at 2.81 Å
Ce ₂ in 6 <i>c</i> (<i>RM</i> ₂ unit)	6 Ni ₃ at 2.85 Å	$\left. \begin{array}{l} 3\text{Ni}_1 \text{ at } 2.89 \text{ \AA} \\ 6\text{Ni}_1 \text{ at } 3.10 \text{ \AA} \end{array} \right\} \text{weighted } d_{\text{Ni}} = 3.06 \text{ \AA}$

For Ce₂ in the deuteride the weighted distance has been calculated assuming half-occupancy factor for Ni₁.

is not the case for the two other nickel atoms lying either within the *RM*₅ unit (Ni₂) or at the boundary between both *RM*_{*i*} units (Ni₃). Similarly, reliable refinements could be obtained only with anisotropic displacement parameters. This fact can be related to the very anisotropic behaviour observed upon hydrogenation leading to volume expansion along the *c*-axis only.

According to previous works [25], it is expected that the valence state of cerium changes upon hydrogenation. Indeed, the value $\nu = 3.36(6)$ observed for the intermetallic compound CeY₂Ni₉ [10] decreases to $\nu = 3.19(1)$ for the fully charged hydride. However, this decrease is less than that observed for CeNi₅-type compounds as reported by Paul-Boncour et al. [25] who obtained a value of $\nu = 3.10$ for a fully charge hydride (i.e. a decrease of -0.26 for all cerium atoms occupying the unique site 1*a* in *P6/mmm* space group). This fact can be interpreted on the basis of the current structural determination. As only *RM*₂ units are hydrogenated, only Ce atoms in the 6*c* position change their valence state whereas those lying on the 3*a* site remain unchanged. As previously published [10], this compound is closer to a pseudo-binary system than a ternary one. The average composition of the *RM*₂ units is equal to Ce_{0.31}Y_{0.69}Ni₂, which correspond to 62% of the Ce atoms on site 6*c* (i.e. atomic position *R*₂). Accordingly, the mean valence for the hydrogenated compound can be calculated assuming two components: $\nu = 3.36 \times 0.38 + 0.62 \times 3.10 = 3.20$ to be compared to the value of 3.19 measured by XAS. Therefore, this metallic hydride should be considered as a mixed intermediate valence compound since two cerium sites (3*a* and 6*c*) coexist with two different intermediate valence states (3.36 and 3.10, respectively) within the same compound. This hypothesis is also supported by the distance calculation for the first nickel shell surrounding the Ce atoms (Table 5). In the intermetallic, this shell consists of 6 Ni atoms at about 2.86 Å for both Ce in sites 3*a* and 6*c*. In the deuteride, Ce₁ in 3*a* is surrounded by 6 Ni₃ atoms at 2.81 Å. For Ce₂ in 6*c* a redistribution appears leading to 3 Ni₁ at 2.89 Å and 6 Ni₃ at 3.10 Å. Assuming half occupancy for Ni₁, this leads to a mean value of 3.06 Å. Then, Ni first neighbour distances are slightly shorter for Ce₁ and significantly larger for Ce₂ in the deuteride by comparison with the intermetallic.

To our knowledge, such heterogeneous mixed valent systems have been already observed for Sm in SmRuSn₃ [26] or for Yb in Yb₅Si₃, Yb₂Pt₃Sn₅ or YbPd₃S₄ [27–29] but it was never reported before for a cerium compound. Such localised effect will of course play a role in the volume expansions. When decreasing its valence state, the metallic atomic radius of cerium increases and such effect is added to that related to hydrogen absorption within the *RM*₂ unit leading to the huge value of $\Delta V/V$ (47%) observed for this unit. However, such effect is rather limited compared to hydrogen absorption since the radius increase related to valence change cannot exceed 5%. Further investigations concerning the relation between valence state and hydrogen composition in Ce*M*₃-type compounds are in progress and will be published elsewhere.

As already mentioned, few crystal structures have been reported so far in the literature for PuNi₃-type metallic hydrides. Burnasheva et al. [14] reported on the occupation of sites 18*h*₁ and 6*c*₁ for HoNi₃D_{1.8} in agreement with the structure observed here for CeY₂Ni₉D_{7.7}. However, this latter structure is significantly different than that found for CeNi₃D_{2.7} for which an orthorhombic symmetry lowering into *Pmcn* space group is observed [16,17]. However, the authors reported that deuterium is located exclusively within the *RM*₂ units as it is in the present case. Similarly, Benham et al. [18] observed significant uniaxial volume expansion for YCo₃D_{*x*} ($1 \leq x \leq 1.9$), a behaviour attributed to the filling of the *RM*₂ units only.

5. Conclusions

The crystal structure of the two deuterides LaY₂Ni₉D_{12.8} and CeY₂Ni₉D_{7.7} have been determined. It is observed that the lanthanum compound exhibits an isotropic behaviour with occupation of both *RM*_{*i*} units, whereas for the cerium compound anisotropy is related to the exclusive occupation of *RM*₂ units by deuterium. From these results, it can be established that:

- Isotropic cell volume expansion is related to full hydrogenation of both *RM*_{*i*} units whereas anisotropic behaviour is obtained when hydrogen occupies crystallographic sites in the *RM*₂ unit only.

- Huge volume expansion of RM_2 units observed for cerium compounds is due to a combination of both volume increase (due to deuterium absorption) and valence change. Moreover, heterogeneous mixed valence state is observed for the first time in a Ce-based metallic deuteride (hydride).
- Capacities observed in $PuNi_3$ -type metallic hydrides can be well explained on the basis of the related binary compounds forming the RM_i units as it was already postulated in our previous paper [10]. On that basis, new ternary compounds can be foreseen from the intergrowth of RM_5 - and RM_2 -type units adopting the $PuNi_3$ -type structure. In all case, the choice of the binary units should to be made with the aim to take profit from the individual properties of RM_5 - and RM_2 -type units in order to obtain compounds with enhance behavior towards hydrogen absorption.

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