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Electronic and crystallographic properties of the system $CeY_2Ni_9D_x$ $(0 \leq x \leq 8.7)$ measured by X-ray absorption spectroscopy

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Abstract

The electronic and crystallographic properties of $CeY_2Ni_9D_x$ $(0 \leq x \leq 8.7\mathrm{D/f.u.})$ have been investigated by X-ray absorption spectroscopy (XAS). The $PuNi_3$-type structure (space group $R\bar{3}m$) is described as a stacking of RM_2 and RM_5 units (R: Y, Ce; M: Ni). Hydrogen occupies the RM_2 units only. The Ce-L_{III} and Ni–K edges have been measured by XAS as a function of hydrogen uptake. A heterogeneous mixed valence state is reported for Ce in the hydride and related to differences in deuterium site occupancies. Huge anisotropic volume expansion is observed and is related to hydrogen absorption and valence change of Ce.

Keywords: Intermetallics; Hydrogen storage materials; Gas–solid reactions; Crystal structure and symmetry; EXAFS; X-ray and neutron diffraction; Anisotropy

1. Introduction

Intermetallic compounds RM_n (R = rare earth or transition metal, M = transition metal, $n = 1, 2, 3$ or 5) absorb reversibly and safely hydrogen near ambient conditions. These compounds are potential materials for energy storage [1–4]. New interests are now devoted to RM_3-type compounds with the recent discovery of ternary systems like RM_2Ni_9 (M = Mg, Ca, Ti or Y) [5–9]. These compounds crystallize in the $PuNi_3$-type rhombohedral structure ($R\bar{3}m$ space group) [10] and are described as a stacking of $CaCu_5$-type and $MgZn_2$-type units [11]. For R = Ce, hydrogenation of RM_3-type compounds shows strong anisotropic behavior and $CeNi_3H_3$ exhibits a huge uniaxial expansion ($\delta a/a = -0.80\%$, $\delta c/c = 30.76\%$) [12]. The structure of $CeNi_3D_{2.7}$ was described by Yartys et al. [13] in an orthorhombic symmetry ($Pmcn$ space group) with deuterium located in the $CeNi_2$ units. Similarly, the crystal structure of $CeY_2Ni_9D_{7.7}$ has been determined recently [14]. The intermetallic compound is described like a pseudo-binary one ($Ce_{0.33}Y_{0.66}Ni_3$ [8]) as Y and Ce atoms are randomly distributed over sites $3a$ and $6c$. The deuteride exhibits strong anisotropy ($\delta a/a = -2.0\%$, $\delta c/c = 27.6\%$) related to the exclusive occupation of RM_2 units by deuterium and Ce atoms in intermediate valence state (IVS) [8,15]. According to this peculiar behavior, the electronic states of Ce have been investigated by XAS as a function of the hydrogen uptake.

2. Experimental

CeY_2Ni_9 was prepared as described in [8]. Powder X-ray diffraction (XRD) and electron probe micro-analysis (EPMA) were used to check composition and homogeneity. XRD patterns were refined using the program FULLPROF [16]. XAS measurements have been performed at DCI (LURE, Orsay, France) by transmission mode on the beam lines D44 and D21 in a special tight cell (see [15] for details). Data have been collected at room temperature on fine powders sieved below 20 μm and dispersed on a Kapton^{TM} foil. Energies were tuned with a Si monochromator from 5675–5790 and 8300–8400 eV at the Ce-L_{III} and Ni–K edges, respectively. The edges were refined by a convolution of Lorentzian, Gaussian and arctangent functions according to [17]. The EXAFS data were analyzed using the method described in [18,19].

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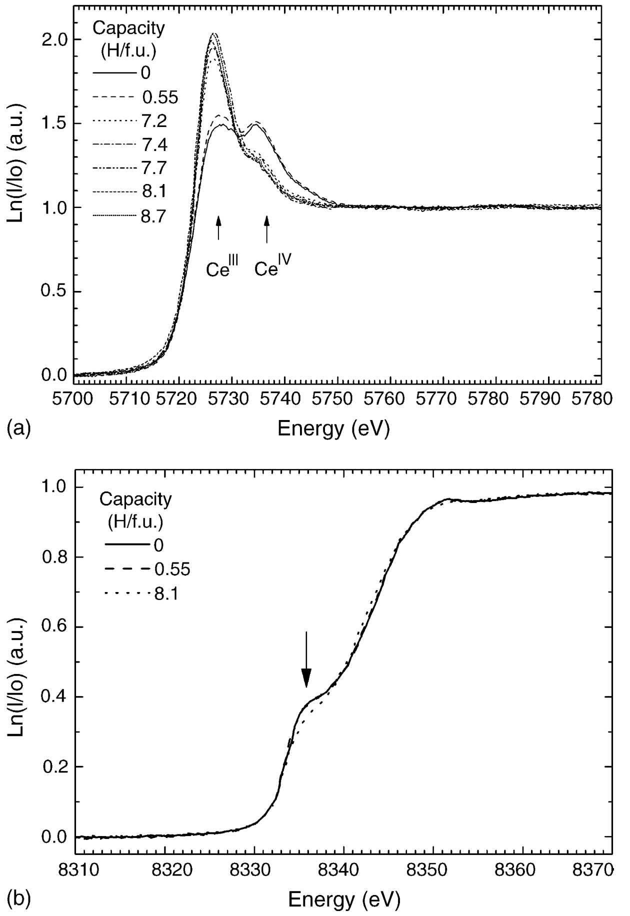

Fig. 1. Evolution of the L_{III} edge of cerium (a) and K edge of nickel (b) for the system $CeY_2Ni_9H_2$ as a function of the state of charge in the range 0–8.7 H/f.u.

3. Results and discussion

In a previous work [8], the IVS $v = 3.36(6)$ was reported for the compound CeY_2Ni_9. When loaded with hydrogen, significant changes are observed (Fig. 1a). Between $x = 0$ and 0.55, two components are clearly visible with few changes as a function of x. The first component at 5725 eV belongs to Ce^{III} and the second one at 5734 eV to Ce^{IV}. When reaching the β branch, the Ce^{IV} component decreases drastically involving a diminution of the IVS down to $v = 3.17(1)$ for $x = 8.7$ H/f.u. Little evolution is observed between $x = 7.2$ and 8.7 H/f.u. and the change occurs mainly during the α–β transformation (Fig. 2).

The Ni–K edge evolution is shown in Fig. 1b for $x = 0$, 0.55 and 8.1 H/f.u. Few changes are observed in the α branch. The main feature concerns the decrease of the prepeak intensity around 8333 eV when crossing the two-phase domain. Such effect, already observed for $LaNi_5$-type compounds [15,20,21], is attributed to the transition from the 1s core level to the empty 4p states strongly hybridized with the 3d ones. The prepeak intensity decrease can be related to the filling of the Ni 4p–3d states by hydrogen electrons.

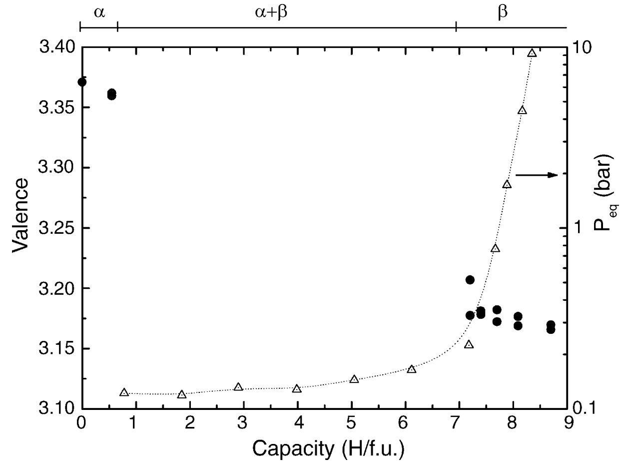

Fig. 2. Evolution of the IVS (full circle, left scale) at the L_{III} edge of Ce for the system $CeY_2Ni_9H_2$ as a function of the capacity. The open triangles represents the equilibrium pressure (right scale) measured at room temperature for the same sample.

According to our works, the IVS of Ce decreases from $v = 3.37(1)$ to $v = 3.17(1)$ upon hydrogenation. However, this decrease is less important than that observed for a fully hydrogen loaded $CeNi_5$-type compound ($v = 3.10$) [15]. This can be understood if one considers that only RM_2 units are hydrogenated here. Then, only Ce atoms lying in the 6*c* position change their valence state whereas those lying on the 3*a* site remain practically unchanged. The average composition of the RM_2 units is $Ce_{0.31}Y_{0.69}Ni_2$ [8] which corresponds to $n_{6c} = 62\%$ (n_i: at.% of Ce on site *i*). Assuming that the valence of Ce_{3a} is unchanged ($v_{3a} = 3.37$), the valence for Ce_{6c} can be estimated as: $v_{6c} = (v - n_{3a}v_{3a})/n_{6c} = 3.05$. This value agrees fairly well with that reported for $CeNi_2H_4$ ($v = 3.03$) [22] at a concentration close to that observed here for the RM_2 block (3.94 H/RM_2). Such a valence change induces an atomic radius increase for Ce_{6c} atoms from 1.71 to 1.81 Å. Therefore, the huge volume increase observed for the RM_2 units (47%) should be decomposed in two parts: hydrogen loading and valence change of Ce. However, despite the additional volume effect attributed to the Ce valence change (about 5%), the whole volume increase remains far above what is commonly observed in metallic hydrides (around 20–30%). Magnetic measurements are foreseen for a better understanding of the electronic states of Ce as a function of *x*.

Correlatively, the RM_5 unit volume remains practically unchanged as there is no hydrogen lying in this unit. Such an empty unit does not allow any expansion in the basal plane involving strong anisotropic elongation of the RM_2 unit along the *c*-axis. A small contraction of the *a* parameter is even observed. Such negative effect can be understood as a response of the structure to the huge elongation along the vertical axis: pulling along the *c*-axis induces a small reduction in the *ab* basal plane (Table 1).

Table 1
Cell parameters and valence state of Ce for $CeYNi_9D_{7.7}$ and for the RM_5 and RM_2 units

Cell parameters				$CeYNi_9H_{7.7}$				RM_5 unit			RM_2 unit		
x	a	c	V	$\delta a/a$	$\delta c/c$	$\delta V/V$	v_{Ce}	$\delta c/c$	$\delta V/V$	v_{Ce}	$\delta c/c$	$\delta V/V$	v_{Ce}
D/f.u.	(Å)	(Å)	($Å^3$)	%	%	%		%	%	($3a$)	%	%	($6c$)
0	4.971	24.54	525.1	–	–	–	3.37	–	–	3.37	–	–	3.37
7.7	4.872	31.31	643.7	−2.0	27.6	22.6	3.17	1.3	−2.7	3.37	53.1	47.1	3.05

Table 2
EXAFS results at the Ni–K edge at room temperature for CeY_2Ni_9 and $CeY_2Ni_9H_{8.1}$

Ni–K edge	N_1	d_1 (Å)	σ_1 (Å)	N_2	d_2 (Å)	σ_2 (Å)	χ
$CeYNi_9$	6.67	2.47	0.088	0.67	3.01	0.092	0.0018
$CeYNi_9H_{8.1}$	4.67	2.43	0.094	2.33	2.99	0.139	0.0032

The coordination numbers N_i were fixed according to the crystal structure results. χ represents the goodness of fit.

The radial distribution functions (RDF) measured at the Ni–K edge for $x = 0$, 0.55 and 8.1 H/f.u. are shown in Fig. 3. The spectra can be simulated considering the distance distributions obtained from the crystallographic structures [8,14]. The main feature of the RDF is seen in the peak located around 2.4 Å attributed to the first Ni–Ni shells. Increasing the hydrogen content induces a redistribution of the number of neighbors and a reduction of the Ni–Ni distances (Table 2) with a sharp decrease of the intensity. Such behavior can be explained again by the partial filling of hydrogen within the cell. As the RM_5 unit is hydrogen-free, its volume remains almost constant keeping the same Ni–Ni distances (or even slightly shorter due to the small volume reduction of this unit). On the contrary, due to the large volume expansion of the RM_2 unit, the Ni–Ni distances are expanded along the c-axis but remain unchanged within the ab plane. Accordingly, the first peak (first Ni neighbors) at about 2.4 Å is not shifted toward larger values but diminishes in intensity as the number of nearest neighbor decreases. The same statement can be applied for the second shell (N_2) despite the vanishing of the EXAFS signal for larger distances.

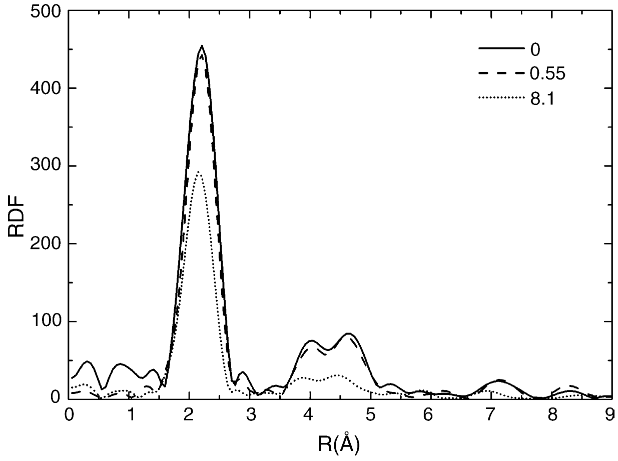

Fig. 3. Partial radial distribution function around the nickel atoms (Ni–K edge) for the system CeY_2Ni_9–H_2 as a function of the hydrogen content at room temperature.

4. Conclusions

The electronic properties of cerium and nickel have been obtained by XAS. $CeY_2Ni_9D_x$ is considered as a mixed intermediate valence compound since two cerium sites coexist with two different IVS's (3.37 and 3.05) in the same compound. This hypothesis is supported by the EXAFS analysis around the Ni atoms. The heterogeneous mixed valence state is observed here for the first time in a Ce-based metallic hydride.

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References

[1] L. Schlapbach, Hydrogen in Intermetallic Compounds I, vol. 63, Springer-Verlag, Berlin, 1988, p. 350.
[2] L. Schlapbach, Hydrogen in Intermetallic Compounds II, vol. 67, Springer-Verlag, Berlin, 1992, p. 328.
[3] F. Cuevas, J.-M. Joubert, M. Latroche, A. Percheron-Guégan, Appl. Phys. A 72 (2001) 225–238.
[4] J.-M. Joubert, M. Latroche, A. Percheron-Guégan, MRS Bull. 27 (9) (2002) 694–698.
[5] K. Kadir, I. Uehara, T. Sakai, J. Alloys Compd. 257 (1997) 115–121.
[6] J. Chen, H.T. Takeshita, H. Tanaka, N. Kuriyama, T. Sakai, I. Uehara, M. Haruta, J. Alloys Compd. 302 (1/2) (2000) 304–313.
[7] K. Kadir, T. Sakai, I. Uehara, J. Alloys Compd. 302 (1/2) (2000) 112–117.
[8] M. Latroche, R. Baddour-Hadjean, A. Percheron-Guégan, J. Solid State Chem. 173 (1) (2003) 236–243.
[9] B. Liao, Y.Q. Lei, G.L. Lu, L.X. Chen, H.G. Pan, Q.D. Wang, J. Alloys Compd. 356/357 (2003) 746–749.
[10] D.T. Cromer, C.E. Olsen, Acta Cryst. 12 (1959) 689–694.
[11] B.D. Dunlap, P.J. Viccaro, G.K. Shenoy, J. Less-Common Met. 74 (1980) 75–79.
[12] R.M. Van Essen, K.H.J. Buschow, J. Less-Common Met. 70 (1980) 189–198.
[13] V.A. Yartys, O. Isnard, A.B. Riabov, L.G. Akselrud, J. Alloys Compd. 356/357 (2003) 109–113.

[14] M. Latroche, V. Paul-Boncour, A. Percheron-Guégan, J. Solid State Chem. 177 (7) (2004) 2541–2548.

[15] V. Paul-Boncour, J.-M. Joubert, M. Latroche, A. Percheron-Guégan, J. Alloys Compd. 330–332 (2002) 246–249.

[16] J. Rodríguez-Carvajal, in: Proceedings of the XV Congress of International Union of Crystallography, Satellite Meeting on Powder Diffraction Toulouse, France, 1990, p. 127.

[17] J. Röhler, in: K.A. Gschneidner Jr., L. Eyring, S. Hüfner (Eds.), Handbook of the Physics and Chemistry of Rare Earths, vol. 10, North-Holland/Elsevier Science, 1987, p. 453.

[18] D. Bonnin, P. Kaiser, J. Desbarres, C. Fretigny, Structures fines d'absorption des rayons X, Ecole du CNRS, Garchy, France, 1988, p. 127.

[19] V. Paul-Boncour, G. Wiesinger, C. Reichl, M. Latroche, A. Percheron-Guégan, R. Cortes, Physica B 307 (1–4) (2001) 277–290.

[20] T. Suenobu, H. Sakaguchi, G.-Y. Adachi, H. Kanai, S. Yoshida, J. Alloys Compd. 190 (2) (1993) 273.

[21] S. Mukerjee, J. McBreen, J.J. Reilly, J.R. Johnson, G. Adzic, K. Petrov, M.P.S. Kumar, W. Zhang, S. Srinivasan, J. Electrochem. Soc. 142 (7) (1995) 2278–2286.

[22] V. Paul-Boncour, A. Percheron-Guégan, J.-C. Achard, in: L.C. Gupta, S.K. Malik (Eds.), Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions, Plenum Press, New York, 1987, p. 647.