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# Crystallographic and hydriding properties of the system $La_{1-x}Ce_xY_2Ni_9$ ($x_{Ce}=0$, 0.5 and 1)

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## Abstract

The structural properties of the system $La_{1-x}Ce_xY_2Ni_9$ with $x_{Ce}=0$, 0.5 and 1 have been investigated by electron probe microanalysis, powder X-ray diffraction and absorption spectroscopy. The compound $LaY_2Ni_9$ adopts a rhombohedral structure of $PuNi_3$-type ($R$-3$m$ space group, $Z = 3$). It can be described as an intergrowth between $RM_5$ (Haücke phase) and $RM_2$ (Laves phase) type structures. Among the two available crystallographic sites for $R$ atoms, lanthanum occupies preferentially the site 3$a$ leading to a partially ordered ternary compound. Substitution by cerium involves anisotropic variations of the cell parameter with a decrease of **a** and an increase of **c** leading to an overall cell volume reduction. Increasing cerium content does not induce any symmetry change but leads to a statistical distribution of the rare earths over the two sites 3$a$ and 6$c$ involving an evolution toward a pseudo-binary compound. This behavior is related to the intermediate valence state of cerium observed by X-ray absorption spectroscopy. The hydriding properties of the two compounds $LaY_2Ni_9$ and $CeY_2Ni_9$ are described in relation with their crystallographic structure.

*Keywords:* $RM_5$; Hydrides; X-ray diffraction; X-ray absorption spectroscopy; Ordering

## 1. Introduction

Intermetallic compounds $RM_n$ ($R$= Y, rare earth, $M$=transition metal, $1\leqslant n\leqslant 5$) are able to store reversibly large amount of hydrogen and are therefore potential materials for energy storage. The $H_2$ absorption–desorption reaction can be performed either by solid-gas or electrochemical routes. It has allowed the development of competitive negative electrode materials to prepare Ni$M$H-type batteries [1] that now widely replace the NiCad ones in the huge market of portable goods. Most of the researches have been focused in the past on binary $RM_5$-, $RM_2$- and $RM$-type alloys. However, these systems still suffer from insufficient capacities, passivation, slow activation and corrosion [2].

To our knowledge, few works have been devoted to ternary compounds. Recently, Kadir et al. [3–6] reported on the $R$–Mg–Ni system ($R$= La, rare earth, Ca or Y) with atomic composition 1:2:9. They found that these compounds crystallize in an ordered variant of the $PuNi_3$-type rhombohedral structure ($R$-3$m$ space group). Among the two available sites 3$a$ and 6$c$ for elements $R$, a strong preference for site 3$a$ is observed whereas Mg is sited on site 6$c$. That leads to the conclusion that these compounds should be considered as fully ordered ternary compounds ($RMg_2Ni_9$) rather than pseudo-binary $RM_3$-type ones ($R_{0.33}Mg_{0.66}Ni_3$) since the repartition of $R$ and Mg is not random. In a matter of fact, the structure can be described as a stacking of $RNi_5$ (Haucke phase) and $MgNi_2$ (Laves phase) units following the scheme: $RNi_5 + 2\,MgNi_2 \rightarrow RMg_2Ni_9$ [7].

Following this scheme, the La–Y–Ni system has been investigated in the present work assuming the reaction: $LaNi_5 + 2YNi_2 \rightarrow LaY_2Ni_9$. Both $LaNi_5$ and $YNi_2$ are well known to react readily with gaseous hydrogen. The compound $LaNi_5$, which crystallizes in the hexagonal $CaCu_5$-type structure (Haucke phase), exhibits

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exceptional thermodynamical properties toward hydrogen absorption storing up to 6.6 H per formula unit (f.u.) [8]. However, its equilibrium pressure ($P = 1.7$ bar at room temperature) is too high for practical applications and the molecular mass of La implies a weight capacity limited to 370 mAh/g. The structural properties of $YNi_2$ have been studied in detail in the past [9,10]. It was shown that this Laves phase is in fact a non-stoichiometric compound with exact formulation $Y_{0.95}Ni_2$. The non-stoichiometry was explained by ordered vacancies distributed on the $Y$ sublattice and involving a symmetry reduction in space group $F$-43$m$. Van Essen and Buschow [11] have investigated the thermodynamical properties of the hydride. They found a solid gas capacity of 3.6 H/f.u. No plateau pressure was observed but the pressure-composition curve was found to increase almost linearly in the range $10^{-4}$ to 10 bar at 50°C indicating that the hydrogen content depends almost linearly on the pressure. More recently, the crystal structure of the deuteride $Y_{0.95}Ni_2D_{2.6}$ was studied by neutron diffraction [12]. From these authors, crystalline hydride can be obtained up to 2.6 D/f.u. at 1 bar and 25°C but any attempt to prepare a deuteride with higher deuterium content leads to a partial amorphization of the compound. Such behavior is commonly observed for $R_{1-x}Ni_2$ hydrides when increasing hydrogen content [13].

According to the thermodynamic properties reported for the binary compounds, the intergrowth between $LaNi_5$ and $YNi_2$ should lead to a compound having an equilibrium pressure close to atmospheric pressure at room temperature and a capacity of about 12 H/f.u. Following this scheme, the compound $LaY_2Ni_9$ has been prepared and studied in this work. Mischmetal is often used in industrial alloys for economical purpose since this mixture of light rare earths is cheaper than pure lanthanum. However it appears that mischmetal composition (and particularly the amount of cerium) is also of great importance for hydride properties [14]. For that reason, the possible replacement of lanthanum by cerium has also been studied and the influence of Ce substitution will be described from a structural and thermodynamical point of view.

## 2. Experimental section

The samples were prepared by induction melting of the pure components (3N purity) under vacuum in a water-cooled copper crucible. The samples were melted five times to ensure good homogeneity. They were then annealed at 750°C for 3 weeks and quenched to room temperature.

Metallographic examination and elemental analysis by electron probe micro-analysis (EPMA Camebax SX100) were performed to check the homogeneity of the alloys. The powder X-ray diffraction experiments (XRD) were performed at room temperature on a Bruker AXS D8 $\theta$–$\theta$ diffractometer using Cu$K\alpha$ radiation (Bragg–Brentano geometry, $2\theta$ range 20–120°, step size 0.02°, backscattered rear graphite monochromator). All the patterns were refined with the Rietveld method using the program FULLPROF [15]. Density measurements were obtained with a Accupyc 1330 pycnometer from Micromeretics.

X-ray absorption spectroscopy (XAS) measurements have been performed by transmission mode on the beam line D21 at DCI (LURE). Data were collected at the Ce–$L_{III}$ edge between 5675 and 5775 eV with a flat Si 311 crystal monochromator. The measurements were done at room temperature on samples made of fine powders sieved below 20 μm and dispersed on a Kapton™ foil.

$P$–$C$ isotherm (PCI) curves were measured at room temperature with a Sievert's-type apparatus using calibrated and thermalized volumes.

## 3. Results

### 3.1. Structural properties

### 3.1.1. The compound $LaY_2Ni_9$

First attempt to prepare the compound $LaY_2Ni_9$ was made using an annealing treatment at 900°C. From microprobe analysis, it was found that the main phase was indeed $LaY_{1.8}Ni_{8.7}$ in fairly good agreement with the nominal composition. However, metallographic examination, EPMA and X-ray diffraction indicate the presence of secondary phases beside the main phase. Those phases were identified to be of $R_2Ni_7$ and $R_xNi_2$-type, in fact the neighbor phases of $RNi_3$ if one refers to the La–Ni phase diagram. Lower annealing temperatures and various nominal stoichiometries were used in order to limit the segregation of these phases. Best results were obtained for a sample annealed at 750°C starting from the composition ratio 1:2:8.9 for which less than 1 wt% of secondary $R_xNi_2$-type phase was detected. Results from EPMA are given in Table 1.

At this stage, a Rietveld's method refinement was performed to fully determine the structural parameters for this phase. As there are two available sites (3$a$

Table 1
Composition obtained by EPMA for the main phase of expected stoichiometry $La_{1-x}Ce_xY_2Ni_9$

| $x$ | 0 | 0.50 | 1 |
|---|---|---|---|
| La | 1.05 (1) | 0.536 (8) | — |
| Ce | — | 0.520 (5) | 1.040(9) |
| Y | 1.98 (1) | 1.95 (2) | 1.93 (5) |
| Ni | 8.97 (1) | 8.98 (2) | 9.02 (4) |

and 6*c*) for La and Y, the occupancy factors for each atom over these two sites can be refined. Assuming no vacancy and that the overall stoichiometry is fixed, the following relation can be written: $N_{Y(3a)}+N_{La(3a)}=3$; $N_{Y(6c)}+N_{La(6c)}=6$; $N_{Y(3a)}+N_{Y(6c)}=6$; $N_{La(3a)}+N_{La(6c)}=3$ where $N_{A(u)}$ represents the number of atoms *A* on the atomic position (*u*). Then, the repartition can be obtained using only one single parameter. According to that, only the occupancy factor $N_{Y(3a)}$ representing the number of yttrium atoms in site 3*a* has been given in Table 2. It is worth to note that if $N_{Y(3a)}=0$ the structure can be described as a fully ordered ternary compound $La_{3a}Y_{6c}Ni_{27}$ isostructural to the $LaMg_2Ni_9$-type structure reported by Kadir et al. [3]. If $N_{Y(3a)}=2$, one have a random distribution of La and Y over the two sites and it corresponds to a randomly distributed pseudo-binary compound of formulation $(La_{0.33}Y_{0.66})Ni_3$.

Table 2
Evolution of the structural parameters as a function of $x_{Ce}$ for $La_{1-x}Ce_xY_2Ni_9$. Atomic positions (space group *R*-3*m*) are: *R*,Y: 3*a* (0,0,0); *R*,Y: 6$c_1$ (0,0,*z*); Ni: 3*b* (0,0,$\frac{1}{2}$); Ni: 6$c_2$ (0,0,*z*); Ni: 18 *h* ($\frac{1}{2}$,$\frac{1}{2}$,*z*)

| $x_{Ce}$ | 0 | 0.5 | 1 |
|---|---|---|---|
| $N_{Y(3a)}$ | 0.69 (7) | 1.03(8) | 1.85(5) |
| $z_{6c1}$ | 0.1396(1) | 0.1395(1) | 0.1389(1) |
| $z_{6c2}$ | 0.3328(3) | 0.3331(3) | 0.3327(2) |
| $z_{18h}$ | 0.0824(2) | 0.0825(2) | 0.0820(1) |
| *a*(Å) | 5.0343(2) | 5.0052(1) | 4.9711(3) |
| *c*(Å) | 24.507(1) | 24.508(1) | 24.538(1) |
| *v*(Å) | 537.90 | 531.73 | 525.14 |
| $R_{Bragg}$ | 5.8 | 7.1 | 7.9 |
| Wt% of $R_xNi_2$ | <1% | — | — |
| $\chi^2$ | 1.16 | 2.02 | 1.2 |

Results of the refinement are given in Table 2. Total number of reflection was 130 for 19 variables. Refined positions are very close to that reported for the $PuNi_3$-type structure. The *x* parameter of the 18 *h* position was first refined but no significant displacement from the ideal value $x=\frac{1}{2}$ can be observed and the position was finally set to $(\frac{1}{2},\frac{1}{2},z)$. The amount of Yttrium in site 3*a* is fairly low ($N_{Y(3a)}=0.7$) which means that this compound is closer to a ternary one despite it is not fully ordered. The secondary $R_xNi_2$-type phase was also taken into account in the refinement of the powder pattern but its weight percentage was found to be less than 1%. The refined pattern is shown in Fig. 1.

### 3.1.2. Effect of cerium substitution

From metallographic observation, it is found that the compounds with $x_{Ce}=0.5$ and 1 are single phase. The results of the EPMA analysis for all compounds are given in Table 1. It confirms the stoichiometry 1:2:9 for the main phase.

These results are confirmed by XRD analysis. For all samples, the main phase can be indexed in the rhombohedral cell of $PuNi_3$-type. The cell parameters for the $La_{1-x}Ce_xY_2Ni_9$ system are given in Table 2 and their evolutions are shown in Fig. 2.

The total replacement of lanthanum by cerium involves a decrease of parameter a (−1.2%) and a small increase of parameter c (+0.13%). The overall effect is a diminution of the cell volume (−2.4%). Using X-ray analysis, it is not possible to distinguish between

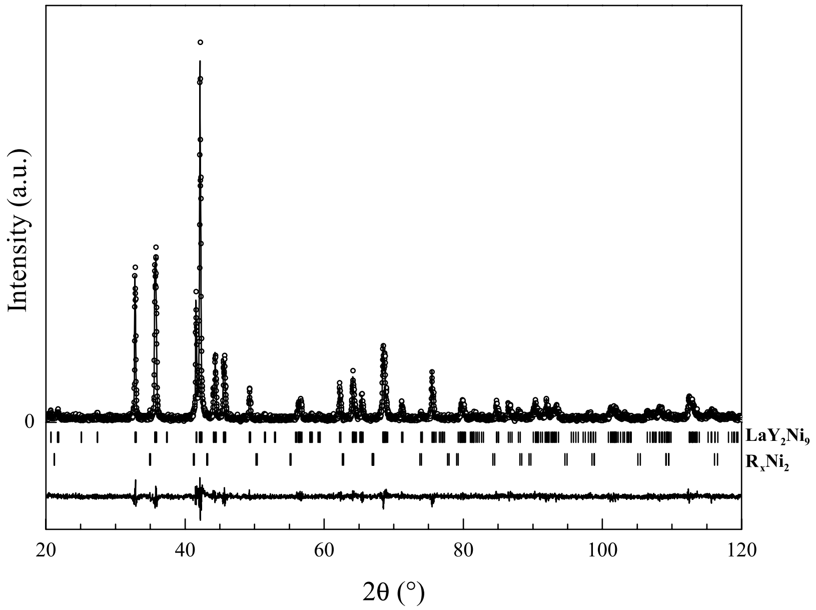

Fig. 1. Refined diffraction pattern of $LaY_2Ni_9$: observed (dots) calculated (solid line) and difference curves (below) are shown. Vertical bars correspond to line positions of the phases.

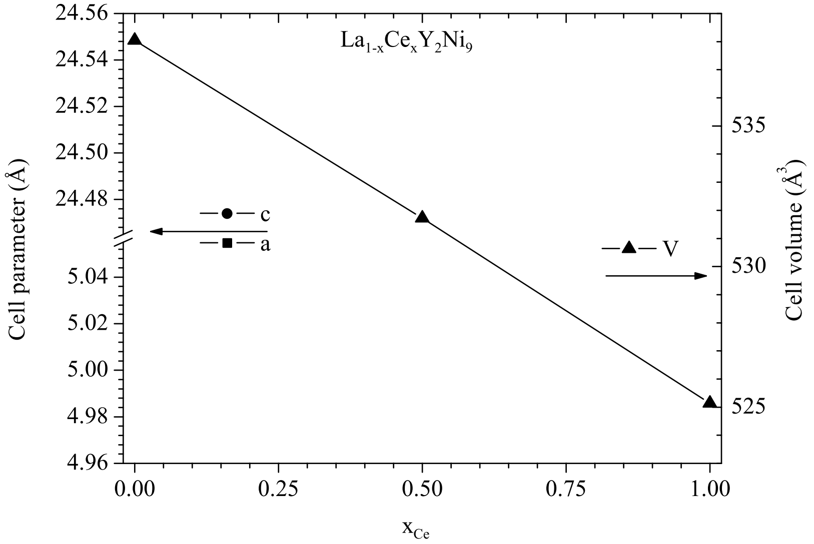

Fig. 2. Variations of the cell parameters and volume as a function of $x_{Ce}$ for $La_{1-x}Ce_xY_2Ni_9$.

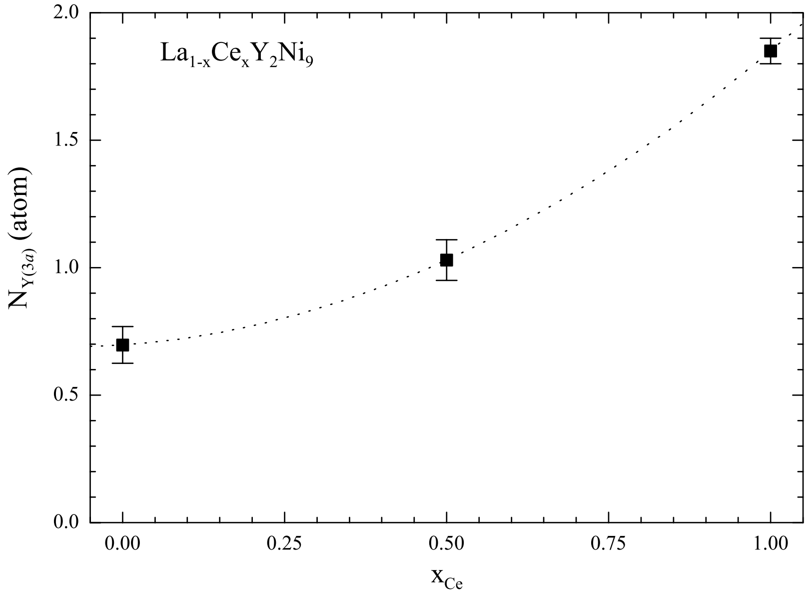

Fig. 3. Evolution of the occupancy factor of Y on site 3$a$. The dot line is only a guide for eyes.

lanthanum and cerium. However, the repartition between the pseudo-atom $R=(La_{1-x}Ce_x)$ and Y can be achieved. The evolution of the parameter $N_{Y(3a)}$ is given in Fig. 3. It is almost constant for low $x_{Ce}$ content but it increases rapidly to reach a value very close to 2 for the pure cerium compound. As it has been already reported [16], cerium is commonly observed in an intermediate valence state in intermetallic compounds. In order to estimate the influence of this valence state on the structural properties of the $La_{1-x}Ce_xY_2Ni_9$ system, the Ce–$L_{III}$ edge has been measured for compounds with $x=0.5$ and 1 by XAS. Typical spectrum is shown in Fig. 4. Two contributions are clearly seen and the spectrum was analyzed assuming two valence states ($Ce^{+3}$ at 5725 eV and $Ce^{+4}$ at 5734 eV) with a convolution of Lorentzian, Gaussian and arctangent functions for each white line. Results of this analysis lead to an intermediate valence state of 3.36(6). No significant evolution can be observed as a function of $x_{Ce}$ and it was therefore concluded that the valence state of cerium is nearly constant in the whole range of concentration.

### 3.2. Thermodynamical properties

The $P$–$C$ isotherm curves for the first hydrogen absorption recorded at room temperature for $LaY_2Ni_9$ and $CeY_2Ni_9$ are shown in Fig. 5. The lanthanum

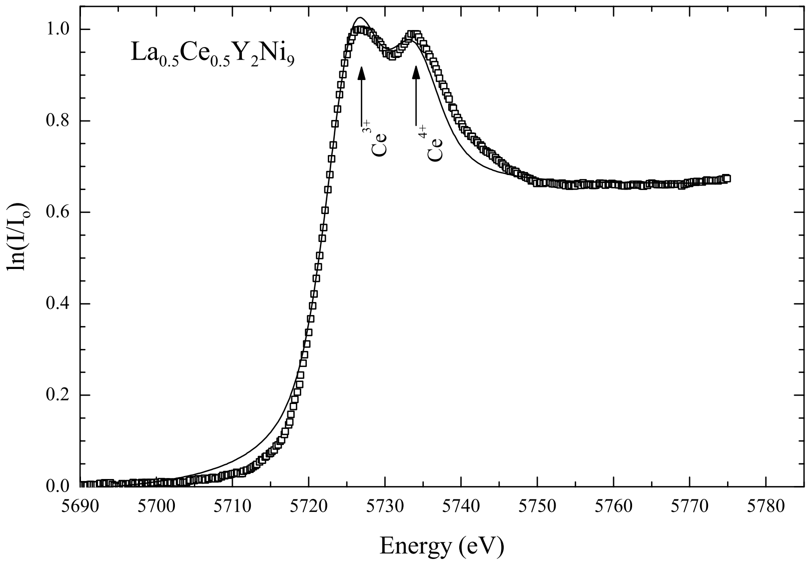

Fig. 4. $L_{III}$ edge of cerium for $La_{0.5}Ce_{0.5}Y_2Ni_9$. The arrows shows the two peaks corresponding to the two different valence states ($Ce^{+3}$ at 5725 eV and $Ce^{+4}$ at 5734 eV) and the full line corresponds to the refinement of the two components.

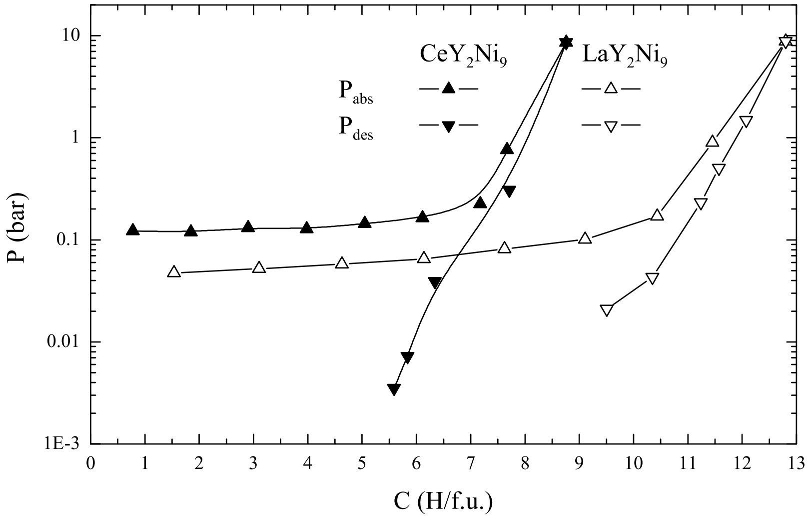

Fig. 5. *P–C* isotherm curves at 25°C for $LaY_2Ni_9$ and $CeY_2Ni_9$.

compound absorbs 12.3 H/f.u. under 1 bar of hydrogen gas at and its plateau pressure is equal to 0.06 bar at 25°C for absorption. Due to the low desorption pressure, to the size of the gauged volume used in the Sievert's apparatus and to the slow kinetic of the alloy, desorption plateau cannot be fully completed. The cerium compound absorbs 7.7 H/f.u. under 1 bar. The absorption plateau pressure is higher than that of the lanthanum compound at 0.128 bar at 25°C. Reversibility is poor and the equilibrium pressure decreases rapidly during desorption. This behavior may be due to amorphization upon hydrogenation and in situ experiments have to be performed to determine the crystalline state of the formed hydrides.

## 4. Discussion

From our structural study, it can be concluded that the intergrowth between $LaNi_5$ and $YNi_2$ to form a new compound of formulation $LaY_2Ni_9$ is possible. From EPMA (Table 1), the stoichiometry for yttrium is equal to 1.98(1). As stated above, the compound $Y_xNi_2$ is under-stoichiometric and exists only for $x = 0.95$. As the $RY_2Ni_9$ structure is obtained from a stacking of $CaCu_5$ and $MgZn_2$ units and because the crystallographic study has shown that a large part of the yttrium atoms are sited in the $RM_2$ blocks, the question arises if one can expect vacancies on site 6*c* by analogy to what is observed for $Y_{0.95}Ni_2$. For that reason, a refinement was performed assuming: $N_{Y(3a)}+N_{La(3a)}=3$; $N_{La(3a)}+N_{La(6c)}=3$ and refining independently $N_{Y(6c)}$ and $N_{Y(3a)}$. From this analysis, the total amount of Yttrium was found equal to 6.1(2) in agreement with the ideal stoichiometric value of 6. Density measurements were also performed and a value of 7.85 was obtained to be compared to the value of 7.83 calculated from the X-ray diffraction. It was therefore concluded that, within the error bars, no vacancies could be detected on the yttrium sites.

When lanthanum is fully substituted by cerium the cell parameter **a** decreases whereas **c** slightly increases. These effects are very similar to what is observed in $RM_5$-type compounds [17,18]. According to Lundin et al. [18] and assuming close packing of spherical atoms, we have $a=\sqrt{3}(r_R+r_M)$ and $c=\sqrt{(15r_M^2-r_R^2-2r_Rr_M)}$. If $r_M$ is fixed, cell parameter **a** follows the variation of $r_R$ but **c** behaves conversely. As cerium radius is smaller than lanthanum, the mean value of $r_R$ decreases as a function of $x_{Ce}$. According to Andresen [19], the $PuNi_3$ structure can also be described as a superstructure of 6 unit cells of $LaNi_5$-type stacked along the $c$-axis and derived by an ordered substitution of 3 La for 3 Ni. Such stacking explains the similarity of **a** and **c** dependence against $x_{Ce}$ for the system $La_{1-x}Ce_xY_2Ni_9$. The behavior of the cell parameters is anisotropic but the final effect logically consists in a linear reduction of the cell volume as a function of $x_{Ce}$.

Though La and Ce are neighbors in the periodic table, the cell volume decrease is important. This can be explained by the intermediate valence state of Ce which is confirmed by the XAS measurements from which the valence $v=3.36(6)$ is obtained. This value is in fairly good agreement with the value observed for related Ce-substituted $LaNi_5$-type compounds [16]. According to its intermediate valence state, the average atomic radius of cerium is estimated at 1.71(2) Å to be compared to 1.87 Å for La and 1.80 for Y. From these values of the atomic radii and assuming that there is no ordering effect between La and Ce, it is possible to calculate the average sizes of the pseudo-atoms lying in sites 3$a$ and 6$c$. These radii $r_{3a}$ and $r_{6c}$ both depends on $x_{Ce}$ and $N_{Y(3a)}$. Results of these calculations are shown in Fig. 6 as a function of $x_{Ce}$. Two regions are clearly identified. Below $x_{Ce}=0.5$, the radius of the site 3$a$ is almost equal to that of the pseudo-rare-earth atom $(La_{1-x}Ce_x)$, whereas the size of the site 6$c$ is almost equal to the value of $r_Y$. This corresponds to an ordered ternary compound which can be described as: $(La_{1-x}Ce_x)_{3a}Y_{6c}Ni_{27}$. For $x_{Ce}=0.5$ both sites have the same radius value of approximately 1.80 Å. Above $x_{Ce}=0.5$, atomic radii of both sites are nearly equal and their variation is close to the expected random distribution. That corresponds to a pseudo-binary compound of general formulation $((La_{1-x}Ce_x)_{0.33}Y_{0.66})_{3a}((La_{1-x}Ce_x)_{0.33}Y_{0.66})_{6c}Ni_{27}$. From these observations, it can be concluded that for a compound of general formulation $RR'_2M_9$ with $r_R>r_{R'}$, a ternary compound should be obtained with $R$ atoms lying on site 3$a$ and $R'$ ones on site 6$c$. This is indeed the case for the compounds $RMg_2Ni_9$ ($R$ = La to Gd) reported by Kadir et al. [3] and this is also in agreement with the results published by Chen et al. [20] on various

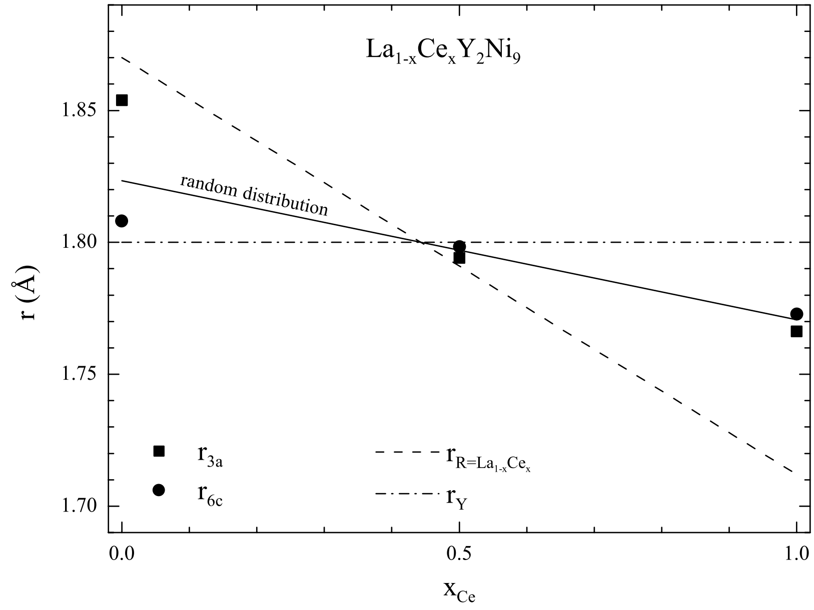

Fig. 6. Variations of the atomic radius sizes for the pseudo-atoms lying on sites 3$a$ and 6$c$ as a function of $x_{Ce}$. Symbols represent the radii $r_{3a}$ (■) and $r_{6c}$ (●). Dotted lines correspond to the radii of Y (constant value) and pseudo-atoms $R=La_{1-x}Ce_x$ (varying as a function of $x_{Ce}$). Average radius expected for random distribution is also shown as a full line.

$LaNi_3$ and $CaNi_3$ substitutes adopting the $PuNi_3$-type structure. In the other case ($r_R \leqslant r_{R'}$), random substitution is possible and a pseudo-binary compound of general formula $(R_{0.33}R'_{0.66})Ni_3$ is more probable.

Concerning thermodynamical properties, the lanthanum compound shows an interesting storage capacity of 12.3 H/f.u. under 1 bar. If one looks at the storage capacity of $LaNi_5$ ($C = 6.6$ H/f.u.) and $Y_{0.95}Ni_2$ ($C' \approx 2.6$ H/f.u. in crystalline domain), the expected capacity for $LaY_2Ni_9$ would be: $C + 2C' \approx 11.8$ H/f.u. very close to the experimental measured value. On the other hand, looking to the storage capacities of $LaNi_3$ and $YNi_3$ (4.5 and 1.2 H/f.u., respectively [20,11]), a pseudo-binary compound would only store $C + 2C' \approx 6.9$ H/f.u. This comparison supports the argument that the compound $LaY_2Ni_9$ must be described as a stacking of $LaNi_5$ and $YNi_2$. Then, the storage capacity of a ternary compound $RR'_2M_9$ can be estimated from the specific capacities of the individual units $RM_5$ and $RM_2$. However, it cannot be excluded that the higher hydrogen absorption capacity observed for $LaY_2Ni_9$ as compared to $YNi_3$ is the result of the decreased hydrogen absorption pressure related to the cell volume increase involved by the replacement of Y by La within the structure.

The equilibrium pressure of $LaY_2Ni_9$ is 0.06 bar, which is convenient for practical applications since it is in the range of reversibility commonly estimated between 0.01 and 1 bar. However, the hysteresis effect is important and the desorption pressure is rather low. It should be reminded that the given $P$–$C$ isotherm curve corresponds to the first absorption/desorption cycle. It is indeed commonly observed that hysteresis effect is reduced upon cycling.

Substituting the lanthanum with cerium involves a decrease of the cell volume and an increase of the plateau pressure. This phenomenon is very classical in metallic hydrides. It has been shown [21] that there is a linear relation between the intermetallic cell volume and the logarithm of the plateau pressure of the hydride. This property has been widely used for adapting the plateau pressure to the application needs and it applies again here. Concerning the capacity, a strong reduction is observed when compared to the lanthanum compound. It can be attributed to the decrease of the cell volume involving diminution of the site sizes available for hydrogen. Another approach can be done referring again to the crystallographic analysis. $CeY_2Ni_9$ is a pseudo-binary compound which formula is better written as $(Ce_{0.33}Y_{0.66})Ni_3$ since Y substitutes randomly the cerium atoms. Therefore, it can be described as the stacking of $CeNi_5/YNi_5$ and $CeNi_2/YNi_2$ units. From the literature, it is known that both $CeNi_5$ and $YNi_5$ absorb very limited quantity of hydrogen at moderate pressure [22]. The capacity of $CeNi_2$ reaches a maximum value of 3.8 H/f.u. [23] whereas that of $YNi_2$ is 2.6 H/f.u. in crystalline form [12]. Thus, assuming a capacity of 0.6 H/f.u. for the $CeNi_5/YNi_5$ layer, the capacity of $Ce_{0.33}Y_{0.66}Ni_3$ can be estimated around 7.0 H/f.u. slightly lower than the value of 7.7 H/f.u. measured in the present work. However, according to Ref. [11], a larger capacity cannot be excluded for $YNi_2$ (3.6 H/f.u.) but such value is expected to induce amorphization of the lattice [12]. This may be an explanation to the non-reversible character of the isotherm curve observed in the desorption branch for this latter compound.

## 5. Conclusions

To conclude, the structural properties of the ternary system $La_{1-x}Ce_xY_2Ni_9$ with $x = 0$; 0.5 and 1 have been investigated. The compounds adopt a rhombohedral structure of $PuNi_3$-type, which can be described as an intergrowth between $RM_5$ and $RM_2$-type structures. It is shown that depending of the atomic radius difference between yttrium and the pseudo-atom $R = (La_{1-x}Ce_x)$ either a partially ordered ternary or a randomly distributed pseudo-binary compound can be obtained. From this assumption, the thermodynamical properties of $LaY_2Ni_9$ and $CeY_2Ni_9$ hydrides can be interpreted. The reduced capacity and the high stability of $CeY_2Ni_9H_{7.7}$ are attributed to the pseudo-binary character of the intermetallic. The compound $LaY_2Ni_9$ presents an interesting capacity of 12.3 H/f.u., which corresponds to 380 mAh/g in equivalent electrochemical units. The properties of this system in electrochemical medium will be presented elsewhere [24].

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## References

[1] A. Percheron-Guégan, J.-C. Achard, J. Sarradin, G. Bronoël, French Patent 7516160, 1975, US Patent 688537, 1978.

[2] F. Cuevas, J.M. Joubert, M. Latroche, A. Percheron-Guégan, Appl. Phys. A 72 (2001) 225–238.

[3] K. Kadir, T. Sakai, I. Uehara, J. Alloys, Compds. 257 (1997) 115.

[4] K. Kadir, N. Kuriyama, I. Uehara, L. Eriksson, J. Alloys Compds. 284 (1999) 145.

[5] K. Kadir, T. Sakai, I. Uehara, J. Alloys Compds. 287 (1999) 264.

[6] K. Kadir, T. Sakai, I. Uehara, J. Alloys Compds. 302 (2000) 112.

[7] B.D. Dunlap, P.J. Viccaro, G.K. Shenoy, J. Less-Common Met. 74 (1980) 75–79.

[8] J.H.N. Van Vucht, F.A. Kuijpers, H.C.A.M. Bruning, Philips Res. Rep. 25 (1970) 133.

[9] M. Latroche, V. Paul-Boncour, A. Percheron-Guégan, J.C. Achard, J. Less-Common Met. 161 (1990) L27–L31.

[10] E. Gratz, A. Kottar, A. Lindbaum, M. Mantler, M. Latroche, V. Paul-Boncour, M. Acet, Cl. Barner, W.B. Holzapfel, V. Pacheco, K. Yvon. J. Phys. Condens. Matter 8 (1996) 8351–8361.
[11] R.H. Van Essen, K.H.J. Buschow, J. Less-Common Met. 70 (1980) 189–198.
[12] A. Percheron-Guégan, V. Paul-Boncour, M. Latroche, J.C. Achard, J. Less-Common Met. 172–174 (1991) 198–205.
[13] M. Latroche, V. Paul-Boncour, A. Percheron-Guégan, Z. Phys. Chem. Bd. 179 (1993) S261–268.
[14] G.D. Adzic, J.R. Johnson, J.J. Reilly, J. McBreen, S. Mukerjee, J. Electrochem. Soc. 142 (1995) 3429.
[15] J. Rodriguez-Carvajal, Abstract of the Satellite Meeting on Powder Diffraction, Congress of the International Union of Crystallography, Toulouse, France, 1990 p. 127.
[16] V. Paul-Boncour, J.-M. Joubert, M. Latroche, A. Percheron-Guégan, J. Alloys Compds. 330–332 (2002) 246–249.
[17] Che Guang-Can, Yu Yu-De, Liang Jing-Kui, Wuli Xuebao, Acta Phys. Sin. 33 (6) (1984) 770–778.
[18] C.K. Lundin, F.E. Lynch, C.B. Magee, J. Less-Common Met. 56 (1977) 19.
[19] A.F. Andresen, in: A.F. Andresen, A.J. Maeland (Eds.), Hydrides for Energy Storage, Pergamon, Oxford, 1978, p. 61.
[20] J. Chen, H.T. Takeshita, H. Tanaka, N. Kuriyama, T. Sakai, I. Uehara, M. Haruta, J. Alloys Compds. 302 (2000) 304–313.
[21] J.-C. Achard, A. Percheron-Guégan, H. Diaz, F. Briaucourt, F. Demany, Proceedings of the Second International Congress on Hydrogen in Metals, Paris, 1977, p. 1E12.
[22] K.H.J. Buschow, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook of the Physics and Chemistry of Rare Earths, Elsevier Sciences Publishers B.N, Amsterdam, 1984, p. 1.
[23] V. Paul-Boncour, C. Lartigue, A. Percheron-Guégan, J.C. Achard, J. Less-Common Met. 143 (1988) 301–313.
[24] R. Baddour-Hadjean, L. Meyer, J.-P. Pereira-Ramos, M. Latroche, A. Percheron-Guégan, Electrochem. Acta 46 (2001) 2385–2393.