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Thermodynamic and structural comparison between two potential metal-hydride battery materials $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$

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Abstract

The thermodynamic and structural properties of $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and their hydrides (deuterides) are compared. The isothermal curves have been measured. The lattice parameters and the occupancies of the various interstitial sites by deuterium have been determined by powder neutron diffraction. Differences between the two compounds as regards the hydrogen absorption are interpreted in terms of the different atomic radii of lanthanum and cerium. The evolution of the valence of cerium as a function of hydrogen content is discussed. © 1998 Elsevier Science S.A.

Keywords: Nickel–metal hydride batteries; Hydrides; Neutron diffraction; Mischmetal

1. Introduction

In the frame of the replacement of negative electrode in nickel–cadmium batteries for portable devices by lighter and denser materials, rare earth based intermetallic compounds are investigated. They can reversibly store hydrogen by forming intermetallic hydrides with hydrogen or protons in gas–solid or electrochemical reactions. All those materials are $LaNi_5$ substituted compounds with $CaCu_5$ structural type. In the transition metal sublattice, substitution by Mn, Al and Co has been found to offer the best compromise between high hydrogen capacity and good resistance to corrosion [1]. For the lanthanum sublattice, mischmetal (natural rare earths mixture) is used for economical reasons. As the exact composition of the mischmetal may vary depending on the source of the ore and on a possible enrichment in a specific rare earth, it is of importance to compare the influence and the role of each rare earth in those compounds in order to design optimal materials for industrial application.

In this work, two intermetallic compounds have been prepared: $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ (La and Ce being the main components of mischmetal). They have been studied by neutron diffraction including deuterated samples of the Ce compound at two different compositions. The results are compared to the closely related results previously obtained on $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_x$ ($x=2.0$, 4.6 [2], 5.6 [3]) and discussed in terms of equilibrium pressure, composition of the hydride phase and nature and occupancies of the crystallographic sites occupied by hydrogen (deuterium).

2. Experimental

Detailed description of the experimental procedures can be found in previous papers [2,3]. The alloys are obtained by induction melting of the pure elements followed by appropriate annealing. They are carefully checked by metallographic examination, electron probe microanalysis (EPMA) and X-ray diffraction. Pressure–composition isotherms at room temperature have been measured by conventional volumetric method (Sievert's device). Samples for neutron diffraction are loaded with deuterium by solid–gas reaction in silica tubes then closed under controlled pressure. All the patterns were recorded on the 3T2 instrument at the Laboratoire Léon Brillouin in Saclay except for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ which was recorded on the D2B diffractometer at the Institut Laue Langevin in

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Grenoble. The analysis of the diffraction patterns is made by Rietveld refinement.

3. Results

The two intermetallic compounds $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ were found single phase by EPMA with homogeneous compositions close to the nominal ones: $La_{0.99(1)}Ni_{3.59(2)}Mn_{0.40(1)}Al_{0.28(1)}Co_{0.75(1)}$ and $Ce_{1.00(1)}Ni_{3.59(1)}Mn_{0.39(1)}Al_{0.29(1)}Co_{0.73(1)}$.

Powder neutron diffraction patterns were measured for those two intermetallic compounds and for two different deuterium compositions for the cerium compound ($CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{3.4}$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{5.1}$). The first composition corresponds to a two phase sample where α and β hydrides coexist, the second one to a pure β phase sample.

The results of the refinements are summarised in Table 1. All the phases (intermetallic compounds and hydrides) have the $CaCu_5$ type structure of $LaNi_5$ (space group *P*6/*mmm*) for which the rare earth (A element) occupies site 1*a* and Ni, Mn, Al and Co (B elements) occupy sites 2*c* and 3*g*. It is impossible from a single pattern refinement to obtain the distribution of Mn, Al and Co over the two possible Ni sites. This has been achieved elsewhere by multiwavelength anomalous dispersion powder diffraction for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ [4]. From a single neutron diffraction pattern, only information about the average scattering lengths at each site can be obtained. Assuming an average sum of the scattering lengths b_{2c} and b_{3g}, which reproduces the nominal composition of the alloy ($3.55\ b_{Ni}+0.4\ b_{Mn}+0.3\ b_{Al}+0.75\ b_{Co}$), refinement of the occupancy factor for these two sites allows us to take into account the non random distribution of the elements over the two sites. This refined value is given in Table 1 in the form of b_{2c} and b_{3g}.

The deuterium when present occupies the same four interstitial sites as it is found in such $LaNi_5$ substituted compounds [5]: 4*h* (1/3, 2/3, $z\approx0.38$), 6*m* ($x\approx0.14$, 2*x*, 1/2), 12*n* ($x\approx_{0.4}6$, 0, $z\approx0.10$), 12*o* ($x\approx0.22$, 2*x*, $z\approx0.32$). Occupancy factors in percent are given in Table 1.

4. Discussion

The refined values for the scattering lengths at sites 2*c* and 3*g* for the intermetallic compounds (for La $b_{2c}=17.8$ fm, $b_{3g}=20.2$ fm; for Ce $b_{2c}=17.9$ fm, $b_{3g}=20.1$ fm) are in good agreement with the values calculated from the distribution obtained by anomalous dispersion experiments on the La compound ($b_{2c}=17.5$ fm, $b_{3g}=20.4$ fm) [4]. It follows that the same distribution of the substituents for Ni in the Ce compound is expected. As indicated by the values found for $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{5.1}$, a change of the distribution induced by hydrogenation is unlikely to occur. Consequently, the values for the average scattering lengths at sites 2*c* and 3*g* for the two phases in $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{3.4}$ have been fixed to the values determined in the intermetallic compounds to limit the number of refined parameters.

Cell volumes of Ce and La intermetallic compounds are found to be very different though these elements are neighbours in the periodic table (Fig. 1). The smaller volume for the Ce compound can be explained by the intermediate valence state of Ce. This has been checked by X-ray absorption edge measurements at the LURE (Fig. 2) where the two contributions (Ce^{3+}, Ce^{4+}) are clearly seen. The analysis of those data leads to 30% of Ce with a valence of four. The corresponding atomic average radius is estimated 1.73 Å, 8% smaller than the lanthanum one (1.87 Å). However, the effect of the replacement of La by Ce on the lattice parameters is not isotropic since it involves a large decrease of the a parameter while c is almost constant. The same behaviour has been previously observed for $LaNi_5$ and $CeNi_5$ [6,7] and was attributed to the fact that contrary to the a parameter, c depends almost entirely on the transition metal radius [8].

The variation of the lattice parameters as a function of the deuterium composition (*x*) can be followed in Fig. 1. For both compounds deuterium uptake involves an increase of the lattice parameters which is linear for the La compound. The increase of the cell volume for the Ce compound is also linear up to $x=4.2$ but deviates significantly for $x=5.1$. This effect could be attributed to a diminution of the Ce valence upon hydrogen absorption leading to an increase of its radius. Such effect has already

Table 1

Results of the Rietveld refinement for the different intermetallic compounds and hydrides

Composition	*a* (Å)	*c* (Å)	*V* (Å^3)	4*h* (%)	6*m* (%)	12*n* (%)	12*o* (%)	Total D content	b_{2c} (fm)	b_{3g} (fm)	Weight (%)	R_{Bragg} (%)
$LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$	5.076	4.055	90.50						17.8	20.2		5.6
$CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$	4.929	4.063	85.47						17.9	20.1		5.4
$CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D^{a}_{3.4}$	4.978	4.116	88.33		15	3		1.3	Fixed	Fixed	25	13.0
	5.171	4.159	96.32	1	37	16		4.2	Fixed	Fixed	75	9
$CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D^{a}_{5.1}$	5.287	4.229	102.37	6	35	21	2	5.1	18.1	19.9		9.2

The occupancy factors are given as a percentage for the different deuterium sites and the total D content are calculated from these values. b_{2c} and b_{3g} are the refined scattering lengths at sites 2*c* and 3*g* in fm.

[a] Due to an experimental difficulty, the compositions given here are those obtained from the refinement and not measured by volumetric method.

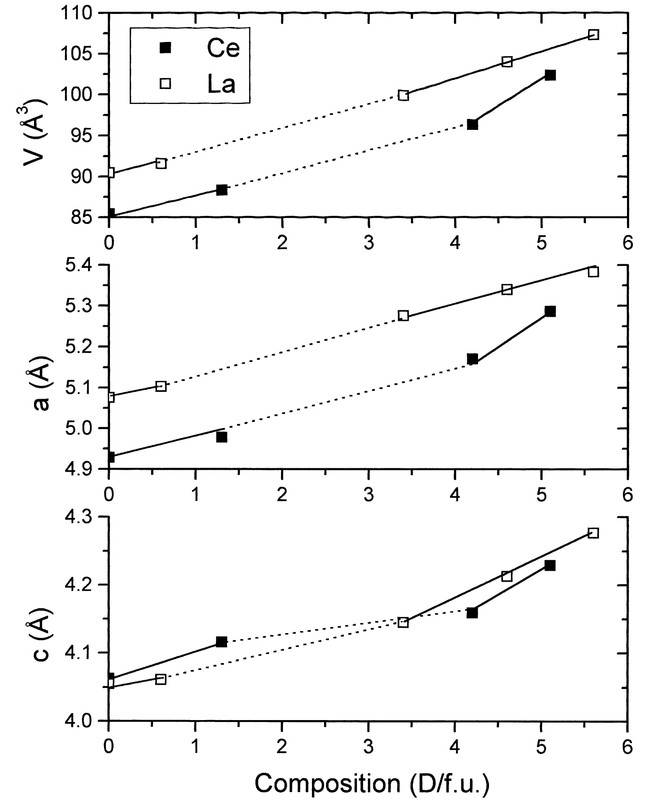

Fig. 1. Change of lattice parameters of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_x$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_x$ as a function of deuterium composition. Dot lines correspond to α–β transition domain and are only a visual guide.

been observed in other systems such as $CeNi_2H_x$ [9] and $La_{1-x}Ce_xNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ [10] and is related to the filling of the conduction band by the electrons coming from the hydrogen atoms.

The isothermal absorption and desorption curves are plotted in Fig. 3 and corresponding data are summarised in Table 2. The hysteresis is comparable for both compounds and is very small. The larger value of the plateau pressure for the cerium compound is consistent with the smaller cell volume of the intermetallic compound [11]. One can notice a shift of the position of the plateau towards higher hydrogen compositions for the Ce compound: the solubility limit in the α phase is larger but the plateau widths remain nearly the same in both cases.

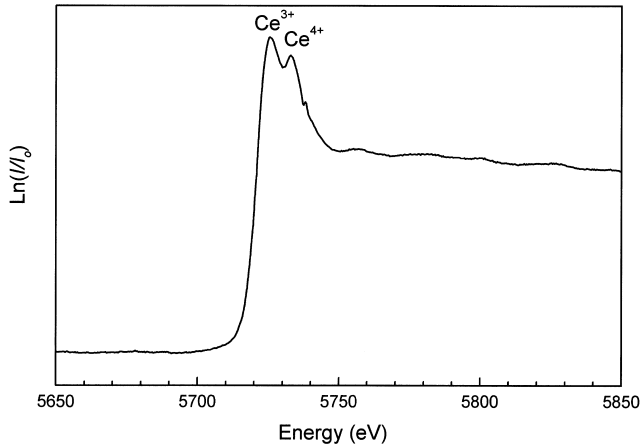

Fig. 2. Ce L_{III} X-ray absorption edge for $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$.

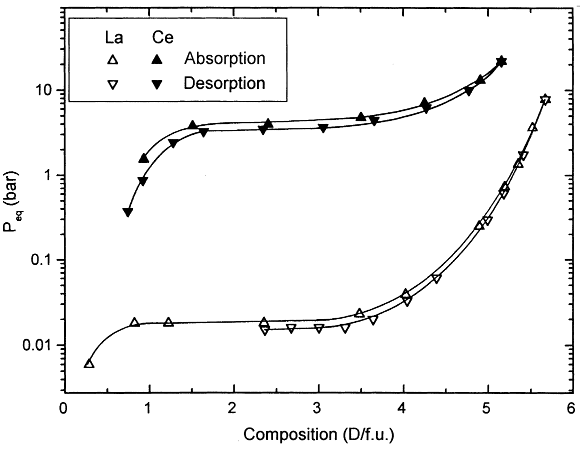

Fig. 3. Pressure–composition curves at 25°C (absorption and desorption) for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$.

The occupancy factors of the deuterium sites are plotted in Fig. 4 for the lanthanum and cerium compounds. The refined total D contents for the two phases found in $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{3.4}$ i.e. 25 wt% of saturated α phase (α_{max}) ($D_{1.3}$) and 75 wt% of under-saturated β phase (β_{min}) ($D_{4.2}$) (Table 1) are in agreement with the limits for the pressure plateau given in Table 2. Again, as observed for the isothermal curves, the width of the pressure plateau is the same as that refined in the case of lanthanum ($\Delta D=2.9$ ($D_{1.3}\rightarrow D_{4.2}$) versus $\Delta D=2.8$ ($D_{0.6}\rightarrow D_{3.4}$) [2]). As can be seen from the figure, this increase in composition for the Ce α_{max} and β_{min} phases is due to a better filling of sites 6*m*, the occupations of the other sites being almost identical.

This difference can be explained if one looks carefully at the deuterium site size calculated for the intermetallic compounds (Table 3). It has been shown that occupancy factors can be directly related to this size parameter [12]. It is defined as the radius of the largest sphere in contact with the metallic atoms forming the tetrahedron. It depends both on the cell parameters and on the metallic atom radii. For the substituted sites 2*c* and 3*g*, the average radii have been calculated following the distribution established in [4] ($R_{2c}=1.248$ Å, $R_{3g}=1.271$ Å).

Therefore, when replacing La by Ce ($R_{La}=1.87$ Å, $R_{Ce}=1.73$ Å) and according to the nature of the sites we observe three different behaviours:

- for the B_4 site (4*h*), no rare earth is present in the coordination tetrahedron, thus this site size decreases in the same way as the cell volume. Therefore, this site

Table 2
Thermodynamic data at 25°C obtained from the pressure–composition curves

Compound	Plateau pressure (abs/des) (bar)	α_{max} (D/f.u.)	β_{min} (D/f.u.)	Capacity/(pressure) (D/f.u.)/(bar)
$LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$	0.018/0.015	0.6	3.6	5.67/(8)
$CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$	4/3.5	1.2	4.3	5.15/(21)

α_{max}: composition of the saturated α phase, β_{min}: composition of the under-saturated β phase.

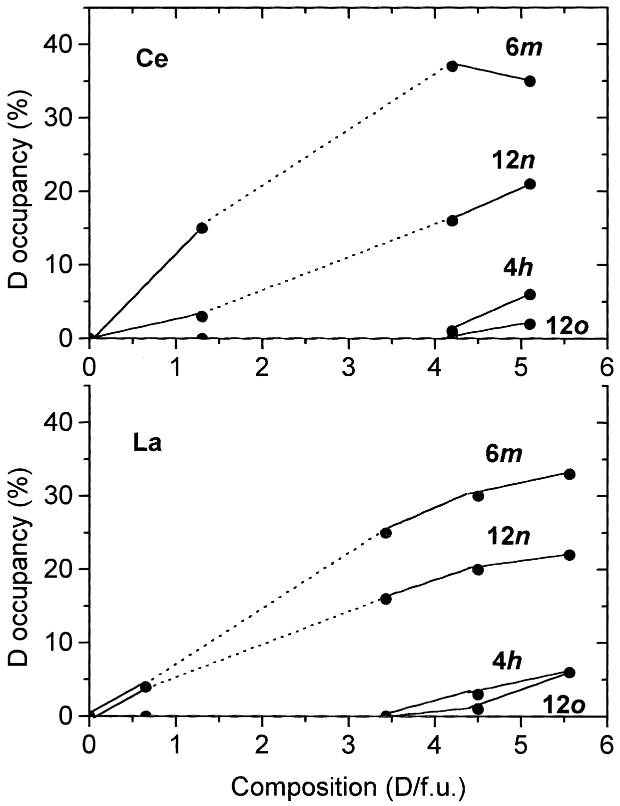

Fig. 4. Occupancies of the deuterium sites as a function of the deuteride composition for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ (from Ref. [2,3] and $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$. Dot lines correspond to α–β transition domain and are only a visual guide.

Table 3
Radii of the interstitial sites calculated in the two intermetallic compounds

D site	Environment	Radii (Å)	
		La compound	Ce compound
4*h*	1 B (2c) 3 B (3g)	0.28	0.25 (−11%)
6*m*	2 A 2 B (3g)	0.42	0.49 (+17%)
12*n*	1 A 2 B (2c) 1 B (3g)	0.34	0.33 (−3%)
12*o*	1 A 1 B (2c) 2 B (3g)	0.31	0.32 (+3%)

A=La or Ce; B=(Ni, Mn, Al, Co). The radius variation rates (%) are given between brackets.

should be less occupied in the Ce compound. However, as it is nearly empty in the La compound for α_{max} and β_{min} phases, it is unlikely to observe such an effect.

- for the AB_3 sites (12*n* and 12*o*), the reduction of the rare earth radius leaves more space for the interstitial site but the decrease of the cell volume compensates for this effect leading to a constant site size in both compounds. Therefore, the same D occupancy factors are expected and indeed observed for these sites.
- for the A_2B_2 site (6*m*), two rare earth atoms are involved in the tetrahedron leading to a larger increase of the site size, the volume decrease does not compensate for this effect and the site is larger for Ce than for the La compound. The larger filling observed for this site agrees with its larger size.

Therefore the shift of the plateau observed for the Ce compound can be directly related to the predisposition of the intermetallic compound to accommodate more atoms in site 6*m* due to its larger size.

The results obtained for the two hydrides measured on the plateau pressure are confirmed to a certain extent by the measurements in the β branch. A small reduction of the occupancy of site 6*m* is observed in $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}D_{5.1}$ and must be explained by a change of the site size. This is in good agreement with the change of Ce valence already proposed to explain the anomalous increase of the cell volume. It involves an increase of the Ce radius and a shrinkage of the 6*m* site size leading to a relative decrease of its occupancy factor.

5. Conclusion

The thermodynamic properties of hydrogen absorption in $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, two potential materials for nickel–metal hydride batteries, as well as the structural properties of their hydrides have been studied and compared. The cerium compound has a smaller cell volume and consequently higher equilibrium pressure. The alpha phase region is more extended in this latter compound and the plateau, keeping the same width, is shifted towards higher hydrogen compositions. This is attributed to a better occupancy of sites 6*m* in both α_{max} and β_{min} phases related to an increased site size in the intermetallic compound. Thus with lanthanum and cerium being the two main constituents of mischmetal, one can predict in such industrial materials the plateau pressure and the extent of the alpha phase domain.

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