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XAS STUDY OF RNi_2 HYDRIDES

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FranceRESUME

Les phases de Laves RNi_2 (R = La, Ce) existent avec un écart à la stoechiométrie (5 % pour $CeNi_2$ et 10 % pour $LaNi_2$) qui se traduit par un désordre structural observé par EXAFS autour des atomes de nickel.

Ces composés absorbent facilement l'hydrogène (4.2 H/mole à 25 C) et deviennent amorphes aux RX pour une concentration supérieure à 3.5 H/mole. L'étude EXAFS des hydrures au seuil K du nickel met en évidence l'augmentation du désordre local autour des atomes de nickel. De plus, l'introduction d'hydrogène dans le composé $CeNi_2$ entraîne un changement de valence du cérium, observé par l'étude des seuils L_{III} du cérium.

ABSTRACT

RNi_2 Laves phases compounds (R = La, Ce) exist with a stoichiometry deviation (5 % for $CeNi_2$ and 10 % for $LaNi_2$) which leads to a structural disorder clearly observed by EXAFS at the Ni K-edge. These compounds easily absorb hydrogen up to 4.2 H/mole at room temperature. X-ray diffraction indicates that they are amorphous for hydrogen contents greater than 3.5 H/mole. EXAFS study at the Ni-K edge gives evidence of the increase of the local disorder upon hydrogenation. In addition a change of cerium valency induced by hydrogen absorption in $CeNi_2$ was observed by a Ce L_{III} edge study.

I - INTRODUCTION

RNi_2 Laves phases compounds (R = La, Ce) easily absorb hydrogen at room temperature up to a concentration of 4.2 H/mole under a hydrogen pressure of 1 atm [1,2]. However these hydrides show no more diffraction lines for an hydrogen content beyond 3.5 H/mole. Magnetization measurements and transmission electron microscopy were used to confirm the amorphous state of the hydrides [2].

In order to understand the crystalline to amorphous phase transformation, EXAFS at the Ni-K edge has been used to characterize the intermetallic compounds and their related hydrides. In addition in the case of $CeNi_2$, the electronic state of cerium was checked by a Ce L_{III} edge analysis.

II - EXPERIMENTAL

The samples were prepared by melting the pure components (La : 99.9 % ; Ce : 99.9 % ; Ni : 99.99 %) in a water cooled copper crucible under vacuum, with subsequent annealing. Their homogeneity, stoichiometry and crystal structure were checked by metallographic examination, electron microprobe analysis and X-ray diffraction.

Hydrides with different hydrogen content were obtained by exposing the samples to a hydrogen pressure of 1 to 10 bar at room temperature. The amount of absorbed hydrogen is measured by a volumetric method.

XAS spectra were collected at 298 K and in some cases 77 K using the synchrotron radiation provided by DCI ring at LURE. Si (220) or Si(311) monochromators were used. EXAFS spectra have been recorded at the Ni-K edge and edge spectra at Ce L_{III} the edge.

III - RESULTS AND DISCUSSION

a - Intermetallic compounds

According to recent work [2] the $LaNi_2$ cubic phase forms peritectically at 800 C with a stoichiometry which varies with the temperature from 2.17 at 660 C to 2.21 at 750 C. The $LaNi_2$ compound studied in this work was obtained after annealing at 660 C. Its composition is $LaNi_{2.17}$ with precipitates of La_2Ni_3 phase (about 10 %). Its X-ray diffraction pattern exhibits only the lines corresponding to the $MgCu_2$ cubic phase with a cell parameter $a = 7.340 \text{ \AA}$. $CeNi_2$ was obtained as a single phase after annealing at 650 C with a $CeNi_{2.08}$ stoichiometry. Its X-ray pattern was indexed with a $MgCu_2$ cubic cell and $a = 7.194 \text{ \AA}$.

Fourier transform (F.T.) of $k^3 X(k)$ function of $LaNi_2$ and $CeNi_2$ compounds are presented in figure 1. A smaller first peak intensity and the disappearance of peaks at larger distances are observed for $LaNi_2$ compared to $CeNi_2$. If the $LaNi_2$ spectrum is collected at 77 K (Figure 2) the first peak intensity increases and peaks located at the same distance as $CeNi_2$ peaks appear. At 77 K the thermal disorder decreases. This shows that the difference observed between $LaNi_2$ and $CeNi_2$ spectra collected at room temperature can be attributed to a disorder effect which is more pronounced for $LaNi_2$.

Each peak of the F.T. (spectra collected at room temperature) has been filtered and analysed with a least square fitting procedure. A $12 \mu\text{m}$ Ni foil was used as reference to determine experimental Ni-Ni phase shifts and amplitudes. The mean free path and the energy edge were kept equal to that of Ni. The refined parameters : N (coordination number), R (distance) and $\Delta\sigma$ (Debye Waller factor variation) are presented in table 1 and compared with the values calculated from crystallographic data. Only Ni-Ni pairs were used to fit the peaks. For $CeNi_2$ the distances are unchanged but the coordination numbers decrease from 2 to 4. In the case of $LaNi_2$ not only N but also R decreases (-0.075 \AA). This decrease could be attributed to a non gaussian distance distribution as it has been observed for a wide range of amorphous compounds [3]. Because this effect increases with the stoichiometry deviation (5 % for $CeNi_2$ and 10 % for $LaNi_2$) we assume that it is due to structural defects introduced by the excess of Ni in the AB_2 phase.

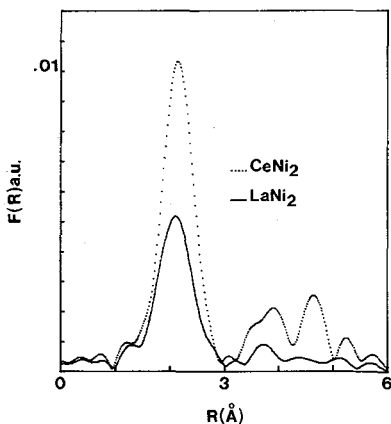


Fig.1 : F.T. of $LaNi_2$ and $CeNi_2$ spectra at 298 K

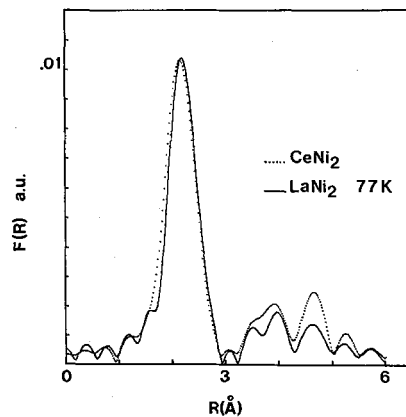


Fig.2 : F.T. of $LaNi_2$ at 77 K and $CeNi_2$ at 298 K spectra

b - Hydrides

X-ray diffraction patterns of the hydrides obtained at room temperature were measured as a function of hydrogen content. Indexing of the diffraction lines shows for both compounds the same $MgCu_2$ cubic structure as for the starting intermetallic. The intensity of the lines decreases continuously up to 3.5 H/mole and beyond that completely disappears. In the case of $LaNi_2$ the cell parameter slightly increases up to $x = 1.1$ H/mole ($\frac{\Delta V}{V} = 1.2\%$) then remain constant, whereas for $CeNi_2$ a slight cell parameter decrease ($\frac{\Delta V}{V} = 0.8\%$) is observed.

From the intensity decrease of the crystalline lines, we assumed that the crystalline phase corresponds to the α phase and the amorphous phase to the β phase which progressively replaces the α phase.

In order to understand this transformation we have studied EXAFS spectra at Ni K edge for various hydrogen concentrations. In figures 3 and 4, F.T. of $LaNi_2$ and $CeNi_2$ respectively with their related hydrides are presented.

The decrease of the first peak intensity and the disappearance of peaks at higher distances are observed. Results of the first peak analysis are given in table 1. For both compounds the distances remain constant. For $LaNi_2$, hydrogen absorption induces a Debye Waller factor increase whereas for $CeNi_2$ a coordination number decrease is also observed. This indicates that if the mean distance is unchanged, the distance distribution is larger for the hydrides.

The influence of hydrogen on cerium atoms was also checked. In Figure 5 Ce L_{III} absorption spectra of $CeNi_2$ and $CeNi_2H_4$ are presented. Each spectra was analysed with a fitting procedure described in [4]. For $CeNi_2$ the first white line at 5723 eV was attributed to a $4f^1$ configuration and the second one at 5732 eV to a $4f^0$ configuration. From the intensity ratio of the two peaks a valence of 3.23 ± 0.03 was calculated in agreement with previous work [5]. For $CeNi_2H_4$ the single white line at 5723 eV shows that cerium has become trivalent. Such a valency change upon hydrogenation has been previously observed for $CeRu_2$ [6]. For $LaNi_2$ and related hydrides no change of lanthanum edge was observed. But as lanthanum always remains trivalent La L_{III} edge study is not a significant means of investigation.

These results have shown the increase of local disorder around Ni atoms and the valency change of cerium atoms upon hydrogenation. As a next step EXAFS at the rare-earth L_{III} edge will be studied to observe the structural changes around La and Ce atoms.

Compounds		$LaNi_2$	$CeNi_2$			$LaNi_2H_{2.5}$	$LaNi_2H_{4.1}$	$CeNi_2H_{4.4}$
	Shell N°	1	1	2	3	1	1	1
EXAFS	$N_{\pm} \pm 10\%$	3.1	3.5	4	3	3.1	3.1	1.5
	$R_{\pm} \pm .01 \text{ \AA}$	2.52	2.53	4.40	5.09	2.52	2.52	2.53
	$\Delta\sigma_{\pm} \pm .005 \text{ \AA}$	0.07	0.03	0.05	0.05	0.09	0.10	0.06
X ray	N	6	6	12	12			
	$R \text{ \AA}$	2.59	2.54	4.40	5.08			

Table 1 : Parameters calculated from EXAFS and X.R.D. data for RNi_2 compounds (R = La, Ce) and related hydrides.

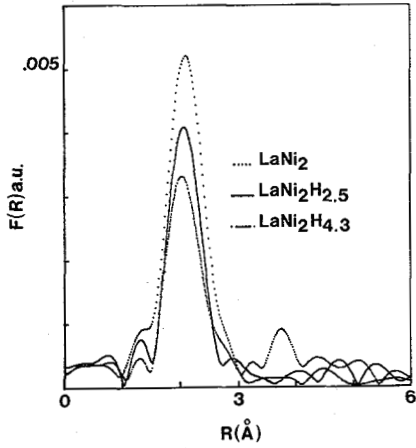


Fig.3 : F.T. of LaNi_2 and related hydrides with various hydrogen contents.

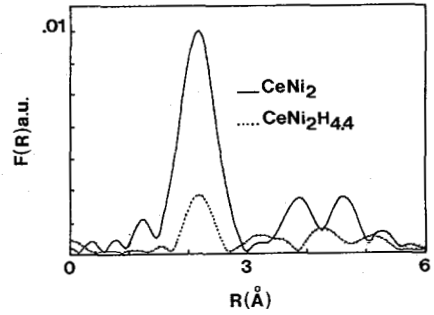


Fig.4 : F.T. of CeNi_2 and $\text{CeNi}_2\text{H}_{4.4}$

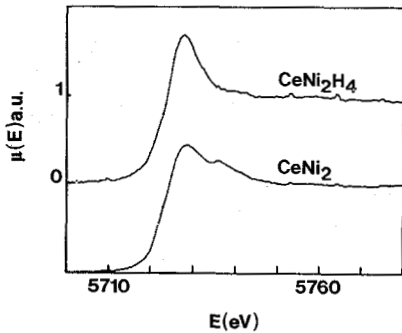


Fig.5 : Ce L_{III} edge absorption spectra of CeNi_2 and CeNi_2H_4

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