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In situ XAS study of the hydrogenation of AB_5 compounds ($A=La$, Ce and $B=Ni_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$)

V. Paul-Boncour*, J.-M. Joubert, M. Latroche, A. Percheron-Guégan

Laboratoire de Chimie Métallurgique des Terres Rares, GLVT, CNRS, 2 rue H. Dunant, F-94320 Thiais, France

Abstract

The XAS spectra of $La_{1-x}Ce_xB_5$ ($B=Ni_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$; $x=0$, 0.5, 1) at the Ce L_{III} and transition metal K edges have been measured in situ upon hydrogen absorption. The evolution of the Ce valence from an intermediate valent state to a trivalent state as the hydrogen content increases leads to an increase of Ce radius, which rules the structural and thermodynamic properties of the hydrides. The decrease of the prepeak intensities of the transition metal K edges, is related to the change of the density of states upon hydrogen absorption. The presence of cerium modify also the filling of the 3d band, and shift the formation of a stable hydride to larger H content.

Keywords: XAS spectra; Transition metal; Hydrogen absorption; Cerium

1. Introduction

$LaNi_5$ type intermetallic compounds have been extensively studied for their properties to store reversibly large amounts of hydrogen. They are now widely used as negative electrode in nickel metal–hydride batteries. The replacement of La by Mischmetal (Mm) and Ni by $B=Ni_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, has been found to be the best compromise for high capacity and good resistance to corrosion [1]. The Mischmetal, used for economical advantages, is a natural mixture of several rare earth elements, mainly lanthanum and cerium. As the composition of Mm varies with the source of the ore, it is important to understand the role of each rare earth element in particular of cerium, on the hydrogenation properties. A previous study of the thermodynamic and structural properties of the LaB_5 and CeB_5 compounds upon hydrogen absorption has shown a different evolution between these two systems [2]. The CeB_5 hydride shows a larger increase of the cell parameter **a** and an unexpected reduction of the 6 m site occupancy in the β branch (solid solution of hydrogen in the hydride phase). It was assumed that these anomalous behaviors can be due to a change of cerium valence, from intermediate to trivalent state, since they can be related to an increase of the Ce atom size.

The variation of cerium valence can be followed through the evolution of the Ce L_{III} X-ray absorption edge [3]. In addition, the modification of the transition metal K edges upon H absorption can be related to the changes of the density of states as it was observed in previous work on $LaNi_5$ and related hydrides by ex situ or electrochemical in situ measurements [4–6]. Therefore to verify whether the structural behavior of CeB_5 hydride is related to a change of cerium valence and to follow the modification of the electronic state of the 3d metals as a function of hydrogen content, we have performed in situ X-ray absorption (XAS) measurements of AB_5 compounds upon gaseous hydrogen absorption.

2. Experimental

The preparation and characterisation of the $(La_{1-x}Ce_x)Ni_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ intermetallic compounds ($x=0$, 0.5, 1) are described in Ref. [2]. The samples were activated by several hydrogen absorption–desorption cycles before experiments. The XAS experiments have been performed at LURE (ORSAY) on the XAFS II spectrometer with a Si 311 monochromator. A special cell was designed to perform the in situ hydrogen absorption experiments. The tight cell was equipped with mylar windows of 100 μm to perform transmission measurements and connected to a volumetric Sievert device to monitor the hydrogen content in the sample. A small amount of powdered sample was deposited on an adhesive kapton layer in beam for the XAS measurements,

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*Corresponding author.

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whereas about 300 mg of sample was introduced inside the cell and out of the X-ray beam, to measure quantitatively the amount of absorbed hydrogen. The XAS spectra were collected at the La and Ce L_{III} edge and at the Mn, Co and Ni K edges. However due to the proximity of the Ce L_I and Mn K edge, it was not possible to analyse the Mn K edge for the Ce containing samples. Each spectrum was then treated by a background subtraction and a normalisation to the height of the absorption edge. The Ce L_{III} spectra were refined by a convolution of lorentzian, gaussian and arctan functions for each white line according to Ref. [7]. The intensity of the prepeak in the transition metal K edges was measured by a surface integration.

3. Results

The evolution of normalized Ce L_{III} XAS spectra of the CeB_5H_x hydrides ($x=0$, 1.3, 4.1 and 5.0) is reported in Fig. 1. These spectra display two white lines designated as Ce^{III} and Ce^{IV} which correspond to the transition from the $2p_{3/2}$ core level to the two final $4f^1(5d\ 6s)^3$ and $4f^0(5d\ 6s)^4$ empty states, respectively. The fractional part of the valence can be obtained by the ratio of the two integrated white line intensities. In both CeB_5 and $Ce_{0.5}La_{0.5}B_5$ intermetallic compounds the cerium is in an intermediate valent state with a Ce valence slightly larger for $Ce_{0.5}La_{0.5}B_5$ compared to CeB_5 (Fig. 2). In the α phase range, the decrease of the Ce valence remains weak. In the β branch a steep decrease of the valence from 3.3 down to 3.10 occurs for a small hydrogen uptake.

The evolution of the Ni K edge of CeB_5H_x compounds versus H content is reported in Fig. 3. The main effect is the decrease of the prepeak intensity at about 8333 eV as the H content increases. This peak has been already observed in the XANES spectra of $LaNi_5$ and substituted compounds [4–6]. It has been attributed to the transition from the 1 s core level to the empty part of the 4p states which are strongly hybridized with the 3d states. Therefore the decrease of this prepeak intensity can be linked to the filling of the Ni 4p–3d states by hydrogen. In order to quantify the filling of the Ni d band, we have measured the relative integrated intensity of this prepeak. The same procedure was applied to the Co and Mn (for LaB_5) K edges. The evolution of the relative prepeak intensities is reported in Fig. 4. For all compounds the decrease of the prepeak intensity shows a similar variation at the Mn, Co and Ni K edge. A significant decrease of the prepeak intensity occurs more rapidly in LaB_5 hydrides than in the Ce containing hydrides.

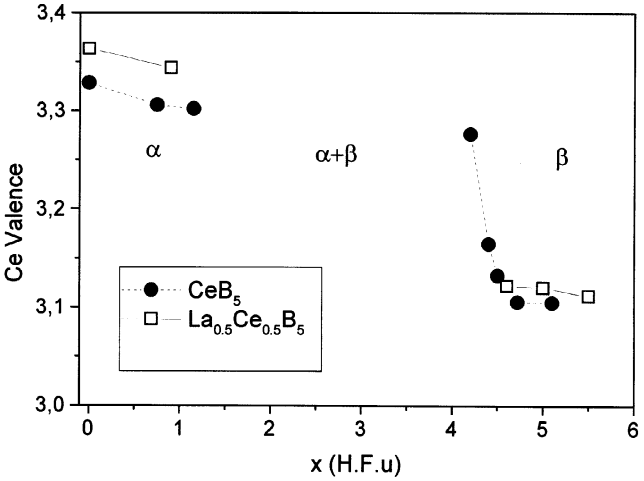

Fig. 2. Evolution of the Ce valence in CeB_5 and $La_{0.5}Ce_{0.5}B_5$ hydrides.

4. Discussion

The previous study of the CeB_5 hydrides compared to the LaB_5 hydrides [2] has shown the influence of the cerium substitution on their thermodynamic and structural properties. It was assumed that the differences between the

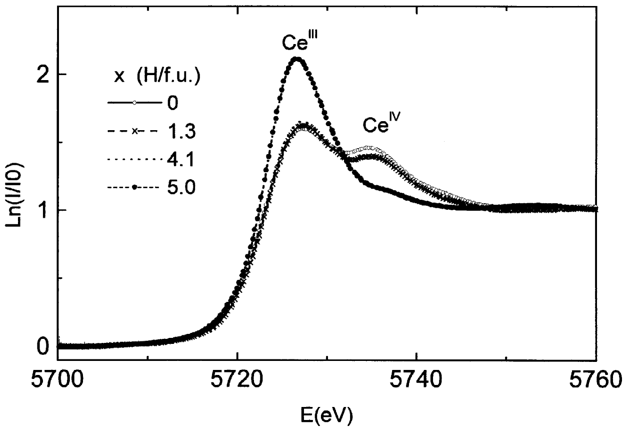

Fig. 1. Evolution of the Ce L_{III} XAS spectra of the CeB_5H_x hydrides. Ce^{III} and Ce^{IV} indicate the positions of the white lines corresponding to trivalent and tetravalent Ce, respectively.

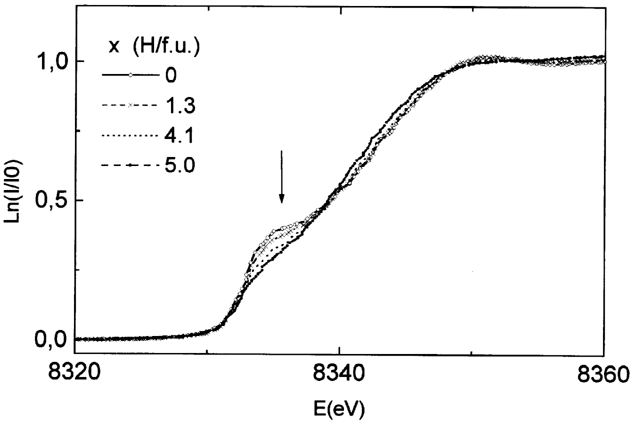

Fig. 3. Evolution of the Ni K edge XAS spectra of the CeB_5 hydrides. The arrow indicates the prepeak corresponding to the transition from 1s to 4p–3d empty states.

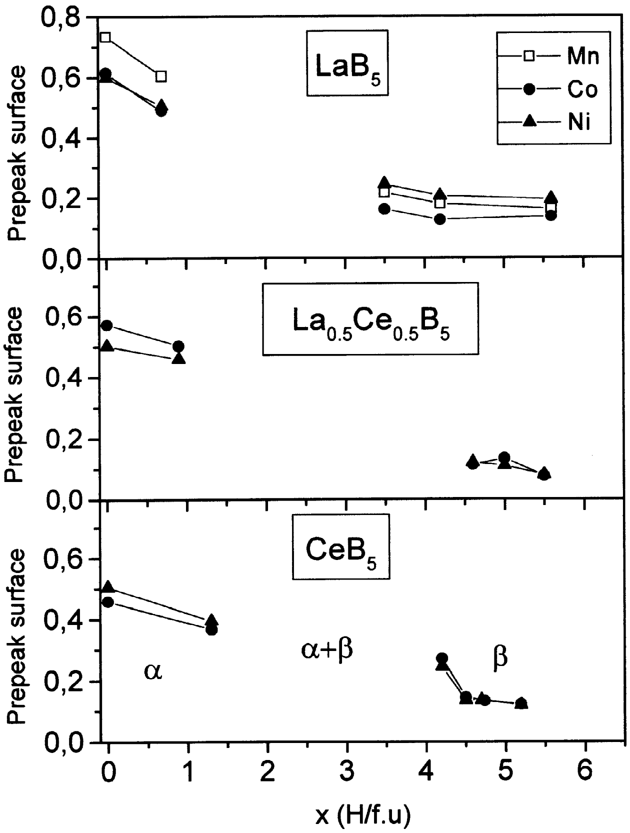

Fig. 4. Evolution of the surface of the prepeak of the Mn, Co and Ni–K edge of the LaB_5, $La_{0.5}Ce_{0.5}B_5$ and CeB_5 hydrides.

two systems were due to a change of cerium valence in the β branch. In the nearly trivalent state (γ-Ce) the cerium radius is 1.83 Å whereas in the intermediate valent state (α-Ce) it is 1.73 Å. This corresponds, respectively, to a size reduction of 2 and 8% compared to that of La atom (1.87 Å) [8]. The study of the transformation of Ce metal under pressure by XAS indicates a jump of the valence of 10% from γ-Ce ($p=0$ kbar) to α-Ce ($p=10$ kbar), then the valence increases continuously up to 30 kbar [7]. The steep decrease of Ce valence for a weak hydrogen uptake can therefore be induced by the increase of the cell volume due to hydrogen absorption, as a negative pressure effect. The presence of additional electrons due to H absorption can also favor the localization of the Ce 4f states below the Fermi level.

The decrease of the Ce valence in the β branch leads to an increase of the Ce radius, and therefore explains the larger increase of the cell volume in the β branch compared to LaB_5 [2]. This effect is more pronounced for CeB_5 than for $La_{0.5}Ce_{0.5}B_5$, due to the larger amount of Ce atoms. The increase of the Ce radius allows also to explain the anomalous decrease of the interstitial 6 m site occupancy observed by neutron diffraction [2] since this site is surrounded by two rare earth and two transition metal atoms. The other interstitial sites which contains no or only one rare earth atoms are less affected and display a normal behavior.

The decrease of the prepeak intensity of the 3d K edges, attributed to a transition towards empty 4p–3d states, can be related to a weaker hybridization between the 4p and 3d orbitals and to the filling of the 3d states, which occurs upon H absorption. The substitution of Ni by Mn, Al and Co, modify the DOS of $LaNi_5$ [9], since the additional Mn and Co 3d sub-bands are located at higher energy than the Ni 3d sub-band. The Ni d states are much more strongly mixed with the Co d band than with the Mn d states. This Mn 3d sub-bands has therefore a larger number of holes than Ni, and this can explain the larger surface of the Mn prepeak compared to those of Ni and Co in the LaB_5 compound. From these DOS calculations, it is remarkable to notice that the estimated number of holes in the transition metal d bands, up to the valley which marks the rise of the La d states is the same, four holes, for both the $LaNi_4Co$ and LaB_5 compounds. In the hydride $LaNi_4CoH_4$ [10] the Fermi level falls just at the bottom of this valley, a factor that was correlated to the stability of this intermediate hydride. For larger H content, the hydrogen pressure is expected to rise. This corresponds to the experimentally observed β branch. In $La_{0.5}Ce_{0.5}B_5$ and CeB_5, the minimum hydrogen content of the β branch (4.1 H/f.u.) is shifted to larger value compared to LaB_5 (3.5 H/f.u.). It is noticeable than the decrease of the Ni and Co prepeak intensities of the Ce compounds are also shifted to larger H content (Fig. 4). This can be related to the presence of the Ce 4f states at the Fermi level, which shift the minimum of the total DOS to higher energy. An hydride phase will therefore be stabilised for larger H content.

5. Conclusions

The evolution of the Ce valence in CeB_5 and $La_{0.5}Ce_{0.5}B_5$ hydrides, studied by in situ X-ray absorption measurements at the Ce L_{III} edge have shown a decrease of the Ce valence from 3.32 to 3.10, which occurs mainly in the β branch. This variation of Ce valence, implies an increase of the Ce radius, and explains the larger cell volume increase and the unexpected decrease of the 6 m site occupancy. The intensity of the prepeak of the 3d K edge, attributed to a transition towards empty 4p–3d states, decrease more rapidly in LaB_5 than in CeB_5. Since the formation of a stable hydride is obtained when the fermi level is located in a minima of the density, this can explain the shift of the β branch to larger H content in the Ce compounds.

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References

[1] H. Ogawa, M. Ikoma, H. Kawano, I. Matsumoto, Power Source 12 (1998) 393.

[2] J.-M. Joubert, M. Latroche, A. Percheron-Guégan, F. Bourée-Vigneron, J. Alloys Comp. 275–277 (1998) 118.

[3] 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, pp. 647–650.

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

[5] 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 (1995) 2278.

[6] D.A. Tryk, In Tae Bae, Y. Hu, S. Kim, M.R. Antonio, D.A. Sherson, J. Electrochem. Soc. 142 (1995) 824.

[7] J. Röhler, in: K.A. Gschneidner Jr., L. Eyring, S. Hüfner (Eds.), Handbook on the Physics and Chemistry of Rare earths, X-ray Absorption and Emission Spectra, Vol. 10, Elsevier Science Publisher, North-Holland, 1987, p. 453.

[8] D.C. Koskenmaki, K.A. Gschneidner Jr., in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare earths, Cerium, Vol. 1, Elsevier Science Publisher, North-Holland, 1978, p. 337.

[9] V. Paul-Boncour, M. Gupta, J.-M. Joubert, A. Percheron-Guégan, P. Parent, C. Laffon, J. Mater. Chem. 10 (2000) 2741.

[10] M. Gupta, J. Alloys Comp. 293–295 (1999) 190.