Effect of hydrogenation on the electronic state of metallic La hydrides probed by X-ray absorption spectroscopy at the La $L$-edges

To cite this article: N Ishimatsu et al 2009 J. Phys.: Conf. Ser. 190 012070

View the article online for updates and enhancements.

Related content
- Effect of Hydrogenation on Photodarkening in CdS-Doped Glass
  Tadaki Miyoshi, Koji Nitta, Ken-ichi Towata et al.
- Effect of Hydrogenation on the Dangling-Bond Free 4H-SiC(1120)/SiO$_2$ Interface Studied by Ab Initio Calculations
  Eiichi Okuno, Toshio Sakakibara, Shoichi Onda et al.
- Effect of Hydrogenation on ZnO Luminescence
  Takashi Sekiguchi, Naoki Chashi and Yoshihiro Terada

Recent citations
- Relationship between element-selective electronic states and hydrogen absorption properties of Pd-M (M=Ru, Rh, Ag, and Au) alloys
  Kanako Fujii et al
Effect of hydrogenation on the electronic state of metallic La hydrides probed by X-ray absorption spectroscopy at the La L-edges

N Ishimatsu¹, R Sasada¹, H Maruyama¹, T Ichikawa², H Miyaoa², T Kimura³, M Tsubota³, Y Kojima³, T Tsumuraya³, T Oguchi⁴, N Kawamura⁴, A Machida⁵

(1) Grad. Sch. of Sci., Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
(2) IAMR, Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan
(3) ADSM, Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan
(4) JASRI/SPring-8, 1-1-1, Kouto, Sayo, Hyogo 679-5198, Japan
(5) SRRC, JAEA, 1-1-1, Kouto, Sayo, Hyogo 679-5148, Japan

naoki@sci.hiroshima-u.ac.jp

Abstract. We have investigated the effect of hydrogenation on La 5d and 6p electronic states in metallic LaHₓ (x=0.0, 2.0, 2.3, and 2.6) by X-ray absorption near edge structure at the La L-edges. As the hydrogen content x increases from 0 to 2.6, white-line intensity at the La L₂,3-edges shows a remarkable increase in the range of x≥2.0. This is interpreted as the increase in La 5d hole induced by interstitial H atoms on the octahedral sites. On the other hand, the shoulder structure at the La L₁-edge disappears in the process of x=0.0→2.0, indicating that the p-d hybridization is weakened by H atoms on the tetrahedral sites. This study demonstrates that H atoms on the two interstitial H sites provide different contribution to the modification of the electronic states.

1. Introduction
In metal-hydride systems, hydrogenation causes remarkable changes in crystal structure, electric conductivity, optical property, and so on. In the case of La-metal with double hexagonal closed pack (dhcp) structure, the hydrogenation partially changes La-metal into fcc structured LaHₓ with increasing x, and then the fcc structure remains in the range of x≥2.0. It is well known that H atoms preferentially occupy tetrahedral sites (Hₜ-site) of the fcc lattice in LaHₓ (x≤2.0) first and subsequently octahedral one (Hₒ-site) in LaHₓ (x>2.0). La hydrides undergo a drastic drop of electric conductivity with increasing hydrogen content in the range of x≥2.0 [1]; a metal-insulator transition eventually occurs at x≥2.8 accompanied with a remarkable enhancement of the optical transparency [1,2]. The drastic changes in the electric and optical properties have attracted great interest in the hydrogen-induced modification in the electronic structure of LaHₓ.
According to the electronic band calculations [3,4], it has been explained that H atom captures an electron from La and forms a two-electron singlet states as an anion H\(_{-}\), resulting in a gap at the Fermi energy (\(E_F\)) for LaH\(_x\) [3,4]. Heat capacity measurement experimentally demonstrated that density of states (DOS) at \(E_F\) gradually decreases with increasing \(x\) from 1.9 to 3.0 [5,6]. Since DOS at \(E_F\) mainly consists of La \(d\) orbitals, La \(d\)-H \(s\) hybridization and charge transfer between La \(d\) and H \(s\) orbitals are important issues to understand the transition. In order to study these phenomena experimentally, X-ray absorption spectroscopy is a useful technique because of its element- and orbital selectivity. Here, we present a study on the electronic states in metallic LaH\(_x\) (\(x\)=0, 2.0, 2.3, 2.6) probed by X-ray absorption near edge structure (XANES) at the La \(L_{1,2,3}\)-edges. XANES spectra allow us to probe the electronic states of La 5\(d\) and 6\(p\) orbitals around \(E_F\). The series of the samples may distinguish modification of the electronic structure due to the different hydrogen sites, \(i.e.,\) H\(_t\) and H\(_o\).

2. Experimental procedure

Powdered LaH\(_{2.3}\) sample was synthesized by hydrogenation under 773 K and hydrogen gas pressure of 0.5 MPa. The other samples were purchased from Goodfellow Co. Ltd. and Kojundo Chemical Lab. Co. Ltd. Since the lattice constant of metallic LaH\(_x\) linearly decreases with increasing \(x\) [7], hydrogen content \(x\) was estimated from the lattice constant measured by X-ray powder diffraction. There was no impurity phase in the sample.

The XANES measurement was carried out at SPring-8 BL39XU using transmission geometry. Since La-metal and La hydrides are easily oxidized, the sample was sealed with an Ar atmosphere during the measurements. From a reproducibility of XANES profile, we confirmed that the sample was not oxidized.

3. Results and Discussion

Figure 1 shows XANES spectra of LaH\(_x\) at the La \(L_{2}\)- and \(L_{3}\)-edges. Each spectrum was normalized at the highest energy side on the basis of the conventional procedure. La hydrides show a narrow profile of white-line (WL) compared with that of La-metal. The hydrogenation, \(x\)=0\(\rightarrow\)2.0, enhances the intensity of WL at the \(L_{2}\)-edge. On the other hand, the WL at the \(L_{3}\)-edge becomes sharper but the peak intensity is almost unchanged. In the range of \(x\)=2.0-2.6, the WL steeply increases, which is observed at both the edges. On the higher energy side, a small change in the oscillatory profile may be due to the structural transition from dhcp to fcc.

![Figure 1. XANES spectrum of LaH\(_x\) at the La \(L_{3}\)- and \(L_{2}\)-edges.](image)

To provide quantitative information about the La 5\(d\) states, the WL profile was extracted by subtracting an arctangent background from the XANES spectrum. For this procedure, the core-hole lifetime broadening of the \(L_{3}\) and \(L_{2}\)-edges was set to be 3.41 eV and 3.68 eV, respectively [9]. Integrated intensity of WL (\(I_{WL}\)) at \(L_{2}\)-, \(L_{3}\)-edges, and the sum of them are shown in Figure 2. The sum
of \(I_{WL}\) is proportional to a number of La 5d holes [8]. The steep increase in the sum of \(I_{WL}\) with \(x=2.0 \rightarrow 2.6\) indicates that the occupation of \(H_o\) significantly induces La 5d hole. In the range of \(x=0.0\) to 2.0, on the other hand, the sum of \(I_{WL}\) exhibits a slight positive slope, indicating that the increase in the La 5d hole due to the occupation of \(H_i\) is small compared with that due to \(H_o\). This result is attributed to the opposite trend of \(I_{WL}\) at \(L_2\)- and \(L_3\)-edges; the remarkable increase in \(I_{WL}\) at \(L_2\)-edge indicates that the occupation of \(H_t\) site preferentially induces the La 5d holes with \(J=3/2\) symmetry if we assume a dipole transition \(2p_{1/2} \rightarrow 5d_{3/2}\) at the \(L_2\)-edge. However, this enhancement is compensated by the decrease in \(I_{WL}\) of the \(L_3\)-edge where the dipole transition \(2p_{3/2} \rightarrow 5d_{5/2}\) dominantly occurs [8]. In this consideration, the interaction between photoelectron and core-hole is not taken into account. For a better understanding of the WL intensity, it should be discussed how the interaction influences the variation of \(I_{WL}\).

![Figure 2](image)

**Figure 2.** Integrated intensity of WL \((I_{WL})\) at \(L_2\)-, \(L_3\)-edges, and sum of them as a function of \(x\). \(I_{WL}\) at the \(L_2\)- and \(L_3\)-edges are multiplied by 3 and 1.5 for comparison, respectively.

![Figure 3](image)

**Figure 3.** XANES spectrum of LaH\(_x\) at the La \(L_1\)-edge.

It is noted that the absorption edge \(E_0\), determined from the inflection point of XANES spectrum, gradually shifts to a higher energy side with increasing \(x\) up to 2.6. However, the shift is small, \(+0.5\) eV for \(L_3\)- and \(+1.0\) eV for \(L_2\)-edge, so that LaH\(_x\) remains metallic. This result is consistent with the metallic conductivity of LaH\(_x\) \((x<2.8)\) [1]. Furthermore, for the WL profile, full width of half maximum (FWHM) of WL is reduced with increasing \(x\) from 0 to 2.6. Therefore, the hydrogenation causes the band width of La 5d DOS to be narrower. These variations in La 5d states are strongly related to the decrease in DOS at the \(E_F\) due to the hydrogenation [5,6]. We consider that the modification leads to a gap at \(E_F\) and gives rise to onset of the metal-insulator transition.

In order to investigate the effect of hydrogenation on the different orbital, we probed La 6p electronic state by XANES at the La \(L_1\)-edge. Figure 3 shows XANES spectra at the La \(L_1\)-edge. The spectral profile of La-metal is characterized by a shoulder structure "A" that is ascribed to the La
$p$-orbital hybridized with the $d$-orbital of the neighboring La atoms [10]. As shown in Figure 3, the shoulder A disappears at the hydrogenation $x=2.0$. Therefore, the occupation of H$_t$ site suppresses the $p$-$d$ hybridization and effectively reduces La $p$ DOS near $E_F$. The collapse of the $p$-$d$ hybridization would influence the La $5d$ states. We also observed that the structural transition from dhcp to fcc gives rise to the remarkable change in the oscillatory profile at the higher energy side.

In contrast to the remarkable change of the shoulder structure A at $x \leq 2.0$, the spectral profile at $x > 2.0$ is unchanged except for the intensity of crest "B"; the crest B is slightly raised at $x = 2.6$. Therefore, the occupation of H$_t$ site leads to a small influence on the La $6p$ states. Although the hydrogenation modifies not only La $5d$ but also $6p$ electronic states, the occupation of H$_t$ site is more effective in the case of La $6p$ states. For the drastic fall in electric conductivity, it is considered that the effect of $p$ states is probably weak compared with that of La $d$ states.

4. Conclusion

We have investigated the effect of hydrogenation on La $d$ and $p$ electronic states in metallic LaH$_x$ ($x \leq 2.6$) by means of XANES at the La $L$-edges. The present results demonstrate that the modification in the electronic states occurs in both La $5d$ and $6p$ states. Major change in $6p$ state is observed due to the occupation of H$_t$ site, which weakens the $p$-$d$ hybridization. On the other hand, the occupation of H$_o$ site dominantly increases La $5d$ holes. The increase in La $5d$ hole and reduction of FWHM for WL well correspond to the decrease in DOS due to the hydrogenation. It is considered that the modification in La $d$ state mainly results in onset of the metal-insulator transition at $x \approx 2.8$.

Acknowledgments

This work was supported by the Grants of the NEDO project “Advanced Fundamental Research on Hydrogen Storage Materials.” XANES measurement was performed at SPring-8 with the approval of PRC-JASRI (Nos. 2007B1512 and 2008B1284).

References

[1] Huiberts J H, Griessen R, Rector J H, Wijngaarden R J, Dekker J P, De Groot D G and Koeman N J 1996 Nature(London) 380 231
[2] Griessen R, Huiberts J H, Kremers M, van Gogh A T M, Koeman N J, Dekker J P and Notten P H L 1997 J. Alloys Compd. 253-254 44
[3] Eder R, Pen H F and Sawatzky G A 1997 Phys. Rev. B 56 10115
[4] Ng K K, Zhang F C, Anisimov V I and Rice T M 1997 Phys. Rev. Lett. 78 1311
[5] Kai K, Gschneidner Jr. K A, Beaudry B J and Peterson D T 1989 Phys. Rev. B 40 6591
[6] Leyer S, Heck S, Kaiser A, Dormann E and Barnes R G, 2005 Phys Rev. B 72 125115
[7] Renaudin G, Yvon K, Wolf W and Herzig P 2005 J. Alloys Compd. 404-406 55
[8] Lytle F W 1987 Phys. Chem. 91 1251
[9] Fuggle J C 1992 Unoccupied Electronic States: Fundamentals for Xanes, Eels, Ips and Bis (Topics in Applied Physics) ed J E Inglesfield (Springer-Verlag) Appendix B pp 347-351
[10] Chaboy J, Garcia J and Marcelli A 1997 J. Magn. Magn. Mater. 166 149