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EXAFS characterization of $LaNi_5$, $LaCo_5$ and their hydrides

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Introduction

$LaNi_5$ and $LaNi_5$ based alloys are important for hydrogen storage materials, such as an electrode in Ni-metal hydride batteries and hydrogen-fuel cells. The crystal structure of $LaNi_5$ is $CaCu_5$-type (space group *P6/mmm*). Its hydride, $LaNi_5H_7$, has hexagonal structure of space group $P6_3mc$. $LaCo_5$ also has $CaCu_5$-type structure, while hexagonal structure distorts to orthorhombic structure when $LaCo_5$ is hydrogenized. Hydride of $LaCo_5$ is represented as $LaCo_5H_3$ rather than $LaNi_5H_7$ for $LaNi_5$, which leads to smaller hydrogen absorption for $LaCo_5$ compared with $LaNi_5$. Their hydrogenation characteristics may correspond to the difference of local structure between $LaCo_5$ and $LaNi_5$ [1].

In this paper, the local structures around Ni, Co and La for $LaNi_5$, $LaCo_5$ and their hydrides are clarified with EXAFS and the mean-square fluctuation of inter-atomic distance, σ^2, is given from EXAFS spectrum due to estimate the influence of the structural fluctuation on the hydrogen absorption and the structural transition.

Experiments

Samples of $LaNi_5$ and $LaCo_5$ are prepared by arc-melting the constituent elements under an argon atmosphere and annealed at 1223 K for 5 days. These samples are hydrogenized under 4MPa hydrogen at 353K.

For XAFS measurements, BN pellets are prepared adjusting optimum absorption thickness. XAFS spectra of the Ni (Co) K-edge and La L_{III}-edge were measured by a transmission method from 20 K to 300K using a double Si(111) monochromator. UWXAFS programs are used to analyze the XAFS data and FEFF program is used for multiple scattering calculations.

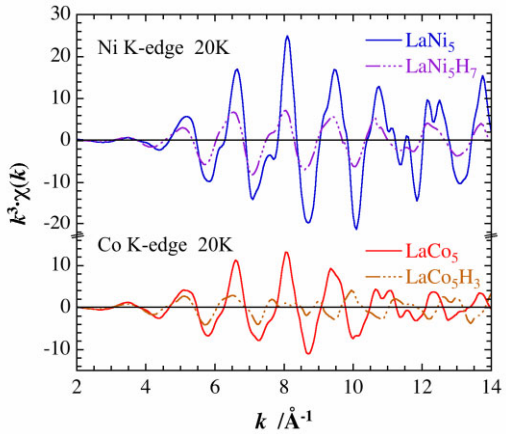

Fig.1 EXAFS spectra of Ni and Co K-edges represented as $k^3\chi(k)$ vs. k at 20K for $LaNi_5$, $LaCo_5$ and their hydrides.

Results and discussion

Fig.1 shows Ni K-edge EXAFS spectra at 20K for $LaNi_5$ and $LaNi_5H_7$ and Co K-edge for $LaCo_5$ and $LaCo_5H_3$. The EXAFS spectrum of $LaNi_5$ exhibits relatively larger amplitude than $LaCo_5$, while the phase of spectrum is almost same as that for $LaCo_5$ because these compounds have same $CaCu_5$-type crystal structure. Small EXAFS amplitude of $LaCo_5$ is supposed that the local structure around Co in $LaCo_5$ has relatively large fluctuation probably due to weak Co-Co bonding compare with Ni-Ni one for $LaNi_5$, which can be associated with transformation from hexagonal to orthorhombic structure through hydrogenation.

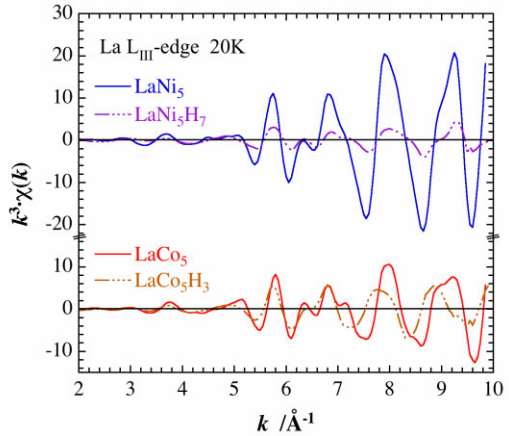

Fig.2 EXAFS spectra of the La L_{III}-edge represented as $k^3\chi(k)$ vs. k at 20K for $LaNi_5$, $LaCo_5$ and their hydrides.

EXAFS $k^3\chi(k)$ spectra of the La L_{III}-edge are shown in Fig.2. The amplitude of spectrum for $LaNi_5H_7$ drastically attenuated from that for $LaNi_5$. Consequently, σ^2(La-Ni) increases from 0.48×10^{-4} [nm^2] for $LaNi_5$ to 1.85×10^{-4} [nm^2] for $LaNi_5H_7$.

Although the XRD patterns of hydrides show long-range structural order, EXAFS spectra indicate that the local structure of hydrides involves large fluctuation of inter-atomic distance. It is interesting that the phase of spectrum for $LaNi_5H_7$ is almost same as that for $LaNi_5$, which disagrees with the calculated spectra for $LaNi_5H_7$. It is indicated that the transformation from $LaNi_5$ to hydride is an isotropic expansion with large structural fluctuation.

Reference

[1] M. Matsuura, et al., J.Alloy Comp. 390, 31 (2005).

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