

Resolving nano-scale atomic arrangements in various materials for understanding their hydrogen storage properties using the atomic pair distribution function

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Summary

We have carried out an in-situ X-ray total scattering experiment on $\text{LaNi}_{4.5}\text{Al}_{0.5}$ to investigate its local structural evolution during the hydrogenation process using the atomic pair distribution function (PDF) analysis. Data were collected at several pressure points at room temperature at BL22XU at SPring-8. Our preliminary results show that all the diffraction data were well explained by the average hexagonal structural model (space group $P6/mmm$). The local structure of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ was also well explained by the $P6/mmm$ structural model but that of $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ was not. The PDF analysis result indicates that the arrangement of Ni atoms on a basal plane of $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ is somewhat distorted probably due to the local arrangement of H atoms.

key words:

Hydrogen storage materials, local structure, total scattering, pair distribution function, LaNi_5

1. Objectives

We have investigated transitional changes in the crystal structure of LaNi_5 -based intermetallic compounds, well-known materials for hydrogen storage, during the hydrogenation process. Via time-resolved measurements using BL22XU beam line, we observed the development of huge diffuse intensities underneath the Bragg peaks during the transition from the solid solution phase to the hydride phase. Such diffuse intensities completely disappeared after the hydrogenation process was completed. It is well known that solid solution and hydride phases coexist during the hydrogen reaction process and most probably such huge diffuse intensities arise from disordered atomic arrangements at an interface between two phases. In order to find out the origin of the diffuse intensities, we propose to carry out the in-situ hydrogen gas loading X-ray total scattering experiments on $\text{LaNi}_{4.5}\text{Al}_{0.5}$ for the atomic pair distribution function (PDF) analysis.

2. Methods

A synchrotron X-ray total scattering experiment was conducted at Japan Atomic Energy Agency (JAEA) beam line of BL22XU [1] at SPring-8. $\text{LaNi}_{4.5}\text{Al}_{0.5}$ powder sample (particle size $< 20 \text{ }\mu\text{m}$) was packed in an in-situ gas loading sample holder made of a kapton capillary with a diameter of 1.4 mm, a valve and couplings. The sample was

activated by heating at 423 K under vacuum for 1 h before hydrogenation. Data were collected at several pressure points using RA-PDF setup [2]. All the measurements were carried out at room temperature and an incident X-ray energy was 69.905 keV ($\lambda=0.17735$ Å). An image plate detector (R-AxisV from Rigaku) was mounted orthogonal to the incident beam with a sample-to-detector distance of 300 mm. The signal from an empty container (a kapton capillary) was subtracted from the raw data, and various other corrections were made [3] before obtaining the PDFs using the program PDFgetX2 [4]. For local structural studies the PDFgui program [5] was used and for average structural studies the RIETAN-FP program [6] was used.

3. Results and Discussion

Rietveld fits of synchrotron X-ray diffraction data of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ using the $P6/mmm$ structural model are shown in Figure 1(a) and (b), respectively. In the $P6/mmm$ model, La is on (0,0,0), Ni(1) on (0.3333, 0.6667, 0), Ni(2) on (0.5, 0, 0.5) and Al on (0.5, 0, 0.5). During hydrogenation, the volume of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ expands but its structure type remains the same [7]. Overall features including peak positions and peak intensities in $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ data are well explained by the model and no extra phase is found (Figure 1). Another model where Al occupies both (0.3333, 0.6667, 0) and (0.5, 0, 0.5) was reported but this model fails to explain some of peak intensities in our diffraction data. The Rietveld fit of the diffraction data obtained at $P=0.047$ MPa, where solid solution and hydride phases coexist, is shown in Figure 2. The data is well explained by two $P6/mmm$ structural models, one for solid solution phase and the other for hydride phase. Refined lattice parameters as well as mass fractions of solid solution (f_s) and hydride (f_h) phases obtained from Rietveld refinement of selected datasets are given in Table 1.

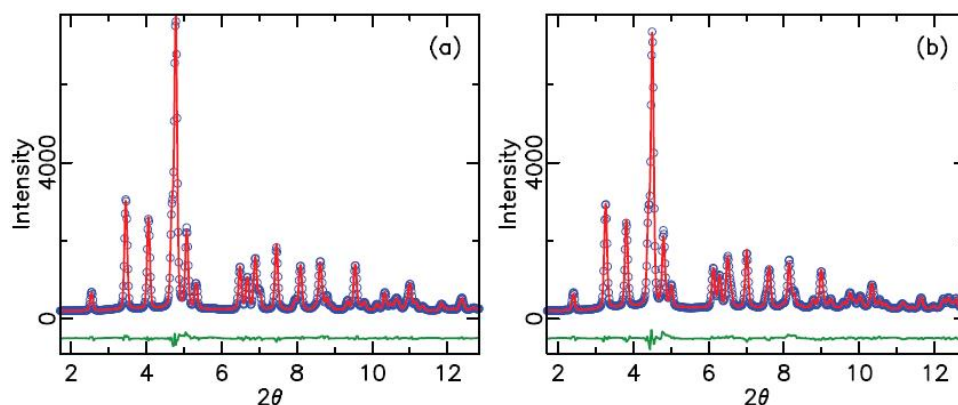


Figure 1. Rietveld fits of synchrotron X-ray diffraction data of (a) $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and (b) $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ obtained at room temperature. A $P6/mmm$ structural model was used. Blue open circles, red solid lines and green solid lines represent data, calculation and difference between data and calculation, respectively. Difference curves are offset for clarity.

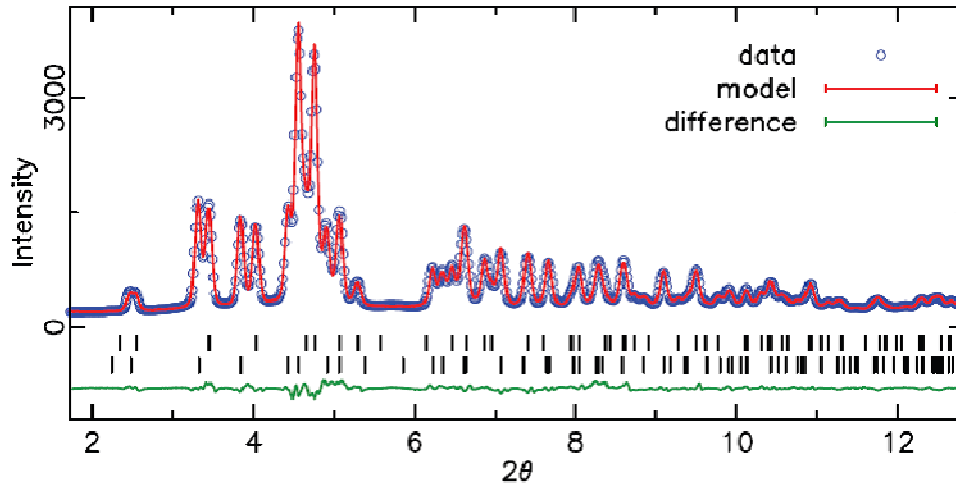


Figure 2. The Rietveld fit of in-situ X-ray diffraction data of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ at $P=0.047$ MPa during hydrogenation. Two $P6/mmm$ structural models were used. Difference between data and calculation is offset.

Table 1. Lattice parameters of the solid solution and hydride phases of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ as well as their mass fractions obtained from Rietveld refinement of in-situ synchrotron X-ray diffraction data. The lattice parameters are in units of Å.

pressure	Solid solution lattice parameters	Hydride lattice parameters	fractions
0 MPa	$a=5.0444(5)$, $c=4.0298(3)$		
0.036 MPa	$a=5.0804(6)$, $c=4.0329(5)$	$a=5.332(2)$, $c=4.164(1)$	$f_s:f_h=0.84:0.16$
0.047 MPa	$a=5.0862(9)$, $c=4.0352(6)$	$a=5.335(1)$, $c=4.1702(7)$	$f_s:f_h=0.48:0.52$
0.054 MPa	$a=5.088(4)$, $c=4.051(2)$	$a=5.3417(8)$, $c=4.1812(6)$	$f_s:f_h=0.09:0.91$
$P > 1$ MPa		$a=5.3673(6)$, $c=4.2578(4)$	

The PDF refinement results using $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ X-ray data are shown in Figure 3(a) and (b), respectively. The average structural model (space group $P6/mmm$) was used. The refinement range was $1.5 < r < 20$ Å but only the range of $r < 10$ Å is shown. A scale factor, lattice parameters, isotropic atomic displacement parameters (U_{iso}) and a peak sharpening parameter [3] were refined until the best fit was obtained. The model explains the X-ray PDF of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ well with reasonable U_{iso} values (Figure 3(a)). It also reproduces overall PDF features of $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ but it does not pick up the positions and intensities of some of the peaks correctly (Figure 3(b)). Especially, the model provides a different shaped peak at ~ 4.3 Å and a smaller peak at ~ 5.2 Å. When we use anisotropic atomic displacement parameters ($U_{11}=U_{22} \neq U_{33}$), U_{11} (and U_{22}) for Ni(1) and Ni(2) becomes twice larger than U_{33} . This result indicates that the arrangement of Ni on a basal plane ($z=0$) of $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ is somewhat distorted. This is probably closely related to local hydrogen occupation. Further analyses of the local distortion in the hydride phase and the local structural evolution during the hydrogenation process are underway.

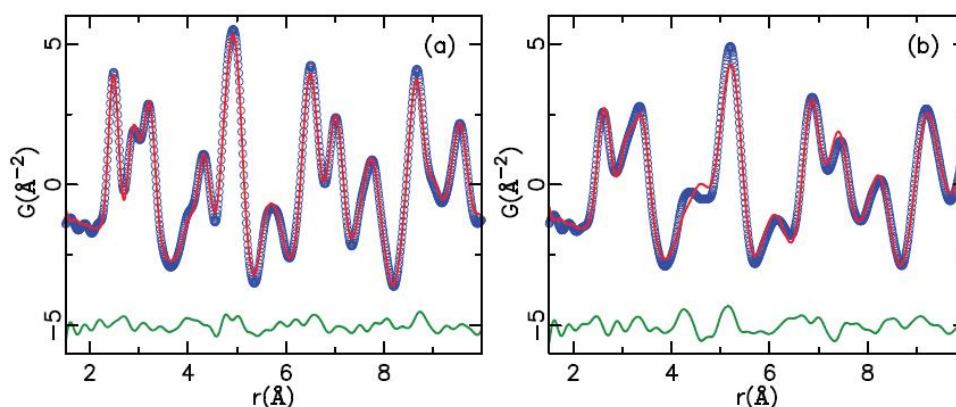


Figure 3. The PDF fits of (a) $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and (b) $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_{4.8}$ data using the $P6/mmm$ structural model. Blue open circles, red solid lines and green solid lines correspond to experimental PDFs, calculated PDFs and difference curves. The difference curves are offset for clarity.

4. References

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