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An in situ Mössbauer study using synchrotron radiation

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Abstract We have been developing a system for in situ Mössbauer studies using synchrotron radiation (SR) to elucidate the mechanism of hydrogenation processes. In the system, samples reacts in a pressure-temperature chamber and SR-based Mössbauer spectra using variable-frequency nuclear monochromator and energy spectra of inelastic nuclear resonant scattering (NRS) of SR are measured. As a feasibility study, the temperature dependence of the Mössbauer and inelastic NRS spectra of ^{57}Fe in c-$GdFe_2H_3$ under vacuum were measured. In both spectra, clear differences were observed between 373 K and 573 K. These differences can be interpreted by the change of microscopic environment around Fe at the dehydrogenation. Thus, it is confirmed that this system works well enough to perform the in-situ Mössbauer study on the dehydrogenation of c-$GdFe_2H_3$.

Keywords Hydrogen desorption · In situ Mössbauer study · Synchrotron radiation · $GdFe_2$ · Nuclear monochromator · Inelastic nuclear resonant scattering

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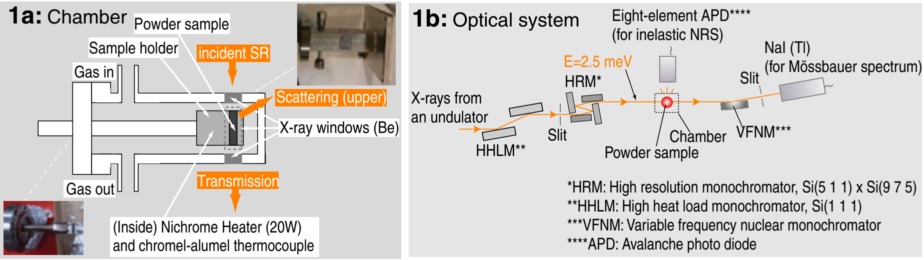


Fig. 1 Schematic drawings; **1a**: the developed chamber for in situ Mössbauer study. **1b**: the optical system at the experiment in BL11XU. The orange bold arrows mean the path of the beam. The upper right and the lower left at Fig. 1a is the photograph of the chamber

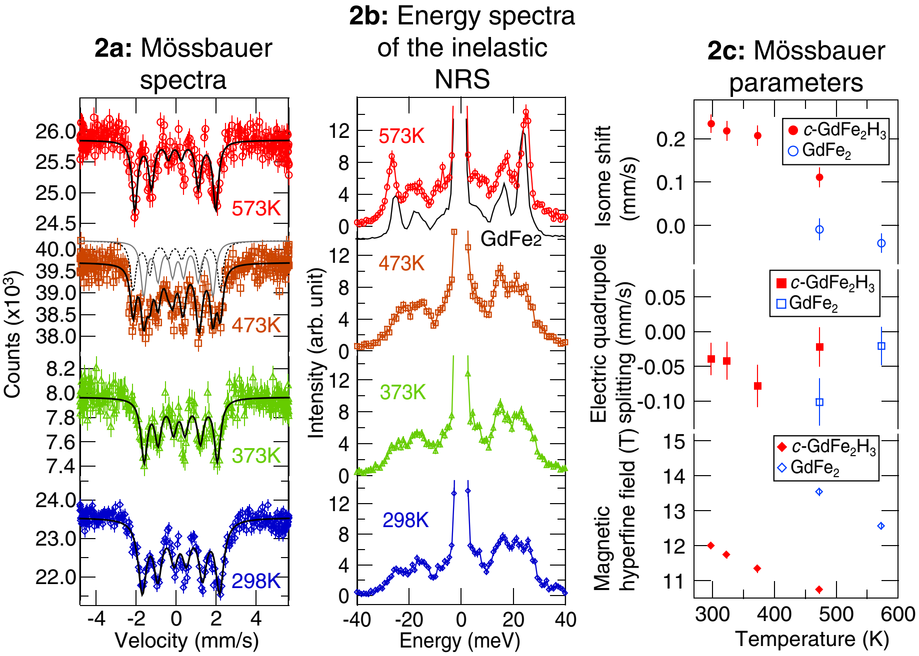
1 Introduction

Hydrogen absorption to materials and desorption from them have been studied by many researchers. These processes are affected by the diffusion of H and the constituent atoms as well as the bonding between them [1]. Thus, their local electronic and vibrational states are important. To study them, we have been developing a system for in situ Mössbauer studies using synchrotron radiation (SR); a sample in a newly developed pressure-temperature chamber is studied by SR-based ^{57}Fe Mössbauer spectra using the variable-frequency nuclear monochromator (VFNM) and energy spectra of the inelastic nuclear resonant scattering (NRS) of SR by ^{57}Fe. Here, we report the system and the feasibility study, in which we observed the dehydrogenation of c-$GdFe_2H_3$ in both spectra.

2 Experiments

The developed chamber is shown in Fig. 1a. All parts with no mention are made of stainless steel to resist H_2 gas. The sample holder of an Al alloy has a cavity to form an edge in the sample cluster; SR transmits the edge and is scattered by the surface of the cluster. The distance between the surface and the outside of the upper X-ray window is typically 7 mm, to detect the isotropic inelastic scattering efficiently.

With this chamber, the SR-based Mössbauer and inelastic NRS spectra of ^{57}Fe were measured at BL11XU of SPring-8. The experimental setup is shown in Fig. 1b. SR monochromatized to 2.5 meV around the energy of ^{57}Fe nuclear resonance was incident on the powder sample of c-$GdFe_2H_3$ (47% enrichment of ^{57}Fe). The chamber was kept in the vacuum of 1 Pa and the temperature of the sample was tuned by the heater in the chamber. The transmitted radiation from the sample was diffracted by VFNM and detected by a NaI(Tl) detector to observe the Mössbauer spectra; the details of the setup are written in [2]. The inelastic NRS from the sample is detected by an eight-element avalanche photo diode detector; the details of the setup are written in [3].



Note:
At 473 K, the hydrogen desorbed from the sample and thus the Mössbauer spectrum at 473 K shows the two sextets corresponding to GdFe2 and c-GdFe2H3. However, the inelastic spectrum at 473 K looks similar to those of *c*-GdFe2H3 below 373 K. This must be due to the relation between the measuring time and the time scale of the dehydrogenation. Because the sample desorbed the hydrogen slowly at 473 K, GdFe2 had formed little in the earlier measurement of inelastic spectra (typically 2 hours measuring time), although GdFe2 was no longer little in the later measurement of Mössbauer spectrum (typically 4 hours).

Fig. 2 Experimental results; **2a**: the SR-based Mössbauer spectra with VFNM (measuring time: typically 4 h per spectrum). **2b**: the energy spectra of the inelastic NRS of SR (typically 2 h per spectrum). **2c**: the Mössbauer parameters from Fig. 2a. The velocity scale of Fig. 2a is calibrated by α-Fe at 298 K. The black bold lines in Fig. 2a show fitting lines. The gray line and the dashed black line above the spectra at 473 K in Fig. 2a are the components of the fitting for the spectrum at 473 K. The lines in Fig. 2b are only eye guides except the black line just below the spectrum at 573 K, which is the inelastic NRS spectrum of $GdFe_2$ at 298 K

3 Results and discussion

The Mössbauer spectra at the temperatures from 298 K to 573 K are shown in Fig. 2a. Although the Mössbauer spectra except at 473 K can be approximately fitted with one Lorentz sextet, the spectrum at 473 K needs two sextets. The obtained Mössbauer parameters are shown in Fig. 2c. The gradual decrease of the isomer shift (IS) on heating below 473 K is well interpreted by the second order Doppler shift, but the abrupt emergence of another site with smaller IS value at 473 K indicates the dehydrogenation at this temperature because the decrease of surrounding H atoms reduces IS value. As for electric quadrupole splitting, there is little change because both *c*-$GdFe_2H_3$ and (dehydrogenated) $GdFe_2$ is C15 Laves structure. The gradual decrease of the magnetic hyperfine field on heating is due to the thermal disturbance of the Fe magnetic moment and its steep increase at 473 K is due to the increase of the Fe magnetic moment caused by the lattice contraction in dehydrogenation. Thus, all changes in the Mössbauer spectra can be interpreted by the effects of the heating or the dehydrogenation.

The inelastic NRS spectra at the temperatures from 298 K to 573 K are shown in Fig. 2b. Below 473 K, the spectra show two broad peaks around 15 and 21 meV. In contrast, the spectrum at 573 K clearly differs from the others and shows two sharp peaks at 18 and 25 meV. This spectrum agrees with the inelastic NRS spectra of $GdFe_2$, as shown in Fig. 2b. In addition, the two sharp peaks of $GdFe_2$ correspond to the Gd-Fe bonding, according to the study on $DyFe_2$[4]. Thus, the broadening of these peaks in the spectra of *c*-$GdFe_2H_3$ below 473 K can be understood by the variation of the Gd-Fe bonding owing to the hydrogen insertion.

From these results, the dehydrogenation of *c*-$GdFe_2H_3$ was successfully observed in situ by both Mössbauer and inelastic NRS spectra. Hence, this system is expected to be applied to the detailed in situ study on hydrogenation processes, such as hydrogen induced amorphization. In fact, a H_2 gas transfer system is ready to connect in BL11XU now. It is noted that the in situ Mössbauer study with various nuclides using this chamber is available by the forward NRS method and the SR-based Mössbauer spectroscopy [5].

4 Summary

We have been developing a system for in situ Mössbauer study, including the newly developed pressure-temperature chamber. It enables us to observe the SR-based ^{57}Fe Mössbauer spectra with VFNM and the energy spectra of inelastic NRS of SR by ^{57}Fe in situ. As a feasibility study, the temperature dependence of *c*-$GdFe_2H_3$ was measured by both spectra and its dehydrogenation was clearly observed. The detailed Mössbauer study with this system would give further comprehension on the microscopic picture of the hydrogenation processes.

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