MLF Experimental Report	提出日 Date of Report Mar. 04, 2011
課題番号 Project No. 2010A0031 実験課題名 Title of experiment The doping effect on the formation of H μ H bond in MgH2 実験責任者名 Name of principal investigator Jun Sugiyama 所属 Affiliation Toyota Central Research and Development Laboratories, Inc.	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/（BL No.） D1 実施日 Date of Experiment October 20, 2011 – October 24, 2011

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Two powder samples of Magnesium hydride were synthesized at TCRDL. One is as hydrogenated powder sample, the other is the powder milled for 24 hours.

Each powder was packed in an Au-sealed titanium cell with Kapton window.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Magnesium is considered to be one of the most promising materials for reversible hydrogen storage, because of its high storage capacity. However, since a magnesium hydride (MgH2) is thermodynamically very stable, its dehydrogenation temperature (T_d) for an as prepared powder sample is reported to be ~ 600 K. But, T_d for a milled sample decreases by about 50 K [1]. In order to understand the bonding nature of Mg and H, MEM/Rietveld analyses were performed using synchrotron radiation x-ray [2]. However, the dynamics for the hydrogenation and/or dehydrogenation is still not well understood. We have, therefore, measured wTF- and ZF-spectra for the two MgH_2 powder samples; namely, a hydrogenated powder and a milled hydrogenated -powder, in the T range between 50 and 500 K in order to study the mechanism for lowering T_d by milling. The obtained spectra were fitted using a combination of H-μ-H signal, a dynamic Gaussian Kubo-Toyabe signal, three oscillatory signals, and an offset background signal; $A_0P(t) = A_{H_\mu H}P_{H_\mu H}(t)\exp(-\lambda_{H_\mu H}t) + A_{KT}G_{KT}(t) + \Sigma A_i\exp(-\lambda_i t)\cos(\omega_i t+\phi_i) + A_{BG}$. Here, A_0 is the initial (t=0) asymmetry, $A_{H_\mu H}$, A_i, A_{KT} and A_{BG} are the asymmetry for each signal, $\lambda_{H_\mu H}$ and λ_i is the exponential relaxation rate of the oscillatory signals, $G_{KT}(t)$ is the GKT function.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Figure 1 shows the T variation of the ZF-spectra for the two samples in the T range between 50 and 500 K. The ZF spectrum for the non-milled sample shows a minimum around 5 μs, indicating the presence of a small random nuclear field (H_{int}^{n}). However, there is no composition of a H-μ-H signal. Since the whole signal from the sample is well fitted by a dynamic Kubo-Toyabe function, the origin of the muon-spin depolarization is assigned as a nuclear magnetic field caused by H.

On the other hand, the ZF-spectra for the milled sample shows a damped oscillation below 250K indicating the formation of the H-μ-H bond. Above 300K, the H-μ-H signal disappears and the whole spectrum shows a dynamic Kubo-Toyabe behavior.

Figure 2 shows the T dependence of the asymmetry of each signal for the milled MgH_2 sample. Below 250K, $A_{H\mu H}$ decreases with increasing T, while A_i (i=1-3) remains. This result suggests that the μ^+ forms H-μ^+-H bond and the extra combination to other H. Furthermore, the bonds between μ^+ and H are supposed to be formed on the surface of the MgH_2 particle, because the surface area of the milled sample is larger than the non-milled sample. The absence of the oscillatory signal above 300 K indicates that the bond between μ^+ and H is unstable and the μ^+ feels only the nuclear magnetic moment of H.

[1] R. A. Varin, *et al.*, Nanotechnology, **17**, 3856 (2006).

[2] T. Noritake, *et al.*, Appl. Phys. Lett., **81**, 2008 (2002).

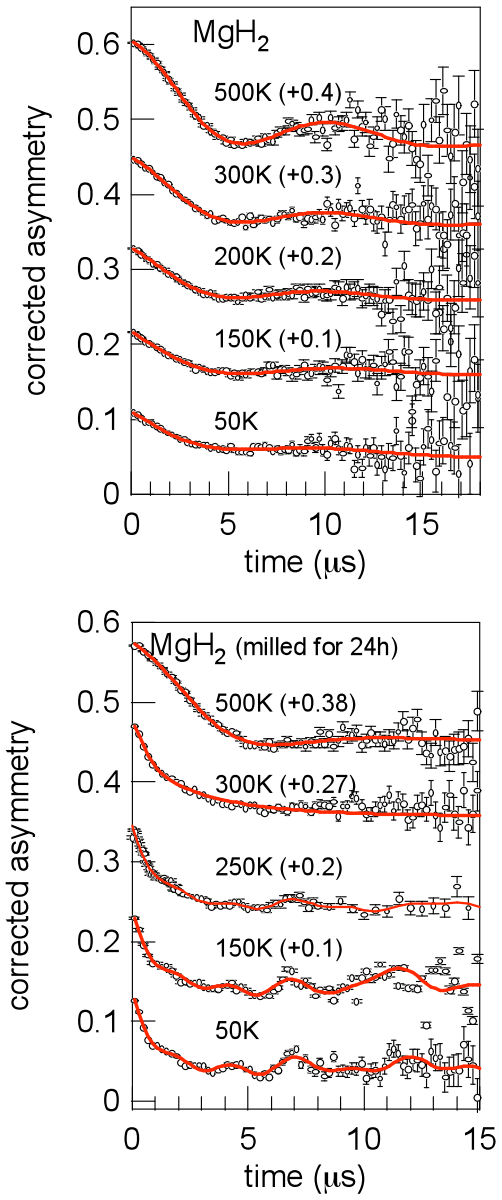

Fig. 1 T variation of the ZF-spectra for MgH_2 (a) as hydrogenated and (b) milled for 24 hours.

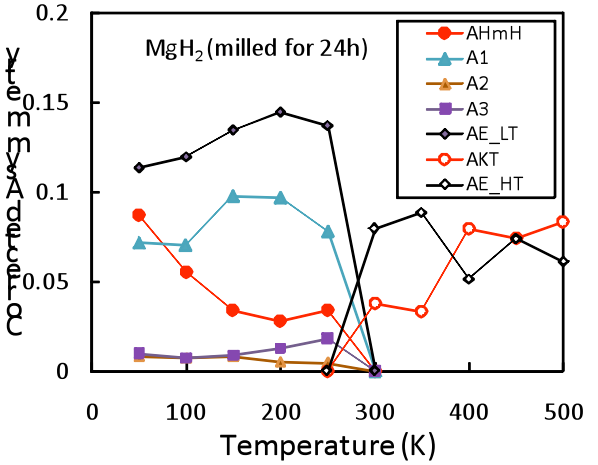

Fig. 2 T dependences of the asymmetry for the ZF-μ^+SR spectra for the milled sample.