MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2015A0201 実験課題名 Title of experiment muSR STUDY OF HYDROGEN DYNAMICS IN NEW MULTIFERROIC COMPOUNDS CO2(OD)3CL AND CO2(OD)3BR USING SINGLE CRYSTALS 実験責任者名 Name of principal investigator Xu-Guang Zheng 所属 Affiliation Saga University	装置責任者 Name of responsible person Y. Miyake 装置名 Name of Instrument/（BL No.） D1 実施日 Date of Experiment 2016. 2.22-2.25

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.

CO2(OD)3CL AND CO2(OD)3BR in powder

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.

We performed a comparative muon-spin-relaxation (μSR) study on $Co_2(OH)_3Cl$ and $Co_2(OD)_3Cl$ basing on the idea that μSR could “see” the dynamics of deuterium or hydrogen atoms through probing the fluctuation of their nuclear fields. This is enabled by the fact that a majority of the positive muon should form a steady water-like combination with the hydroxyl OD^{-1}.

Polycrystalline $Co_2(OD)_3Cl$ and $Co_2(OH)_3Cl$, as synthesized from hydrothermal reaction of NaOD/NaOH and $CoCl_2$, was used for the μSR experiments at the JPARC as well as RIKEN-RAL Muon Facility of the Rutherford Appleton Laboratory, Didcot, UK. The powder samples of $Co_2(OD)_3Cl$ and $Co_2(OH)_3Cl$, respectively, were pressed into a pellet 3 cm in diameter and 1 mm thick, and then tightly covered with a 25-μm thick high-purity silver foil and mounted to a silver sample-holder. A double-pulsed positive surface muon beam was used with the temperature controlled by a standard He-4 gas flow cryostat.

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

Examples of μSR spectra at two typical temperatures for $Co_2(OD)_3Cl$ under zero-field (ZF) and longitudinal-field (LF), are given in Fig. 1. Although $Co_2(OD)_3Cl$ showed magnetic transition at T_C = 10.5 K, the μSR experiments revealed the existence of magnetic couplings at much higher temperatures.

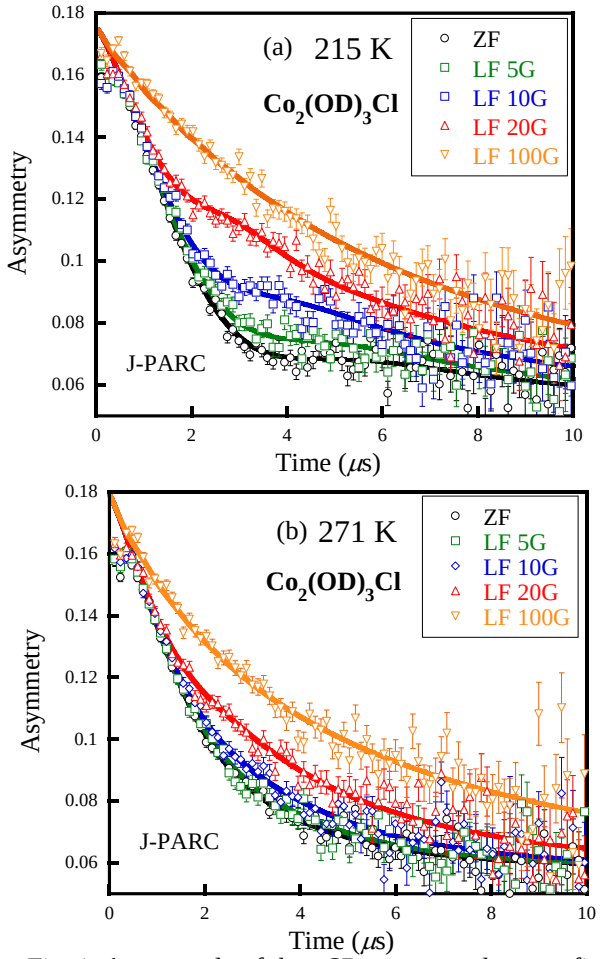

Fig. 1. An example of the μSR spectra under zero-field and longitudinal fields for $Co_2(OD)_3Cl$ at 215 K and 271 K, respectively, showing the change in the dynamics of nuclei. The solid lines are fitted lines according to Eq. (1).

The ZF-μSR spectrum consists of Kubo-Toyabe relaxation or dynamic Kubo-Toyabe relaxation due to the nuclear field of D and Cl nuclei, and exponential relaxations due to the magnetic spins of Co^{2+}. For example, for $Co_2(OD)_3Cl$ at 215 K, the depolarization due to the nuclear fields was almost decoupled under a small longitudinal field of 100 G (Fig. 1a). Meanwhile, the dynamics of the nuclear field at 271 K are apparently different from those at 215 K (Fig. 1b). Therefore, by analyzing the ZF-μSR and LF-μSR spectra, the distribution of the nuclear fields and their evolution with temperature, i.e., the dynamics of the deuteriums on the lattice of $Co_2(OD)_3Cl$ at various temperatures, can be estimated.

In summary, the present study has revealed that the newly-identified ferroelectric response in the geometrically frustrated magnet $Co_2(OD)_3Cl$ occurs with a drastic change in the dynamics of the deuterium atoms.