


(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

 MLF Experimental Report	提出日 Date of Report 2014.07.30
課題番号 Project No. 2013B0252 実験課題名 Title of experiment INVESTIGATION OF A UNCONVENTIONAL HYDROGEN GEOMETRIC EFFECT IN HYDROXYL SALTS CO ₂ (OH) ₃ CL, CO ₂ (OD) ₃ CL, CO ₂ (OH) ₃ BR AND CO ₂ (OD) ₃ BR II 実験責任者名 Name of principal investigator X.G. 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 3/1 9:00 - 3/3 9:00

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.
Co ₂ (OD) ₃ Cl in powder form

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.
<p>Hydroxyl salts of the type $M_2(\text{OH})_3X$ have been known for a long time. The $M_2(\text{OH})_3X$ compounds with the magnetic ions Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+} are all magnetic materials. The most familiar might be the hydroxyl chloride $\text{Cu}_2(\text{OH})_3\text{Cl}$ (atacamite), which forms naturally on copper and bronze as a green patina and is widely recognized as imparting the characteristic hue to the Statue of Liberty. It may also exist as a bio-minerals in living organisms such as in the jaws of the marine bloodworm and crocodile, where it enhances hardness and stiffness. However, only in recent years their magnetic properties became clear and they are known as “frustrated magnets” due to our research efforts. Our latest finding is a universal strong magnetic--dielectric-lattice coupling in all such compounds. Measurements of their dielectric constants and lattice parameters revealed simultaneous changes at their respective T_N (T_C) for all hydroxyl salts of the type $M_2(\text{OH})_3X$, and $M(\text{OH})X$, which demonstrates strong magnetic--dielectric--lattice coupling. Then we further found that for $\text{Co}_2(\text{OH})_3\text{Cl}$, the deuterated compound $(\text{Co}_2(\text{OD})_3\text{Cl})$ clearly showed ferroelectricity at exceptionally high temperatures.</p>

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

To understand its mechanism, we performed a comparative synchrotron X-ray diffraction experiment for $\text{Co}_2(\text{OH})_3\text{Cl}$ and $\text{Co}_2(\text{OD})_3\text{Cl}$. Remarkable and anisotropic change in the unit cell lengths occurred upon deuteration, with notable difference along the a ($a=b$) axes than the c -axis direction. More obvious changes appeared in the atomic bonding lengths with deuteration. We can see that the distances between the ions neighbored with nearby hydrogen, for example, the bond length between the Co ions on the kagome plane (Co1-Co1) and those between the O and Co (O-Co1 and -Co2), all notably increased upon deuteration. This is surprising because H and D have almost equivalent ion radii.

Therefore, we expect that the ferroelectricity in $\text{Co}_2(\text{OD})_3\text{Cl}$ can be attributed to the hydrogen ions, which may result from a quantum atomic effect. We thus performed μSR experiment on $\text{Co}_2(\text{OD})_3\text{Cl}$. We observed a change in the dynamics of D atoms in $\text{Co}_2(\text{OD})_3\text{Cl}$ through the nuclear field of D (Fig. 1 left). The analyzed fluctuation rate of D in $\text{Co}_2(\text{OD})_3\text{Cl}$ shows a turning point at around the ferroelectric transition temperature $T_E = 230$ K (Fig. 2 right), suggesting that the hydrogen (D) dynamics plays a critical role in the ferroelectric response of $\text{Co}_2(\text{OD})_3\text{Cl}$.

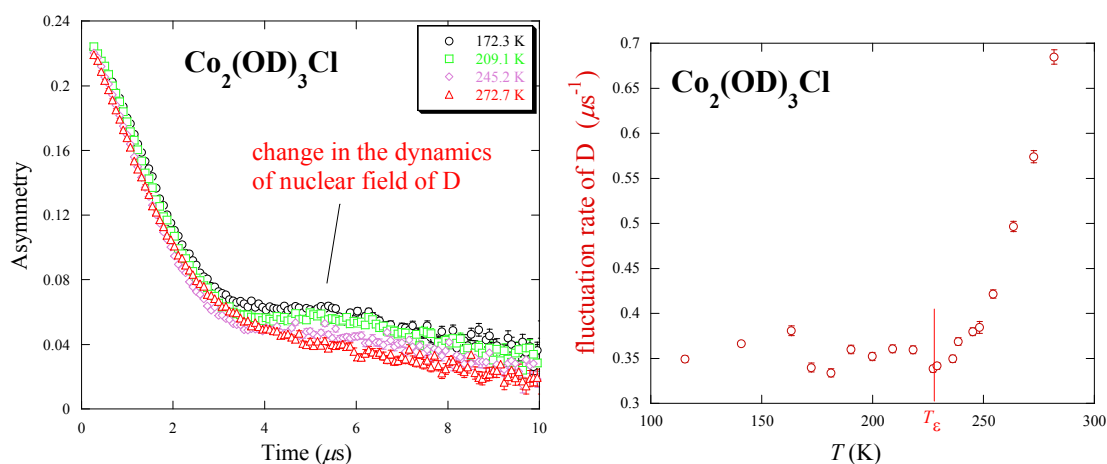


Fig. 1 Left: muon-spin-relaxation spectra indicating a change in the dynamics of D atoms in $\text{Co}_2(\text{OD})_3\text{Cl}$. Right: the analyzed fluctuation rate of D.

This makes an important progress in understanding the mechanism for the reported exotic ferroelectricity in $\text{Co}_2(\text{OD})_3\text{Cl}$.