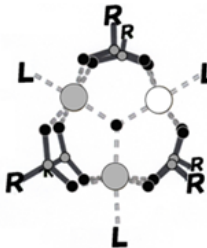


(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

| | |
|--|---|
|  MLF Experimental Report | 提出日 Date of Report Jul. 22, 2013 |
| 課題番号 Project No. 2013A0154 実験課題名 Title of experiment Muon spin researches of valence-trapping and detrapping in mixed-valence trinuclear carboxylate iron complexes 実験責任者名 Name of principal investigator Yoichi Sakai 所属 Affiliation: Daido University | 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 May 3-4, 2013 |

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.

| |
|---|
| <p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>Name: Mixed-valence trinuclear iron pentafluorobenzoate complex with dichloromethane as crystalline solvent Chemical form: $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$ (“Fe₃” is “Fe³⁺Fe³⁺Fe²⁺” or “Fe^{2.7+}”.) Mixed-valence trinuclear iron acetate complex with water as crystalline solvent Chemical form: $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ (“Fe₃” is “Fe³⁺Fe³⁺Fe²⁺” or “Fe^{2.7+}”.)</p> <p>Physical state: Polycrystalline powder</p> |
|---|

| <p>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。)</p> | | | | | | | | | | | | | | | |
|---|---|---|---|--|---|---|--------------------------------------|-----|-----------------|------------------|--------------------|-----|-------------------------------|---------------------------------|---------------------------------|
| <p>Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.</p> | | | | | | | | | | | | | | | |
| <p>For two solid samples of $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$, muon spin relaxation ($\mu\text{SR}$) experiments were carried out in the MUSE D1 area of MLS/J-parc in May 2013. Details of the two compounds are shown in Figure 1, both of which are mixed iron-valence coordination compounds, containing two Fe^{3+} ions and one Fe^{2+} ion. We have investigated iron-valence fluctuation in these compounds by Mössbauer spectroscopy. For an example, as illustrated in the temperature-dependent Mössbauer spectra of $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ (Figure 2) measured by us,</p> |  | <p>(1) $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ (2) $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$</p> <p>Large gray circle; Fe³⁺ Large white ; Fe²⁺ Small gray; C Small black; O</p> | <table border="1"> <thead> <tr> <th></th> <th>R</th> <th>L</th> <th>Cryst alline solvated molecules (nS)</th> </tr> </thead> <tbody> <tr> <td>(1)</td> <td>CH₃</td> <td>H₂O</td> <td>2 H₂O</td> </tr> <tr> <td>(2)</td> <td>C₆F₅</td> <td>C₅H₅N</td> <td>CH₂Cl₂</td> </tr> </tbody> </table> | | R | L | Cryst alline solvated molecules (nS) | (1) | CH ₃ | H ₂ O | 2 H ₂ O | (2) | C ₆ F ₅ | C ₅ H ₅ N | CH ₂ Cl ₂ |
| | R | L | Cryst alline solvated molecules (nS) | | | | | | | | | | | | |
| (1) | CH ₃ | H ₂ O | 2 H ₂ O | | | | | | | | | | | | |
| (2) | C ₆ F ₅ | C ₅ H ₅ N | CH ₂ Cl ₂ | | | | | | | | | | | | |
| <p>Figure 1. Molecular structure of $\text{Fe}_3\text{O}(\text{RCOO})_6\text{L}_3 \cdot n\text{S}$</p> | | | | | | | | | | | | | | | |

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

there is found a valence-detrapped (averaged to $\text{Fe}^{2.7+}$) state of three iron cations at higher temperatures, while contrarily a valence-trapped (localized in Fe^{3+} and Fe^{2+}) state at lower temperature. Almost same result was obtained in our temperature-dependent Mössbauer spectra of $\text{Fe}_3\text{O}(\text{C}_6\text{F}_5\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{CH}_2\text{Cl}_2$, being a novel compound synthesized for the first time by us [1]. ($\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ is a well-known one.)

Time-spectra of positive-muon spin relaxation, under a zero field (ZF) and longitudinal fields (LFs) were measured for the two compounds in this beam-experiment. Typical μSR time spectra, under a zero field (ZF) and longitudinal fields (LFs) of 10 G and 100 G, are shown for $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ at 300 K and 100 K in Figures 3 and 4, respectively.

As seen in the figures, spin polarization (“Asymmetry” of the ordinate) was decreased or relaxed swiftly under a ZF at both the temperature of 300 K and 100 K, while a large part of relaxed under a ZF were recovered under a LF of 10 G, which might be due to decoupling-effect between muon spins and static nuclear magnetic moments with a random direction. Other part of muon spins not decoupled under higher LFs should be relaxed through the interaction with electronic spins of iron ions. The detail and systematic data analysis is in progress.

[1]. Y. Sakai et al. *Hyperfine Interactions*, **205**, 1-5 (2012)

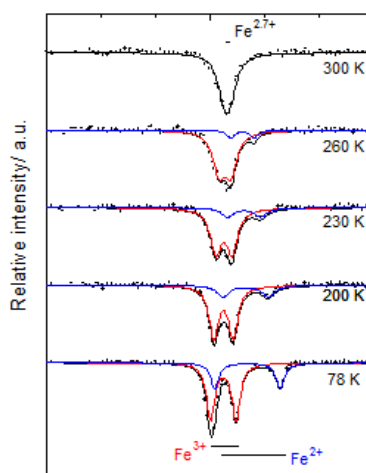


Figure 2. Temperature-dependent Mössbauer spectra of $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$

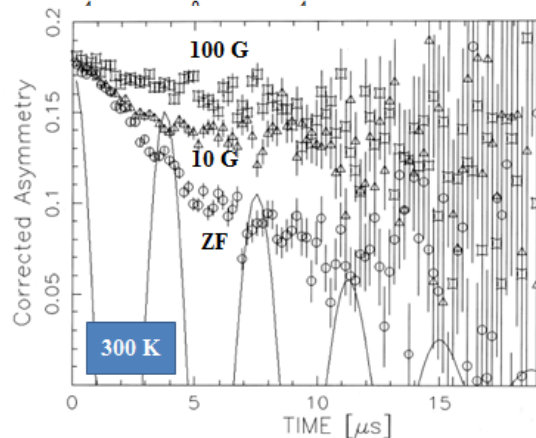


Figure 3. Time-spectra of positive muon spin relaxation of $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ at 300 K, under ZF and LFs of 10 G and 100 G

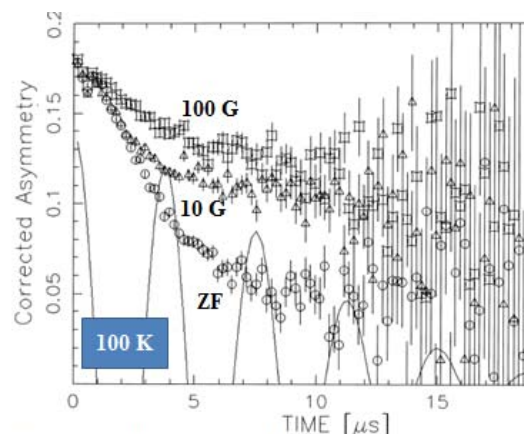


Figure 4. Time-spectra of positive muon spin relaxation of $\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ at 100 K, under ZF and LFs of 10 G and 100 G