

Characterizations of Core Level Electronic Structure and Interaction of Ln-M Cyano DMF Complex by Soft-X-ray Spectroscopy (in 2009)

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Introduction

A 3d-4f complex, $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$, was known to exhibit photo-induced magnetic changes [1]. The factors of this unique behavior were investigated in view of crystal structures [2] and metal-substitution [3] in order to design photo-magnetic materials [4]. As one of viewpoints, we focused on flexibility of crystal structures $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$. In 2008 we found that it showed negative thermal expansion along the a-axis. Intermolecular hydrogen bonds play an important role in this behavior. In order to elucidate <1> effect of Ln(III) ion size <2> effect of H/D isotope of intermolecular hydrogen bonds, and <3> separate observation between lattice (hydrogen bonds) and coordination sphere (electronic states of low-spin Fe(III) ion), we compared with various analogous Ln $(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ or $\text{Ln}(\text{DMF})_4(\text{D}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{D}_2\text{O}$ complexes and measured XAS under variable temperature condition.

Experimental section

Preparation

Slow diffusion of aqueous solution (10 mL) of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.1 mmol) onto DMF solution (10 mL) of $\text{Nd}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.1 mmol) gave rise to yellow prismatic single crystals of $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ at 298 K [1]. The other samples were prepared in a similar way with the corresponding Ce, Sm, Gd, and Er metal sources and water or DMF ligands of different isotopes.

Soft X-ray absorption spectra

The XAS of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ peaks were measured with BL-19B at 70-298 K. The spectra were corrected by the standard sample of Au.

Results and discussion

For example, Figure 1 shows XAS of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ for $\text{Sm}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ (SMFeHH) at 298 and 70 K and $\text{Sm}(\text{DMF})_4(\text{D}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{D}_2\text{O}$ (SmFeDH) at 298 K. In contrast to thermally-induced anisotropic structural changes of the crystal lattice, all the spectra suggest low-spin Fe(III) ions at both temperature. Moreover, H/D isotope of intermolecular hydrogen bonds were observed slightly. One of the important factors of the thermal behavior may be not local coordination environment but intermolecular hydrogen bonds.

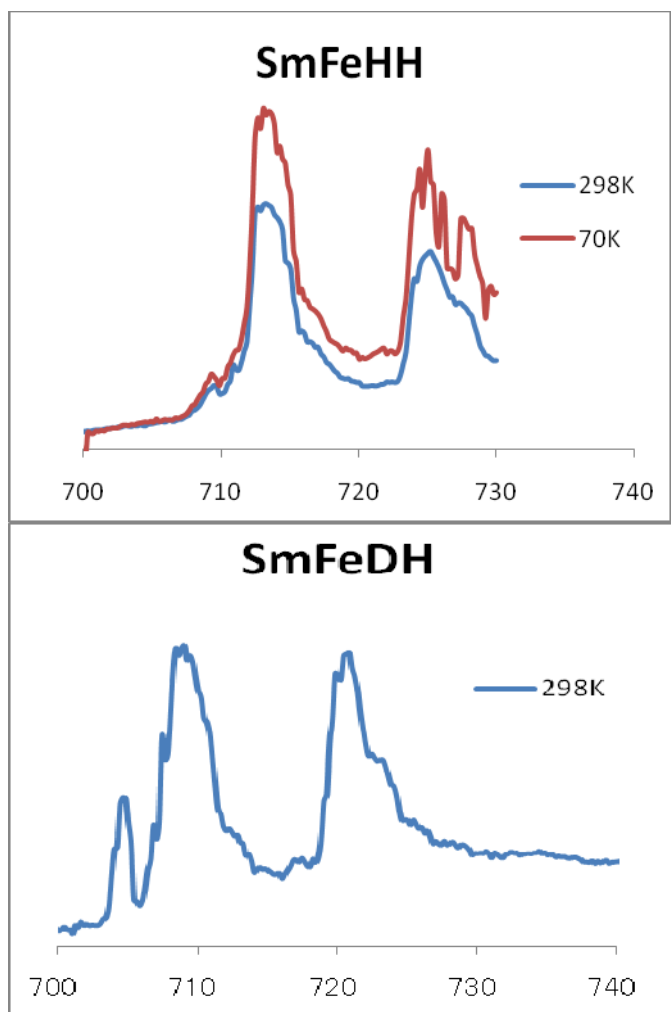


Figure 1: XAS of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ for $\text{Sm}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ (HH) at 298 and 70 K and $\text{Sm}(\text{DMF})_4(\text{D}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{D}_2\text{O}$ (DH) at 298 K.

References

- [1] G. Li, T. Akitsu et al., *J. Am. Chem. Soc.* 125, 12396 (2003).
- [2] T. Akitsu et al., *Polyhedron* 25, 2655 (2006).
- [3] T. Akitsu et al., *Inorg. Chim. Acta* 359, 1421 (2006).
- [4] T. Akitsu et al., *J. Magn. Magn. Mater.* 320, 1586 (2008).

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