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分子磁鐵的電荷密度研究(中法國合計畫)(1/2)

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Charge Density study of molecule magnets

Progression Report

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The primary goal of this joint research effort at National Taiwan university and LCM³B (University of Henry Poincaré) on the molecular magnets, is to attain fundamental understanding of the molecular magnetic properties of the remarkable materials. For the past three months this collaborate project is undergoing in the respective labs. We (both France and Taiwan teams) chose $\text{Fe}(\text{btr})_x(\text{NCS})_y$ (btr = 4,4'-bis-1,2,4-triazole) system which exhibit spin crossover phenomenon as the first example. The exchange of personnel has not been exercised. We plan to do the exchange after we both have some preliminary studies. Following is the Taiwan part of the studies.

Two complexes, $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$ ^[1] and $\text{Fe}(\text{btr})_3(\text{ClO}_4)_2$ ^[2] were concerned in our work. $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$ (**1**) behaves a temperature dependent abrupt spin transition at 120K (Figure 1) with a hysteresis of 25K ($T_{c\downarrow} = 119.8\text{K}$ and $T_{c\uparrow} = 145.1\text{K}$) which is consistent with those of previous report^[1]. $\text{Fe}(\text{btr})_3(\text{ClO}_4)_2$ (**2**) shows a two-step spin crossover (Figure 2). Two unique Fe sites were found in **2** from single crystal X-ray diffraction^[2]. By comparing the local structure of these two Fe sites at different temperature (150K, 190K and 260K), Yann Garcia et al.^[2] speculated that with temperature decreasing from RT to 190K only one Fe site undergoes a gradual spin transition while the other one maintains at HS state. Further temperature decreasing from 190K to 150K causes the other Fe site undergoes an abrupt spin transition. Our aim is to get insight the evolution of electronic configuration associated with temperature changing by performing soft and hard X-ray absorption spectroscopy. All the spectra were collected at NSRRC, Taiwan.

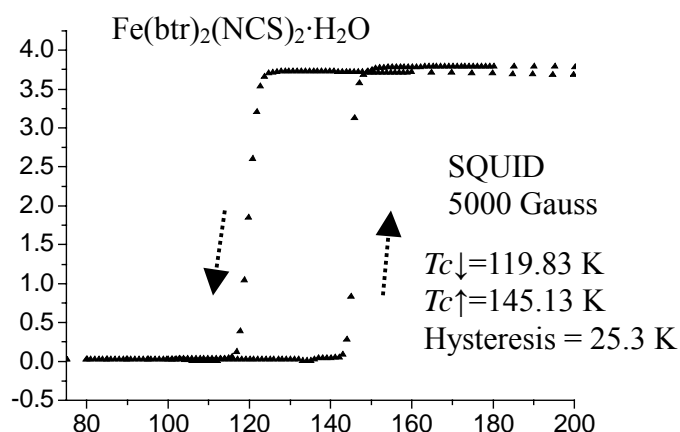


Figure 1. Susceptibility measurement of **1**

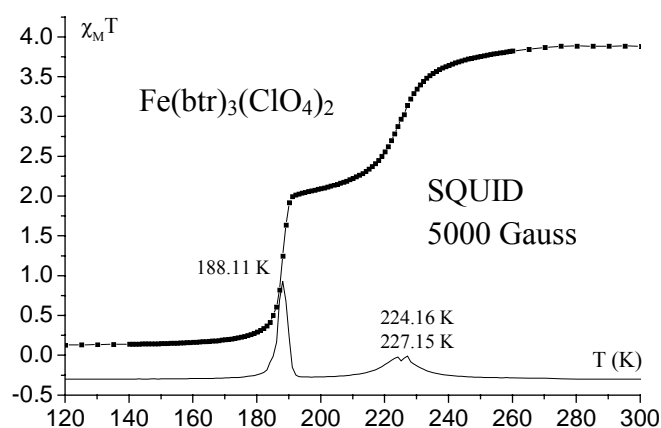


Figure 2. Susceptibility measurement of **2**

Fe K-edge spectra of **1** were shown in Figure 3. With temperature increasing from 80K to 120K, the similarity of the three curves indicate that local structure around Fe atom and its electronic configuration were almost the same during temperature changing in this range. A slight

increasing absorption was found in 7126.6 eV with further heating from 120K to 130K. A dramatic increase of this absorption was observed after heating from 130K to 137K. Thus the change in K-edge absorption does not correspond to the abrupt spin transition observed with SQUID. This may be caused by the temperature gradient between sample and the holder and/or the hysteresis effect. Complimentary theoretical calculations may provide great help to understand the correlation between structure, susceptibility and electronic configuration. Fe L-edge spectra of **1** were also collected (Figure 4). However due to the necessity of high vacuum of 10^{-9} the solvent water molecule must be lost and resulted in the loss of spin crossover phenomenon.

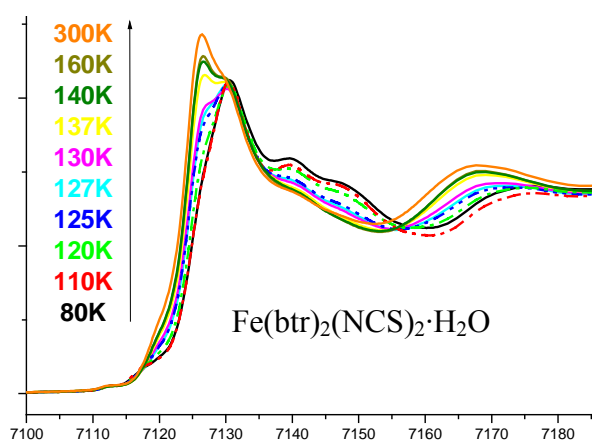


Figure 3. Fe K-edge spectra of **1**

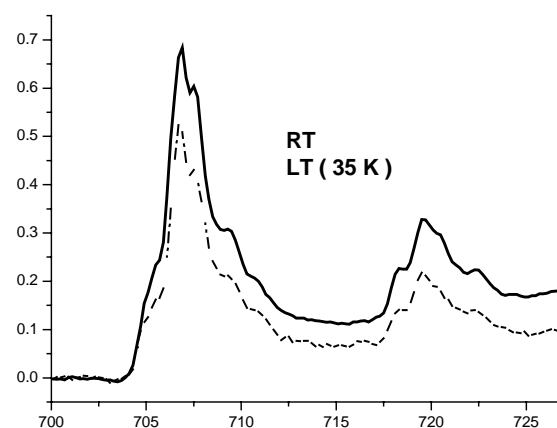


Figure 4. Fe L-edge spectra of **1**

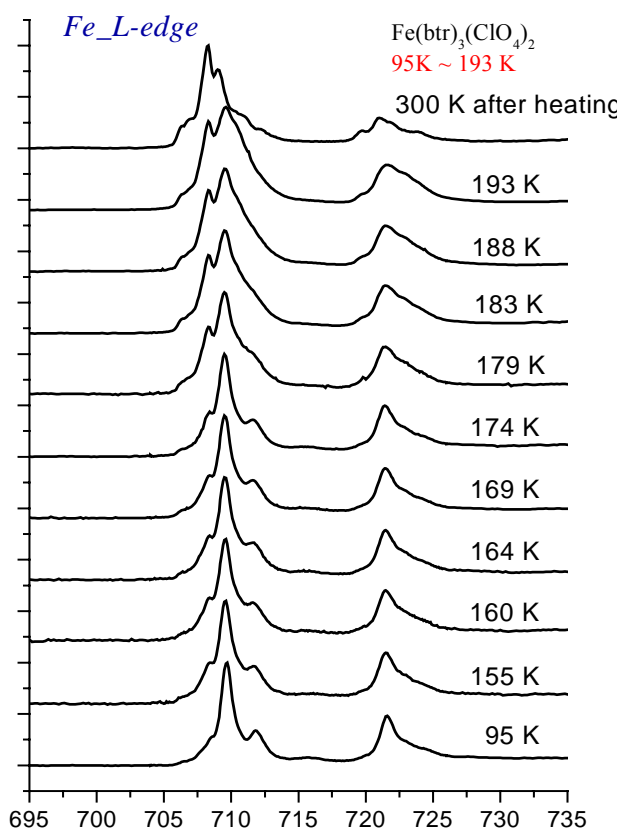
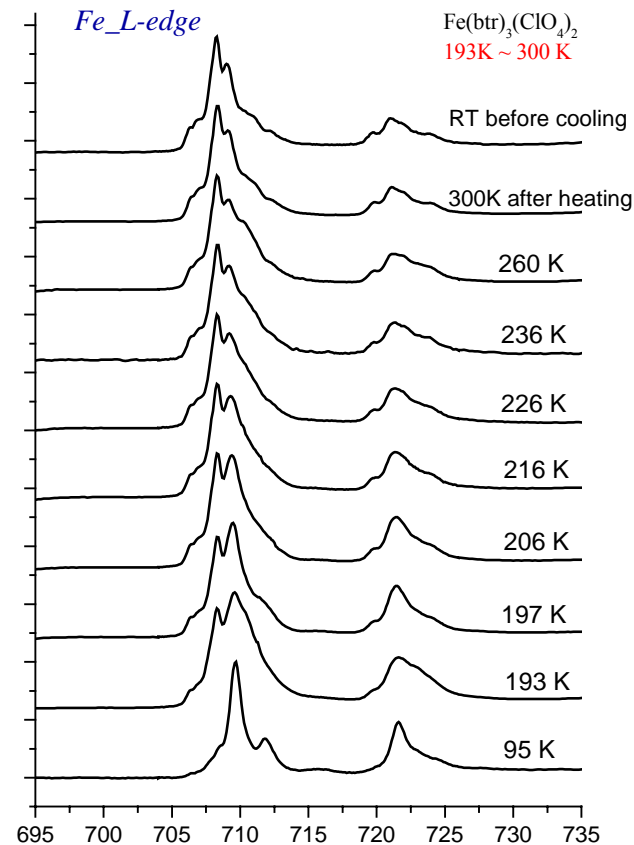


Figure 5. Fe L-edge spectra of **2**



Fe L-edge spectra of **2** (Figure 5) illustrate a consistent two-step spin transition, which consist with the magnetic susceptibility measurement. A dramatic change in L^{III} was observed while heating from 174K to 179K. A simulated spectrum obtained by taking half RT spectrum and half 95K spectrum was very similar to those collected between 179K to 197K and provided a powerful evidence of one Fe site being at LS state while the other one at HS configuration during this temperature range. Further heating from 197K to 300K gradual decrease of absorption peak at 709.4 eV and simultaneously gradual increase of peak at 708.3 eV were observed and attributed to the spin crossover of the other Fe site. The similarity between RT spectrum collected before cooling and the 300K spectrum collected after heating indicates the reversibility of **2**. Further studies in the light induced excited spin state will be investigated soon.

Reference:

- [1] W. Vreugdenhil et al., *Polyhedron*, **9**, 2971, (1990)
- [2] Yann Garcia et al. *Inorg. Chem.*, **38**, 4663, (1999)