

Solid-to-Solid Progressive Crystal Transformation Involving Ligand Exchange, Solvent Insertion, Air Oxidation, Coordination Re-arrangement and Ferromagnetism to Antiferromagnetism

Introductory part, Abstract: Clear light yellow rhombic crystals of $\text{Fe}^{\text{II}}_4(\text{mbm})_4\text{Cl}_4(\text{MeOH})_4$ (**1**), (*Hmbm* = (1-methyl-1H-benzo[d]imidazol-2-yl)methanol) changes their color gradually to opaque black in the atmosphere and converted to $[\text{Fe}^{\text{III}}_4(\text{mbm})_4(\text{OH})_4\text{Cl}_4] \cdot 4\text{H}_2\text{O}$ (**2**) through single-crystal-to-single-crystal (SC-SC) transformation. High field electron spin resonance measurements proved that $\{\text{Fe}^{\text{II}}_4\}$ cubane of **1** is converted into $\{\text{Fe}^{\text{III}}_4\}$ cubane of **2** during the SC-SC transformation process.

Solid-to-solid phase transformation, a change of structure, usually occurs as a function of external physical stimuli such as light, temperature, pressure, mechanical force, as well as their synergic effect [1]. In some rare cases, it occurs by chemical reaction without damaging the crystallinity. A survey shows that only 36 examples related to SC-SC transformation start from clusters has been reported. Among these examples, only three examples involving gas-solid redox reaction upon SC-SC transformation were studied

We have synthesized $\text{Fe}^{\text{II}}_4(\text{mbm})_4\text{Cl}_4(\text{MeOH})_4$ (**1**) with the (1-methyl-1H-benzo[d]imidazol-2-yl)-methanol (*Hmbm*) ligand. It is interesting to see observed that the color of the crystals changed through light-yellow, yellow–brown, brown and finally black after exposure in air under ambient condition (Figure 1 top). Crystallography of the black crystal reveals the same $\{\text{Fe}_4\text{O}_4\}$ core of a different molecule, $[\text{Fe}^{\text{III}}_4(\text{mbm})_4(\text{OH})_4\text{Cl}_4] \cdot 4\text{H}_2\text{O}$ (**2**), within a slightly reduced unit cell of the same space-group but with three chemical changes.

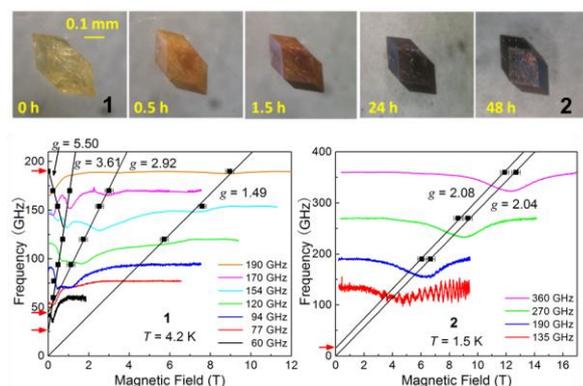


Fig. 1 (Top) Optical photograph of fresh Fe_4 after exposure in air for 0, 0.5, 1.5, 24, and 48 h. (Bottom) HF-ESR spectra of 0 h and 48 h samples at various frequencies. Solid lines are the linear fit to each resonance branch.

Structural and magnetization studies indicate there has been oxidation of the Fe(II) to Fe(III). In order to further confirm the charge value of iron ions and study the SC-SC transformation process, high field electron spin resonance (HF-ESR) measurements were carried out on two polycrystalline samples **1** and **2**. Fig. 1(bottom) shows the frequency dependence of the HF-ESR spectra at low temperatures. The spectra of the two compounds show very different features: four strong signals were observed for **1**, and the linear extrapolations to the resonance fields give three energy gaps of 27, 46, and 190 GHz, implying the existence of large zero-field splitting in **1**, consistent with fitting results to $\chi_m T$. Four effective *g*-values of 1.49, 2.92, 3.61, 5.50 were obtained. The displacements of *g*-values from 2.00 could be due to the strong spin-orbital coupling within Fe(II), or the occurrence of the level mixing with excited spin states at the high magnetic field (considering the small J_1 and J_2 values) [2]. In contrast, the HF-ESR spectra of **2** contain only two peaks, and the linear extrapolations to the resonance fields give the energy gaps of ~20 GHz with *g*-values of 2.08 and 2.04. This is consistent with the nature of Fe(III) ions with very small zero-field splittings [2], and is also consistent with the susceptibility analysis, proving that all the iron ions in **2** are Fe(III).

In sum, HF-ESR has proved that $\{\text{Fe}^{\text{II}}_4\}$ cubane of **1** is converted into $\{\text{Fe}^{\text{III}}_4\}$ cubane of **2** during the SC-SC transformation process.

References

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