

Heat Capacities and Phase Transitions of a Molecule-Based Magnetic Material : $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$, $\text{Bu} = n\text{-C}_4\text{H}_9$; ox = oxalate

Molecule-based magnetism is a current topic of increasing scientific interest. Current research in this field aims to prepare materials exhibiting ferro / ferrimagnetic transitions as well as to understand the mechanism of magnetic interactions involved. Among several materials reported so far, the oxalate ligand bridged mixed-valence molecule-based two-dimensional layered material $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ is of special importance due to its curious magnetic properties. This compound was found to be ferrimagnetic ($T_N = 43\text{K}$) with the anticipations of a spin-glass like state below 40K and a structural phase transition around 38K . A rarely occurring negative magnetization phenomenon was observed in this compound below 30K when pre-cooled under low magnetic fields [A.Bhattacharjee et al, J. Phys. Soc. Jpn., **68** 1679 (1999)]. As heat-capacity calorimetry can detect the existence of phase transition and elucidates the various aspects of magnetic interactions based on precise heat capacity measurements, it is worth while to study the heat capacity of $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$, with the hopes that this study (i) may give new insights into the low temperature magnetic properties, mechanism of the phase transition involved, and (ii) may identify any other phase transition occurring.

The heat capacity measurements in $0.1\text{--}300\text{K}$ range have revealed three heat capacity anomalies at 16.3K , 43.3K and 217K for $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ (Fig. 1 and Fig. 2). The small anomaly at 16.3K seems to be due to a spin glass like disordered state, as anticipated from other measurements.

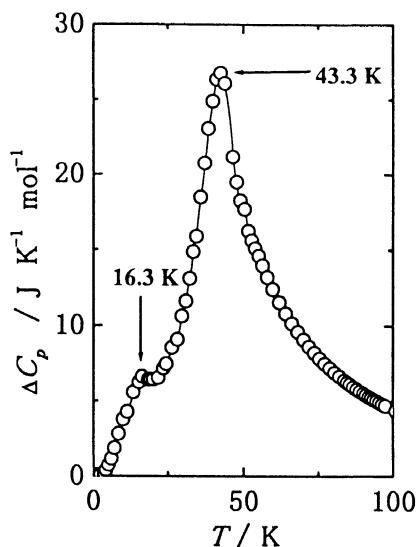


Fig. 1. Magnetic heat capacities ΔC_p vs T plot.

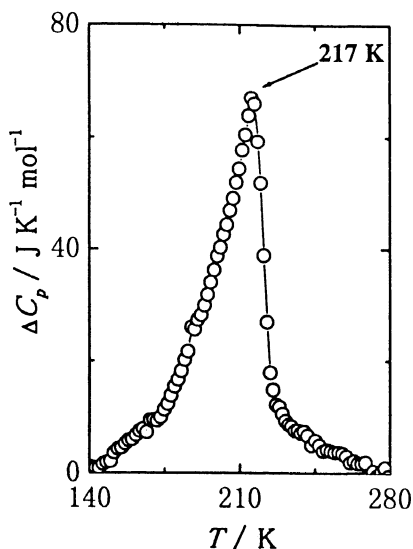


Fig. 2. Excess heat capacities due to order-disorder transition ΔC_p vs T plot.

The anomaly at 43.3 K is due to the magnetic phase transition, as this temperature corresponds to the ferrimagnetic transition temperature. The spin alignment of the trivalent Fe^{III} and divalent Fe^{II} spins in the $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ lattice is due to an antiferromagnetic superexchange interaction between $\text{Fe}^{\text{III}}(S=5/2)$ and $\text{Fe}^{\text{II}}(S=2)$ spins through the anionic oxalate ligand. The agreement between the observed and the expected values of magnetic entropy is fairly good. No evidence of expected structural phase transition around 38 K has been detected in the present study.

The observed heat capacity anomaly at 217 K in $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ is certainly of nonmagnetic origin and originates in the order-disorder phenomenon due to various

configurational changes in the butyl chains of the organic cation and is interpreted in terms of a proposed model. Above 217 K the butyl moieties of the cation execute large thermal motions, while the anionic metal-oxalate layers oscillate as a whole, thus leading to the thermal disorder in $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$. Further systematic studies are presently going on with its different structural analogs.

(Ashis Bhattacharjee)

Presentation

A. Bhattacharjee, M. Sorai, R. Feyerherm and M. Steiner, 2nd International and 4th Japan-China Joint Symposium on Calorimetry and Thermal Analysis (Tsukuba), 1A1620 (1999).

分子磁性体 $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ ($\text{Bu} = n\text{-C}_4\text{H}_9$; ox = oxalate) の熱容量と相転移

層状構造を持つ標題化合物は、43.3 K をネール温度として持つフェリ磁性体であるが、さらに冷却すると補償温度 30 K 以下で自発磁化の向きが逆転するという興味深い現象が起きる。38 K 付近に構造相転移が存在する可能性も指摘されてきた。この化合物について室温以下で熱容量を測定した。43.3 K を頂点とする磁気秩序の発生に伴う熱異常を見いだした。一方、補償温度付近や構造相転移が期待される温度には熱異常は見られなかった。16.3 K 付近にも磁気的な熱異常を見いだした。217 K 付近に構造相転移による熱異常を見いだした。