Multiple Magnetic Pole Reversals and Mössbauer Studies in Molecular-based Mixed Valency Ferrimagnet \{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]}_n (M=Zn, Fe)

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Abstract

The Molecule magnets Materials \{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]}_n (M=Zn, Fe) were investigated by magnetic measurements and Mössbauer spectroscopy. In the complex \{[N(n-C_4H_9)_4][Zn^{II}0.03Fe^{II}0.97Fe^{III}(C_2O_4)_3]}_n detailed investigation of the ferromagnetism behaviour, and a compensation temperature has found with the field being less than 1KOe. And the 57Fe Mössbauer measurements had been carried out in \{[N(n-C_4H_9)_4][Fe^{II}Fe^{III}(C_2O_4)_3]}_n to investigate the mixed valency character and antiferromagnetic coupling. Some ferrimagnets consisting of magnetic anisotropy ions and two or more types of antiferromagnetically ordered magnetic ions exhibit this behavior. As the temperature was lowered to 40 K, the Fe^{III} doublet subspectrum almost completely turns into a sextet subspectrum. The hyperfine magnetic field increases as the temperature decreasing.

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1. Introduction

Molecule-based magnets have been extensively studied because they show novel magnetic properties[1-5]. The phenomenon of multiple magnetic pole inversions have been reported on several
compounds. This properties is the basic of most magnetic storage devices. However, the mechanisms responsible for the multiple magnetic pole inversions have not yet been fully rationalized. The molecular-field theory (MFT) proposed by O. Cador et al. can explain the phenomenon well [1]. Many years ago, Neel predicted that the spontaneous magnetization of two sub-lattices might cancel each other at the so called “compensation temperature” T_{comp}[4-5].

In the paper we report the complex \{[N(n-C4H9)4][ZnII0.03FeII0.97FeIII(C2O4)3]\}_n detailed investigation of the ferromagnetism behaviour, and a compensation temperature has found with the field being less than 1KOe. The phenomenon of magnetic pole reversals is rare. And the 57Fe Mössbauer spectroscopy measurements had been carried out in \{[N(n-C4H9)4][FeIIFeIII(C2O4)3]\}_n to investigate the mixed valency character and antiferromagnetic coupling. As the temperature was lowered to 40 K, the FeIII doublet subspectrum almost completely turns into a sextet subspectrum. The hyperfine magnetic field increases as the temperature decreasing.

2. Experiment section

2.1. Materials and physical measurements

Starting materials were used as commercially obtained. K3[Fe(C2O4)] was prepared according to literature methods [6]. NBu4Br, ZnSO4·7H2O, FeSO4·7H2O and FeCl2 are reagent grade. The powder x-ray diffraction pattern was measured with a Rigaku RINT 2100 instrument(Cu-ka). Magnetic measurements were made using a Quantum Design MPMS 7 SQUID. The radioactive source used for Mössbauer measurements was 57Co (Pd). All spectral patterns were fitted with the MössWin3.0 software.

2.2. Synthesis

The compound \{[N(n-C4H9)4][ZnII0.03FeII0.97FeIII(C2O4)3]\}_n was prepared by the following method: An aqueous solution of K3[Fe(C2O4)] (0.5 mmol mmol) was added to an aqueous solution of ZnSO4·7H2O (0.015 mmol) and FeSO4·7H2O (0.485 mmol) under Ar atmosphere in the dark at room temperature. After 30 minutes, the solution was filtered to remove the remaining small amount of Fe(C2O4). The precipitate was dialyzed by adding a methanol solution of NBu4Br (0.75 mmol) to the filtrate. Thereafter the resulting precipitate was washed with distilled water and dried.

The compound \{[N(n-C4H9)4][FeIIFeIII(C2O4)3]\}_n was prepared by the following method: An aqueous solution of K3[Fe(C2O4)] (2.0 mmol) was added to an aqueous solution of FeCl2 (2.0 mmol) under Ar atmosphere in the dark. After 30 minutes, the solution was filtered to remove the remaining small amount of Fe(C2O4). The precipitate was dialyzed by adding a methanol solution of NBu4Br (2.2 mmol) to the filtrate. Thereafter the resulting green precipitate was washed with distilled water and dried.

3. Results and discussion

3.1. Infrared analyse

Infrared analysis, thermogravimetric analysis, elemental analysis and ICP-AES are used to characterize the samples. The FT-IR spectrum of the compound is shown in Figure 1. The figure of sample \{[N(n-C4H9)4][ZnII0.03FeII0.97FeIII(C2O4)3]\}_n shows C2O4 stretching bands at 1625.28 cm⁻¹, 1449.36 cm⁻¹ and 793.65 cm⁻¹. It shows indicating the existence of Oxalate-bridged group in this compound[10-12]. Meantime, the broad peak at 3430.475 cm⁻¹ correspond to the v(O-H) of the crystal water.
3.2. Magnetism analyses

The temperature dependent magnetic susceptibility measurement for the compound \([\text{[N(n-C4H9)4][Zn}^{II}0.03\text{Fe}^{II}0.97\text{Fe}^{III}(\text{C}_2\text{O}_4)_3]}\) were carried out in the temperature range 2-300 K at the external field of 1 kOe. The result is presented in Figure 2 and Figure 3. The Weiss constant \(\theta\) was obtained by extrapolating the linear portion of \(\chi^{-1}\) versus \(T\) to \(\chi^{-1} = 0\). \(\chi_m\) value above 50 k obey the Curie-Weiss law with a Curie constant of \(C=6.667 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}\) and Weiss paramagnetic Curie temperature of \(\Theta\leftarrow -88.54\text{K}\).

In temperature dependence of \(x_mT\) curve for \([\text{[N(n-C4H9)4][Zn}^{II}0.03\text{Fe}^{II}0.97\text{Fe}^{III}(\text{C}_2\text{O}_4)_3]}\) (as shown in Figure 4), A compensation temperature has found with the field being less than 1KOe. The magnetic susceptibilities indicate that there exist a ferrimagnetic exchange interaction in the compound, and magnetic transition at 23K. The phenomenon of magnetic pole reversals is rare[13-16]. Some ferrimagnets consisting of magnetic anisotropy ions and two or more types of antiferromagnetically ordered magnetic ions exhibit this behavior.
3.3. Mössbauer Spectroscopy

The Mössbauer spectra of \{[N(n-C4H9)4][FeFe(C2O4)3]\}_n have been measured as a function of temperature and selected paramagnetic spectra (as shown in Figure. 5). The value of isomer shift (IS), quadrupole splitting (QS) and hyperfine magnetic field (Hhf) are listed in Table I.

Table I. Mössbauer parameters of \{[N(n-C4H9)4][FeFe(C2O4)3]\}_n at various temperatures

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>FeII doublet</th>
<th>FeIII doublet</th>
<th>FeIII sextet</th>
<th>FeII sextet</th>
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<tr>
<td></td>
<td>IS (mm/s)</td>
<td>QS (mm/s)</td>
<td>Area (%)</td>
<td>IS (mm/s)</td>
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<td></td>
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<td></td>
<td>QS (mm/s)</td>
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<td></td>
<td></td>
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<td></td>
<td>Area (%)</td>
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<tr>
<td>40 K</td>
<td>1.25</td>
<td>1.96</td>
<td>47.4</td>
<td>1.67</td>
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<td></td>
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<td>2.60</td>
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<td>1.23</td>
<td>1.53</td>
<td>33.8</td>
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</table>

The isomer shift (IS) values relative to α-Fe at room temperature (+0.02 mm/s). QS, quadrupole splitting; T, temperature.

As the temperature was lowered to 40 K, the FeIII doublet subspectrum almost completely turns into a sextet subspectrum. The hyperfine magnetic field increases as the temperature decreasing. The Hhf value (46.5T) is typical of high spin FeIII [7]. The results of Mössbauer show that the sample is in the ferrimagnetic state below 40 K. When the sample was cooled to 15 K. The magnetic splitting spectrum was designated as FeIII sextet and another as FeII sextet. The spectrum recorded at 15 K shows a six-line FeIII spectrum corresponding to an internal field of 53 T, while the Hn value estimated at the same temperature for FeII spectrum is 58.7 T. Thus the Mössbauer results indicate that the FeII sublattice spontaneous magnetization increases more steeply below TC than that of the FeIII sublattice. Two magnetic sublattices are defined. Temperature dependent magnetic measurements were performed in the cooling and warming modes [5] (as shown in Figure. 6). Full arrows denote MFe(III) and dashed arrows denote MFe(II). The first line corresponds to the cooling mode, the second to the warming mode.
In order to explain perfectly the magnetic properties, the magnetic hysteresis must be introduced. Fe(II) ions show single-ion anisotropy due to spin-orbit coupling [7-8]. In zero field, the spontaneous magnetization $M_s$ can be calculated as follows:

$$M_i = N g_i \mu_B S_i B_i \left( \frac{g_i \mu_B S_i}{K_i} H_i \right) \quad \text{and} \quad M_s = \sum_i n_i M_i \quad \text{(1)}$$

The temperature dependence of coercive field $H_C$ can be given as follows:

$$H_C(T) = \left( M_{Fe(III)}(T) / M_{Fe(III)}(0) \right) \times \left( M_{Fe(II)}(0) / M_{Fe(II)}(T) \right) H_C(0) \quad \text{(2)}$$

It is not difficult to find that $H_C$ should diverge at $T_{comp}$ due to $M_s(T_{comp}) = 0$. So the fact that $H_C$ is stronger at $T_{comp}$ is described in this model. This is usually observed in compensated ferrimagnets [9]. From Eq (1), we can conclude that the two sublattice magnetizations have different temperature dependences due to the difference of their spin carries. The Mössbauer studies have confirmed the conclusion. Moreover, the Fe(II) sublattice magnetization increases more steeply below $T_C$ than that of the Fe(III) sublattice comes from Mössbauer results. We now consider the magnetic measurements in the CM for the case of $H < H_C(0)$.

As a result, we have not observed the multiple magnetic pole inversions in the CM. The reason why the magnetization remain antiparallel to the field is that $H < H_C(T)$ and M blocked by $H_C$ remains its orientation. This corresponds to the first line in Fig 6. As the magnetic measurements of the sample were carried out in the WM. We think that the easy axis in the CM parallels to some direction. Then the easy axis in the WM should change to another direction in order for the minimal free energy. By Eq (2), we know that the $H_C(T)$ decreases with the reducing $K_{Fe(II)}(T)$. As $H > H_C(T)$ in the WM, the magnetization jumps to a large positive value. The dominant part $M_{Fe(II)}$ is parallel to $H$. Above $T_{comp1}$, $M_{Fe(III)}$ dominates over the sublattice contribution of Fe(II). So the magnetic poles reverse firstly at $T_{comp1}$. $H_C$ is bigger than $H$ at $T_{comp1}$. Then $H_C$ decreases as temperature goes up and eventually becomes smaller than $H$. The magnetization returns to its “normal” orientation. Where the dominant $M_{Fe(III)}$ is parallel to $H$. $M$ becomes positive again. The second magnetic pole reversal is observed. This corresponds to the second line in Fig 6 (Schematic illustration of the temperature dependence of the magnetization orientation). The phenomenon of multiple magnetic pole reversals is rare. Some
ferrimagnets consisting of magnetic anisotropy ions and two or more types of antiferromagnetically ordered magnetic ions exhibit this behavior.

The ferrimagnetic behavior is further characterized by the measurements of hysteresis behavior for $\{\text{[N(n-C4H9)4][ZnII0.03FeII0.97FeIII(C2O4)3]}\}_n$ as shown in Figure 7. The observed value of coercive field ($H_c$) and remanent magnetization ($M_r$) for the compound are 15KOe and 572.2 cm3·G·mol⁻¹.

4. Conclusion

The mixed valency character and antiferromagnetic coupling in Molecule magnets Materials $\{\text{[N(n-C4H9)4][MIIFeIII(C2O4)3]}\}_n$ (M=Zn, Fe) were investigated by magnetic measurements and Mössbauer spectroscopy. In the complex $\{\text{[N(n-C4H9)4][ZnII0.03FeII0.97FeIII(C2O4)3]}\}_n$, we observed a compensation temperature has found with the field being less than 1KOe. The phenomenon of magnetic pole reversals is rare. In the complex $\{\text{[N(n-C4H9)4][FeIIFeIII(C2O4)3]}\}_n$ to investigate the mixed valency character and antiferromagnetic coupling. Some ferrimagnets consisting of magnetic anisotropy ions and two or more types of antiferromagnetically ordered magnetic ions exhibit this behavior. As the temperature was lowered to 40 K, the FeIII doublet subspectrum almost completely turns into a sextet subspectrum. The hyperfine magnetic field increases as the temperature decreasing.

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