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Mössbauer spectroscopy under a magnetic field to explore the low-temperature spin structure of the layered ferrimagnetic material— $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$

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Abstract

⁵⁷Fe Mössbauer spectroscopy of the metal-assembled layered ferrimagnetic material $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ was performed under a high external magnetic field at 4.2 K. This study successfully detected different types of Fe^{II} and Fe^{III} high spin sites in the lattices. The hyperfine field values estimated for all the Fe^{III} high spin sites are close to the expected values, whereas those for Fe^{II} high spin sites are substantially different to those expected usually. A large fraction of magnetically disordered Fe^{III} high spin sites were found. It is understood that the layered structure of the compound may have two kinds of sub-lattices—(Fe_A^{II}–ox–Fe_A^{III}–…) and (Fe_B^{II}–ox–Fe_B^{III}–…)—along with randomly placed magnetically disordered Fe_C^{III} sites, where the Fe_A^{III} and Fe_B^{III} are antiferromagnetically aligned. The existence of the magnetically and/or structurally non-equivalent spin sites in the same lattice has been held responsible for the coexistence of different ferrimagnetic interactions leading to the spin glass state, as observed through earlier magnetic and calorimetric measurements.

1. Introduction

For the first time in the field of magnetism of assembled-metal complexes, the oxalato-bridged layered ferrimagnet $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ has exhibited the rarely occurring negative magnetization phenomenon below 30 K while cooled under a magnetic field of less than 5 kOe [1, 2]. So far, no single crystal structural information is available for this material, though some of its analogues are reported to form a quasi-two-dimensional bi-metallic

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honeycomb lattice bridged by oxalato ligands interleaved with the organic cations (e.g. $N(n-C_4H_9)_4^+$) [3, 4]. Heat capacity calorimetry of this compound under zero magnetic field [5] detected the ferrimagnetic transition at 43.3 K and a structural phase transition at 217 K, along with a small heat capacity anomaly around 16.3 K. In the magnetic-field-dependent heat capacity study of this material performed afterwards [6], the temperature variation of the parameter β in $C_{mag} = \alpha H^\beta$ (where C_{mag} is the magnetic heat capacity) exhibited two sharp minima around 32 and 42 K. This was assumed to be the manifestation of the existence of different spin structures around those temperatures. A recent report [7] on the detailed ac magnetic susceptibility measurement of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ demonstrated the existence of a spin glass-like state below 30 K.

Spin glass behaviour is often observed in the transition of metal-based alloys. In metal-assembled complexes, it was first observed in $\{N(n-C_4H_9)_4[Fe^{II}Fe_x^{III}Cr_{1-x}^{III}(C_2O_4)_3]\}_\infty$ [8]. In the case of polycrystalline ferrimagnetic materials, various exchange interactions between different sublattices often lead to canted spin configurations, and the competing interactions may develop due to the differences between those sublattices at low temperatures. This leads to a spin glass state [9]. To understand the origin of the spin glass state in $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ at low temperatures, it is essential to explore the spin structure in the different sublattices of this compound and then look for the possible magnetic interactions that lead to the observed spin glass phenomenon. Though a report is available on the neutron diffraction study of deuterated $\{P(C_6H_5)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ [10], it should be recalled that the magnetic properties of that material are entirely different [1] from the material under study. Thus, it is not worth correlating the low-temperature spin structure of these two compounds. Mössbauer spectroscopy is a powerful tool for studying magnetic systems with complicated magnetic structure, as this method offers the possibility of observing local spin configurations of different types [11] as well as providing a quantitative estimation of different spin sites in a solid lattice [12]. A few reports are available of Mössbauer spectroscopic studies on the present compound [10, 13–15], but none were aimed at unearthing the low-temperature spin structure. We have attempted to investigate this problem with the help of Mössbauer spectroscopy under a high magnetic field. Our results clearly resolved the coexistence of different Fe^{II} and Fe^{III} spin sites in the lattices at low temperatures, which gives rise to the coexistence of different ferrimagnetic interactions that lead to the spin glass state. These results are discussed in this paper.

2. Experimental details

Polycrystalline material of the $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ used for the present study is from the same batch that was used earlier for magnetic [2, 7] and heat capacity studies [5, 6]. Mössbauer spectra were measured using a conventional constant-acceleration spectrometer with a liquid helium bath cryostat. A superconducting magnet was used to create a magnetic field of 50 kOe parallel to the γ -ray propagation. The sample and the Mössbauer source $^{57}Co/Rh$ were immersed in liquid helium. The hyperfine parameters were obtained by least-squares fitting to Lorentzian lines using the Recoil (1.03a) Mössbauer Software Analysis program.

3. Results and discussion

The ^{57}Fe Mössbauer spectra of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ recorded at 4.2 K under zero field and under a magnetic field of 50 kOe are shown in figures 1 and 2. The spectra were

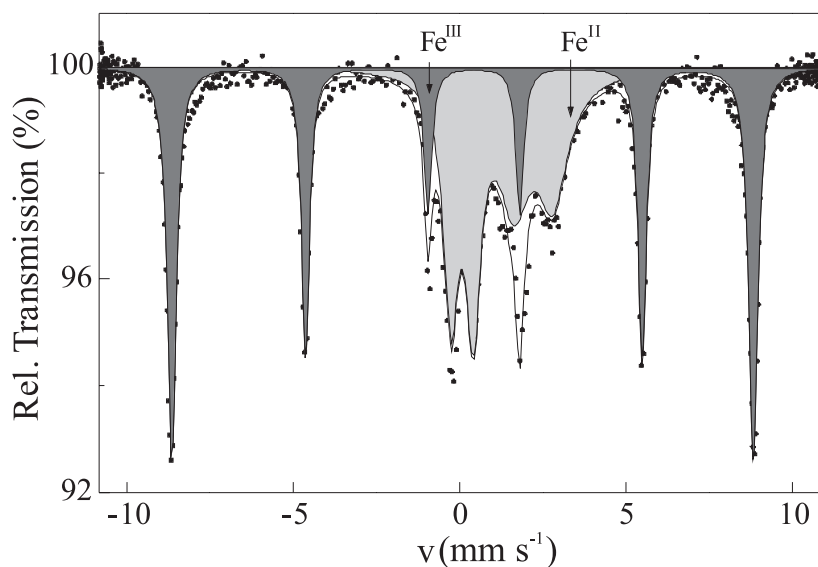


Figure 1. $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ at 4.2 K under zero applied magnetic field.

fitted to Lorentzian lines with isomer shift δ , quadrupole interaction ΔE_Q , hyperfine field H_n and the line-width as the variable parameters for a given component in the spectral fits. The zero-field spectrum is a combination of two sextets, where each one corresponds to Fe^{II} and Fe^{III} spin sites (figure 1). However, it is apparent that the inclusion of one more Fe^{III} sextet of low intensity is required to fit the spectral components associated with Fe^{III} . All the previously reported zero-field Mössbauer spectra at 4.2 K for the present compound [10, 13–15] and analogous compounds [10, 14, 16] could resolve only two high spin sites, corresponding to one each of Fe^{II} and Fe^{III} . However, Carling *et al* [10] mentioned that an additional sextet for Fe^{III} might have been necessary for better fitting of their spectra. The spectrum obtained under a magnetic field in the present study can be resolved further (figure 2), which gives rise to the existence of different high spin sites: two of Fe^{II} and three of Fe^{III} (say, Fe_A^{II} , Fe_B^{II} , Fe_A^{III} , Fe_B^{III} and Fe_C^{III}). The corresponding hyperfine parameters estimated from the best-fit spectra are presented in table 1, along with the previously reported hyperfine parameters for the present compound at 4.2 K. Attempts to fit the observed spectrum under a 50 kOe magnetic field with two spin sites, each for Fe^{II} and Fe^{III} , did not give an appreciably good result. This led us to introduce another Fe^{III} site, which resulted in a better fit and reasonably good results.

For the Fe^{III} high spin site under zero external applied magnetic field, the saturation value of the hyperfine field H_n is 550 kOe [16]. The H_n values estimated for all the Fe^{III} high spin sites without applied magnetic field are significantly close to the saturation value and also in agreement with the previous reports on this compound [13, 15]. The magnetic interaction between the high-spin Fe^{II} ($S = 2$) and Fe^{III} ($S = 5/2$) in the present compound is known, from magnetic studies, to be antiferromagnetic. From figure 2, it is clear that there is a significant variation in the intensity among the border-line sextets corresponding to Fe_A^{III} , Fe_B^{III} and Fe_C^{III} . The observed H_n values under the 50 kOe magnetic field for Fe_A^{III} and Fe_B^{III} correspond to 503 and 577 kOe, whereas that for Fe_C^{III} is 540 kOe. Interestingly, the latter is close to the saturation value. Under the applied magnetic field of 50 kOe, the Mössbauer spectrum of an antiferromagnetic single crystal that has two Fe^{III} ions coupled antiferromagnetically may exhibit two sextets, giving rise to H_n values close to 550 ± 50 kOe for the Fe^{III} ions parallel and

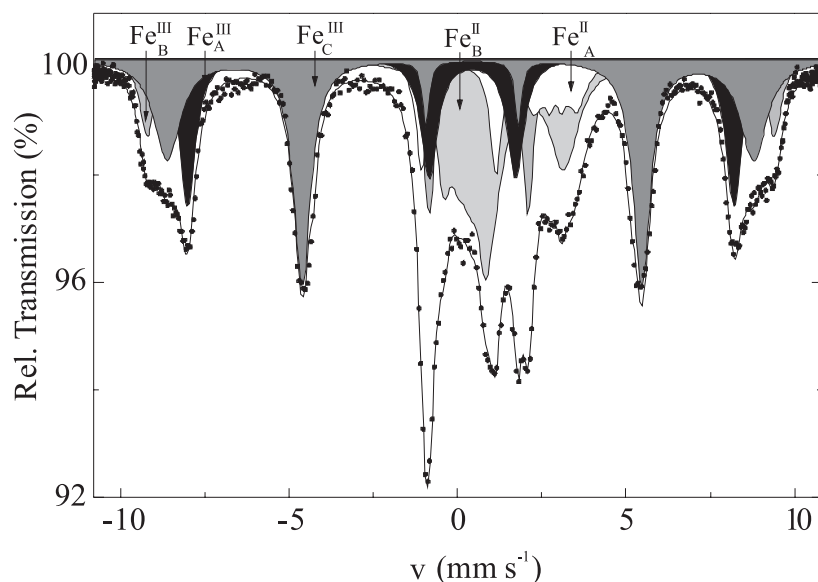


Figure 2. Mössbauer spectra of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ at 4.2 K under a 50 kOe applied magnetic field.

Table 1. Hyperfine parameters of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ obtained from Mössbauer spectra under zero and 50 kOe magnetic fields at 4.2 K. (Note: H_{ext} —external magnetic field; H_n —internal magnetic field; δ —isomer shift; ΔE_q —quadrupole splitting.)

H_{ext} (kOe)	Spin sites	δ ($mm\ s^{-1}$)	ΔE_q ($mm\ s^{-1}$)	H_n (kOe)	Population (%)
0	Fe^{II}	1.39	2.14	36	—
0	Fe^{II} [13]	1.32	1.92	52	—
0	Fe^{II} [10]	1.33	1.79 ^a	57	—
0	Fe^{III}	0.5	0.34 ^b	541	—
0	Fe^{III} [13]	0.51	0.6	537	—
0	Fe^{III} [10]	0.52	0.67 ^b	544	—
50	Fe_A^{II}	1.5	2.86 ^b	68	10.5
50	Fe_B^{II}	1.37	1.88	66	23.9
50	Fe_A^{III}	0.5	0.34 ^b	503	21.4
50	Fe_B^{III}	0.59	0.53 ^b	577	13
50	Fe_C^{III}	0.49	0.5 ^b	540	31.2

^a Fixed at the 78 K value of [9].

^b Electric field gradient $V_{zz} < 0$.

antiparallel to the applied magnetic field direction, respectively. Thus, the spectra observed here under the 50 kOe and H_n values certainly indicate that the Fe_A^{III} and Fe_B^{III} spins are coupled antiferromagnetically, and Fe_A^{III} spins are aligned antiparallel whereas Fe_B^{III} are aligned parallel to the external magnetic field. The deviation from the expected values for Fe_B^{III} may be due to the polycrystalline nature of the present compound.

Besides Fe_A^{III} and Fe_B^{III} , the spectra indicate the existence of another Fe^{III} site (i.e. Fe_C^{III}), which corresponds to the H_n value of 540 kOe. This indicates that these Fe_C^{III} sites are randomly

oriented between the directions of magnetic moments of Fe_A^{III} and Fe_B^{III} . The population of this site is higher than the other Fe^{III} sites. Besides Fe_C^{III} , the total populations of the Fe^{II} and Fe^{III} sites are in the ratio 1:1. The present results, obtained under a high magnetic field, estimate the total population ratio of Fe^{II} and Fe^{III} sites as approximately 1:2, in contrast to the expected ratio of 1:1. Similar disparity is often observed for this compound in elemental analysis in all earlier reports [1, 10]. Moreover, the saturation magnetization of this compound at 5 K was observed from magnetic studies to be $0.07 \mu_B$ [2], which is only 7% of the expected magnetization when Fe^{II} ($S = 2$) and Fe^{III} ($S = 5/2$) spins are perfectly antiferromagnetically aligned. This $0.07 \mu_B$ value of magnetization indicates that only 7% of the spins are effectively aligned in the direction of the applied magnetic field, the rest being randomly oriented. The present observation of the magnetically disordered Fe^{III} sites in the compound also adds reason to the observation of lower values of magnetization. Thus, our consideration of an additional third Fe^{III} site (for a better fit of the observed Mössbauer spectra) is justified.

The observed zero-field H_n value for the Fe^{II} high spin site is lower but within the range reported earlier for the Fe^{II} high spin site at 4.2 K for the present compound (57 kOe [10], 52 kOe [13]) as well as analogous compounds (38 kOe [13] and 45 kOe [14] for $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$; 54 kOe [17] for $\{\text{N}(n\text{-C}_3\text{H}_7)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$; 65 kOe [10] for $\{\text{P}(\text{C}_6\text{H}_5)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$). However, with an applied magnetic field, the estimated H_n values for two different Fe^{II} high spin sites are 68 and 66 kOe, which are also in the range of those reported earlier for the Fe^{II} high spin site at 4.2 K without an applied magnetic field [10]. For Fe^{II} spin sites, as the magnitudes of the contributions due to a non-zero orbital magnetic moment and dipolar interaction can be of the order of the Fermi contact term, the resultant $|H_n|$ value can be anywhere between 0 and 450 kOe. The exceptionally low values of H_n for the Fe^{II} high spin sites at 4.2 K for all these analogous compounds are, in general, thought to be due to a large contribution of the orbital moment to H_n , which is comparable in magnitude and opposite to the negative Fermi contact term (typically 440 kOe for Fe^{II}) [13, 14, 16].

The observed values of δ for Fe^{II} and Fe^{III} are in general agreement with the reported values. However, some remarkable differences appear in the values of ΔE_Q between the present and previously reported values both for Fe^{II} and Fe^{III} . The ΔE_Q values observed for Fe^{II} are quite a lot higher than the reported values, irrespective of the magnetic field condition, but the sign and magnitude are well within the range usually observed for Fe^{II} . On the other hand, the observed ΔE_Q values for Fe^{III} are smaller than the reported values. Both negative and positive electric field gradients for Fe^{III} in the present compound have already been observed [10]. Carling *et al* tried to fit their spectral data, taking the fixed value of ΔE_Q as 78 K in [13], but their model failed to fit adequately with the Fe^{II} spectral profile [10]. They also noticed a dramatic difference in the temperature dependence of ΔE_Q values for Fe^{II} sites in $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ and $\{\text{P}(\text{C}_6\text{H}_5)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$, although in both compounds Fe^{II} and Fe^{III} ions are in the same distorted octahedral coordination environment. Surprisingly, our attempts to fit the observed spectra with the reported hyperfine parameters for Fe^{II} and Fe^{III} at 4.2 K [10, 13] did not give any acceptable fit. This led us to fit our spectrum with all free variable parameters.

The observed differences in the estimated hyperfine parameters among the reports (see table 1) may originate from a proper fitting model consideration and the subtle differences in the compound due to the different synthesis procedures. The magnetic property of these mixed-valence oxalates are remarkably sensitive to the minute changes in the structure/composition due to the synthesis procedure [18]. This is why the analogous compound $\{\text{N}(n\text{-C}_3\text{H}_7)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ prepared in two different batches exhibited quite different Néel's Q- and N-type ferrimagnetism, respectively [1, 18]. Ovanesyan *et al* pointed out that, from the $R3c$ space group consideration of the $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$

group of compounds (M being a transition-metal ion), three of the six anionic layers in the cell incorporate levo-rotatory units, whereas the other three incorporate dextro-rotatory units [19]. This gives the impression that these crystals contain blocks with a different alternation in chirality in the $[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$ fragments in the neighbouring layers. Some blocks exhibit a ‘ Λ - Δ ’ alternation and the others a ‘ Δ - Λ ’ alternation. The type of layer packing in the isomers is of great importance from the viewpoint of magnetism in layered magnets. If interlayer exchange interactions are of some importance; the type of stacking may influence the magnetic ground state. An attempt to model the effect of stacking faults on the magnetic interactions for the case of the present class of layered magnetic materials has been made by Nuttal *et al* [20]. Thus, one may argue that the actual structure/composition of $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ may vary for different synthesis conditions, affecting the spin environment in the crystal. This phenomenon might have contributed to the observed differences in the hyperfine parameters obtained from similar measurements under the same conditions for apparently the same sample of $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ in different laboratories. Though this discussion is not conclusive, it can be discussed elsewhere as it does not fit the goal of the present work.

Reports on the crystallography of some structural analogues of $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ find that these compounds, in general, form a quasi-two-dimensional bi-metallic honeycomb lattice bridged by oxalato-ligands (ox), and that the organic cations (e.g. $\text{N}(n\text{-C}_4\text{H}_9)_4^+ = \text{N}(\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3)_4^+$) are located between the anionic $\text{Fe}^{\text{II}}\text{-ox-Fe}^{\text{III}}$ layers [3, 4]. Within each layer the trivalent and divalent metal sites have the opposite chirality, making the whole structure non-chiral [19, 21]. Three of the organic cationic chains lie in between the anionic layers, whereas the fourth is placed near the threefold axis that threads a honeycomb of the upper anionic layer, thus allowing disorder in the chain around the axis. In terms of the magnetic interactions, it has been concluded that these are quasi-two-dimensional magnetic systems. The magnetic interaction is realized via the super-exchange mechanism between two dissimilar spins through the oxalato ligand in the $\text{Fe}^{\text{II}}\text{-ox-Fe}^{\text{III}}$ layers. Both of the Fe^{II} and Fe^{III} are in the high spin state even down to 4.2 K [13]. If the magnetic interaction between the neighbouring dissimilar spins is antiferromagnetic, it is anticipated that the spins are ordered in an antiparallel arrangement, with nonzero net magnetic moment resulting in a ferrimagnetic lattice.

The magnetic hyperfine field estimated by Mössbauer spectroscopy gives a powerful probe of the properties of the magnetic atoms and their immediate environment [11]. The magnitude of the hyperfine field provides a measure of the magnetic moment on the atoms, though it is not exactly proportional to it. Generally, for iron, the variations of the atomic magnetic moment (Slater–Pauling curve) and the hyperfine field with electron concentration in the neighbourhood in metallic alloys are very close. For magnetically ordered materials, the Mössbauer spectrum is always split by the hyperfine field, and this may be used to determine the nature of magnetic ordering. In this light, we have attempted to visualize the lattice-spin structure of $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ in the following way.

From the present Mössbauer studies it is understood that, in this compound, there are well resolved $\text{Fe}_\text{A}^{\text{II}}$, $\text{Fe}_\text{B}^{\text{II}}$, $\text{Fe}_\text{A}^{\text{III}}$, $\text{Fe}_\text{B}^{\text{III}}$ and $\text{Fe}_\text{C}^{\text{III}}$ sites. The application of a magnetic field not only resolved three sites of the Fe^{III} but also indicated the antiferromagnetic interaction between the $\text{Fe}_\text{A}^{\text{III}}$ and $\text{Fe}_\text{B}^{\text{III}}$ sites. Now, considering this point and the existing intralayer antiferromagnetic interaction between two neighbouring Fe^{II} and Fe^{III} sites, it is understood that the compound may have two types of sub-lattices, i.e. $(\text{Fe}_\text{A}^{\text{II}}\text{-ox-Fe}_\text{A}^{\text{III}}\text{-ox-Fe}_\text{A}^{\text{II}}\text{-ox-Fe}_\text{A}^{\text{III}}\text{-}\dots)$ and $(\text{Fe}_\text{B}^{\text{II}}\text{-ox-Fe}_\text{B}^{\text{III}}\text{-ox-Fe}_\text{B}^{\text{II}}\text{-ox-Fe}_\text{B}^{\text{III}}\text{-}\dots)$. As the $\text{Fe}_\text{A}^{\text{III}}$ and $\text{Fe}_\text{B}^{\text{III}}$ sites are antiferromagnetically aligned with each other, they should be the interlayer nearest neighbours. Otherwise, if $(\text{Fe}_\text{A}^{\text{II}}$ and $\text{Fe}_\text{B}^{\text{III}})$ and $(\text{Fe}_\text{B}^{\text{II}}$ and $\text{Fe}_\text{A}^{\text{III}})$ are the interlayer nearest neighbours, this will give rise

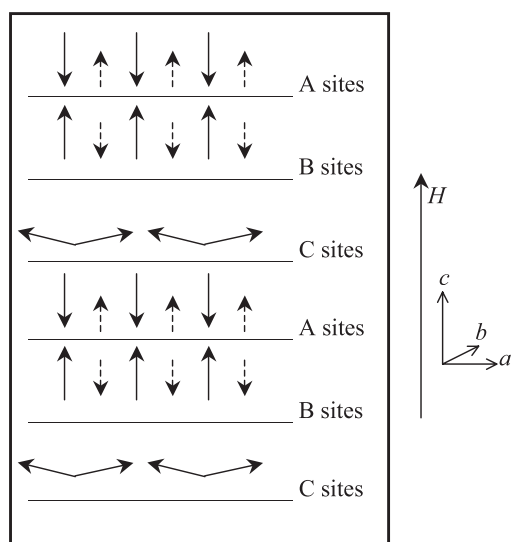


Figure 3. The schematic ferrimagnetic arrangement of spins at different sites along the c -axis in the $\{N(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ lattice. Spin canting and $\text{Fe}_\text{C}^{\text{III}}$ spin sites are not shown (solid arrow: Fe^{III} spin, $S = 5/2$; dashed arrow: Fe^{II} spin, $S = 2$).

to interlayer ferromagnetic interaction. This is not acceptable since, for this compound at temperatures below the magnetic transition temperature, an antiferromagnetic three-dimensional spin-wave excitation was predicted from calorimetric studies [5]. Thus, the calorimetric prediction of the existence of antiferromagnetic interlayer interaction—however small that might be—supports the visualization of the magnetic lattice structure for the present compound. A schematic arrangement of the sub-lattices with different spin sites is shown in figure 3. The layer or lattice structure of this compound consists of two different sub-lattices ($\text{Fe}_\text{A}^{\text{II}}\text{-ox-Fe}_\text{A}^{\text{III}}\text{-ox-Fe}_\text{A}^{\text{II}}\text{-ox-Fe}_\text{A}^{\text{III}}\text{-}\dots$) and ($\text{Fe}_\text{B}^{\text{II}}\text{-ox-Fe}_\text{B}^{\text{III}}\text{-ox-Fe}_\text{B}^{\text{II}}\text{-ox-Fe}_\text{B}^{\text{III}}\text{-}\dots$), each of which is again the combination of two further sub-lattices of Fe^{II} and Fe^{III} , respectively, arranged antiferromagnetically with or without spin canting. The magnetically disordered $\text{Fe}_\text{C}^{\text{III}}$ spins might be randomly placed in the layers on the sites of $\text{Fe}_\text{A}^{\text{III}}$ and $\text{Fe}_\text{B}^{\text{III}}$, giving rise to frustration in the lattice.

Regarding the possible formation of a spin glass state in this compound, it is well known that the spin glass state is a collection of spins (i.e. magnetic moments) whose low-temperature state is a frozen disordered state rather than the kind of uniform or periodic pattern seen in conventional magnets. It appears that, in order to produce such a state in solids, two ingredients are necessary: (i) there must be competition among the different interactions between the moments, in the sense that no single configuration of the spins is uniquely favoured by all interactions (called frustration) and (ii) these interactions must be at least partially random. Many physical properties of the spin glass states support the view that the details of the magnetic interactions are not so important for the formation of a spin glass. Rather, one just needs randomness and frustration in the molecular systems, arising from the competition between different magnetic interactions due to some disorder [22]. In classical spin glass materials, these conditions are mostly the consequences of randomly placed moments that interact through the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction [23]. However, the systems in which the exchange is uniform but either random fields [24] or random anisotropies [25] are present can show the onset of spin glass-like behaviour at low temperatures. Even

molecular systems of frustrated lattices can show spin glass-like behaviour at low temperatures, provided that some disorder is introduced. In the case of ferrimagnetic compounds, the spin glass-like state is characterized generally by correlated ferrimagnetic regions of different size [22], which are a result of the increased frustration determined by the coexistence of antiferromagnetic interactions competing between themselves. Observations of more than one site for both Fe^{II} and Fe^{III} as well as one additional disordered Fe^{III} site are the most remarkable result of the present study in relation to the exploration of the origin of spin glass states in $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$.

The hyperfine field H_n at any spin site may be correlated with the net atomic magnetic moment as proportional to the sum of magnetic moments of that site and the contribution due to magnetic interactions with the nearest neighbours. This can be written as $H_{n\alpha}^\beta = a \cdot \mu_\alpha^\beta + b \cdot \mu'$, where $\mu' = f(z, \theta)$ is the contribution due to magnetic interactions with the nearest neighbours (in units of μ_α^β); α is the spin site A or B; β is the valence state of Fe²⁺ or Fe³⁺; μ is the magnetic moment of the Fe atom; z is the number of nearest neighbours; θ is the spin-canting angle; and a, b are the proportionality constants. Thus, the $H_{n\alpha}^\beta$ value for any particular spin site will reflect the change in its magnetic environment, since μ' is a function of the number of nearest neighbours and their respective spin-canting angles with the spin at the site under consideration. The presence of local spin configurations with different magnetic environments, which leads to a varying amount of μ' , may lead to the appearance of fine structure in the lattice's hyperfine field distribution. Now, from the description of the magnetic lattice structure of the present compound and the analogy between the hyperfine field and atomic magnetic moments of the different Fe^{II} and Fe^{III} sites, it is evident that the random positioning of the magnetically disordered Fe^{III} sites in the (Fe^{II}_A-ox-Fe^{III}_A-ox-Fe^{II}_A-ox-Fe^{III}_A-...) and (Fe^{II}_B-ox-Fe^{III}_B-ox-Fe^{II}_B-ox-Fe^{III}_B-...) layers will certainly create a frustration in the magnetic interactions between different Fe^{II} and Fe^{III} spin pairs. The effect due to frustration on the near-neighbour magnetic interactions will be more prominent intralayer than interlayer, since the former dominates the overall magnetic property of this compound. This situation can easily be held responsible for the various competing magnetic interactions leading to the spin glass state. Moreover, within the same layer, the antisymmetric exchange interaction due to the large spin-orbit coupling of the Fe^{II} spins in the octahedral environment's ⁵T_{2g} ground state will be a weak perturbation superimposed on the strong antiferromagnetic interaction, often leading to a spin-canting phenomenon [26]. Carling *et al* [10] also suggested some amount of canting of the Fe^{II} and Fe^{III} spins in the present compound. This situation certainly generates a difference in the nature of the antiferromagnetic interactions between each spin pair of (Fe^{II}_A and Fe^{III}_A) and (Fe^{II}_B and Fe^{III}_B). All these factors certainly lead to the frustration in the lattice required for generating spin glass behaviour in this compound at low temperatures.

Nuttal and Day [18] expected a structural phase transition in $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ around 38 K associated with a jump in the low field magnetization. However, the calorimetric measurement [5] could not detect any heat capacity anomaly characteristic of a phase transition around that temperature. Ovanesyan *et al* [19] observed two different Fe^{II} hyperfine patterns in the Mössbauer spectra of the analogous compound $\{N(n-C_5H_{11})_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$, which suggests the possible presence of two structurally and/or magnetically non-equivalent Fe^{II} sites. This might be associated with the close proximity of two available sites for the terminal CH₃ groups of the disordered organic cation. However, so far no magnetic studies have been undertaken to look into the existence of a low-temperature spin glass state in this compound. From the heat capacity calorimetry of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$, a structural phase transition was detected at 217 K, which is attributed to an order-disorder phase transition due to an increasing conformational change of the butyl groups in the organic cation [5]. Ordering of the butyl groups below 217 K may

introduce possible structural non-equivalence of different sites in the present material. This may be another reason behind the formation of the observed magnetically and/or structurally non-equivalent Fe^{II} and Fe^{III} sites in this compound, causing a spin glass-like state in the material at low temperatures.

4. Conclusion

A Mössbauer spectroscopic study of $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ under a high external magnetic field has resolved different Fe^{II} and Fe^{III} high spin sites in the solid lattice. The population of different spin sites and associated hyperfine parameters was estimated. This study indicated the nature of spin alignment between different sites as well as helping to visualize the magnetic lattice structure consisting of several sub-lattices. The complex magnetic lattice structure gives rise to some frustration in the magnetic interactions between the spins at various sites with different magnetic environments, leading to a spin glass state—observed earlier through magnetic and calorimetric measurements. As the present measurements were performed on a zero-field-cooled sample, similar studies with a field-cooled sample under a low magnetic field might be interesting since, under those conditions, $\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ exhibits a negative magnetization phenomenon. Although much research work (both experimental and theoretical) is available on the conventional spin glass (metal alloy) materials, very little is known about the spin glass-like behaviour observed in the assembled-metal magnetic materials. Moreover, it is not clear if the mechanisms for conventional spin glasses can be related to the cause of the spin glass behaviour observed in the present compound.

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References

- [1] Mathoniere C, Nuttal C J, Carling S G and Day 1996 *Inorg. Chem.* **35** 1201
- [2] Bhattacharjee A, Feyerherm R and Steiner M 1999 *J. Phys. Soc. Japan* **68** 1679
- [3] Atovmyan L O, Shilov G V, Lyubovskaya R N, Zhilyaeva E I, Ovanesyan N S, Pirumova S I and Gusakovskaya I G 1993 *JETP Lett.* **58** 766
- [4] Pellaux R, Schmalte W H, Huber R, Fischer P, Hauss T, Ouladdiaf B and Decurtins S 1997 *Inorg. Chem.* **36** 2301
- [5] Bhattacharjee A, Miyazaki Y and Sorai M 2000 *J. Phys. Soc. Japan* **69** 479
- [6] Bhattacharjee A, Saito K and Sorai M 2000 *Solid State Commun.* **113** 543
- [7] Bhattacharjee A, Nakazawa Y, Kobayashi H and Sorai M 2002 *J. Phys. Soc. Japan* **71** 2263
- [8] Bhattacharjee A, Iijima S and Mizutani F 1996 *J. Magn. Magn. Mater.* **153** 235
- [9] Yafet Y and Kittel C 1952 *Phys. Rev.* **87** 290
- [10] Carling S G, Visser D, Hautot D, Watts I D, Day P, Ensling J, Gütlich P, Long G J and Grandjean G 2002 *Phys. Rev. B* **66** 104407
- [11] Johnson C E 1996 *J. Phys. D: Appl. Phys.* **29** 2266
- [12] Ksenofontov V, Spiering H, Reiman S, Garcia Y, Gaspar A B, Molinar N, Real J A and Gütlich P 2001 *Chem. Phys. Lett.* **348** 381
- [13] Iijima S, Katsura T, Tamaki H, Mitsumi M, Matsumoto N and Ōkawa H 1993 *Mol. Cryst. Liq. Cryst.* **233** 263
- [14] Ovanesyan N S, Shilov G V, Atovmyan L O, Lyubovskaya R N, Pyalling A A and Morozov Y G 1995 *Mol. Cryst. Liq. Cryst.* **273** 175
- [15] Reiff W M, Kreis J, Meda L and Kirss R U 1995 *Mol. Cryst. Liq. Cryst.* **273** 181

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- [16] Greenwood N N and Gibb T C 1971 *Mössbauer Spectroscopy* (London: Chapman and Hall) p 103
- [17] Iijima S and Mizutani F 1997 *Mol. Cryst. Liq. Cryst.* **306** 227
- [18] Nuttal C J and Day P 1998 *Chem. Mater.* **10** 3050
- [19] Ovanesyan N S, Shilov G V, Sanina N A, Pyalling A A, Atovmyan L O and Bottyan L 1999 *Mol. Cryst. Liq. Cryst.* **335** 803
- [20] Nuttal C J and Day P 1999 *J. Solid State Chem.* **147** 3
- [21] Decurtins S, Schmalte H and Pellaux R 1998 *New J. Chem.* 117
- [22] Belanger D P and Young A P 1991 *J. Magn. Magn. Mater.* **100** 272
- [23] Kubo R and Nagamiya T 1969 *Solid State Physics* (New York: McGraw-Hill) p 577
- [24] Moorjani K and Coey J M 1984 *Magnetic Glasses* (New York: Elsevier) ch 6
- [25] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
- [26] Kahn O 1993 *Molecular Magnetism* (New York: VCH) p 138