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Mössbauer spectroscopic study of low-temperature spin structure and magnetic interactions in $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$

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Abstract

⁵⁷Fe Mössbauer spectroscopy of the layered ferrimagnetic material $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ has been performed at 100 and 4.2 K under different external magnetic field conditions. This study has successfully detected two different types of Fe^{III} high-spin sites in the lattices. The hyperfine field values for all the Fe^{III} high-spin sites are estimated. The magnetic field dependence of the spin canting angle of both the Fe^{III} spin sites has been realized. It is understood that the layered structure of the compound may have two kinds of sub-lattices as (Mn^{II}-ox-Fe_A^{III}-...) and (Mn^{II}-ox-Fe_B^{III}-...), where Fe_A^{III} and Fe_B^{III} are aligned to give rise to a ferromagnetic interlayer interaction. The present observations clearly support the earlier results made on this material through magnetic and low-temperature calorimetric studies.

1. Introduction

The $\{A[M^{II}M^{III}(ox)_3]\}_\infty$ series of metal-assembled complexes with A = tetra *n*-alkyl/aryl ammonium/phosphonium cation, M^{II} and M^{III} = transition metal ions, and ox = oxalate ligand have been widely studied due to their illustrious magnetic properties [1–10]. The magnetic interactions observed in these complexes have originated from the super-exchange interaction between the two intralayer nearest-neighbor M^{II} and M^{III} metal ions mediated by oxalate ligands [1]. Anticipating that a magnetic system $\{A[Mn^{II}Fe^{III}(ox)_3]\}_\infty$ with both metal ions in the same electronic ground states (3d⁵, *S* = 5/2; ⁶A₁) would mimic a two-dimensional (2D) classical antiferromagnet [11], a number of studies on the magnetic and structural properties and Mössbauer effect studies of $\{A[Mn^{II}Fe^{III}(ox)_3]\}_\infty$ complexes

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synthesized with various ‘A’ but with the same $\text{Mn}^{\text{II}}\text{-ox-Fe}^{\text{III}}$ layers have been made [2, 12–16]. Magnetic interactions in this system of materials depend on the nature of non-magnetic organic cations [2] affected by the intralayer organic cation–cation ‘bite-angle’ subtended by the oxalate ligand and the degree of trigonal distortion around the cation. Most of the $\{\text{A}[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]\}_\infty$ compounds exhibit Néel temperatures (T_N) of around 27 K and Curie–Weiss constants between -121 and -128 K [2]. A broad maximum in the $\chi(T)$ plots around 53 K, usually expected for 2D antiferromagnets at higher temperatures [11], was reported from the magnetic susceptibility measurements of $\{\text{A}[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]\}_\infty$ compounds [2]. Below T_N these compounds exhibited a jump in the magnetization arising probably from the uncompensated magnetic moments [2, 14]. Vissar *et al* [12] proposed the uncompensated magnetization observed in $\text{d}_{20}\text{-}\{\text{P}(\text{C}_6\text{D}_5)_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]\}_\infty$ as the manifestation of weak ferromagnetic alignment of Mn^{II} and Fe^{III} spins at low temperatures. From the single-crystal magnetization study of $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$, Carling *et al* [15] observed an uncompensated magnetization below 27 K. A Mössbauer spectroscopic study of this compound held a canted spin structure responsible for the observed uncompensated magnetization [16].

A recent study of the magnetic susceptibility of $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ by us [7] exhibited a significantly large bifurcation in the $\chi(T)$ plots below T_N obtained under field-cooled and zero-field-cooled measuring protocols, which was traceable even at an applied magnetic field of 5 T. The observed bifurcation temperature was magnetic field dependent for the lower range of magnetic fields. More interestingly, the isothermal magnetization curves obtained below T_N deviated significantly from linearity above 3 T, and above this field the magnetization value became increasingly sigmoidal with decreasing temperature. From this observation, a magnetic-field-induced transition in this compound was postulated [7]. A heat capacity study of $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ [8] detected the antiferromagnetic transition at 27.1 K associated with a small hump around 23 K. The estimated magnetic entropy confirmed the high-spin state of both Mn^{II} and Fe^{III} ions in this compound. The magnetic heat capacities above T_N represented an $S = 5/2$ 2D Heisenberg antiferromagnet with a honeycomb lattice structure with an intralayer exchange parameter $J/k_B = -3.3$ K. The spin wave theory applied to the measured heat capacity data below T_N revealed the existence of a very weak interlayer exchange interaction ($J'/k_B = \pm 0.0014$ K). Though the sign of this interlayer interaction could not be assigned, this particular result indicated that $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ is a three-dimensional (3D) or a quasi-2D magnet.

Mössbauer spectroscopy is a powerful tool for studying magnetic systems with complicated magnetic structure, which provides a quantitative estimation of different spin sites of a solid lattice [9]. The estimated magnetic hyperfine field is also a powerful parameter of the magnetic properties of the atoms and their immediate environment [17]. The magnitude of the hyperfine field provides a measure of the magnetic moment on the atoms, though it is not exactly proportional to it. However, for iron, the variations of the atomic magnetic moment (Slater–Pauling curve) and the hyperfine field with its electron concentration in the neighborhood in metallic alloys are generally very close. A recent Mössbauer spectroscopic study under high magnetic field of $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ allowed detection of the presence of different spin sites of Fe^{II} and Fe^{III} at low temperatures as well as their role in determining inter- and intralayer magnetic interactions [9]. There are only two reports of Mössbauer spectroscopic studies on this antiferromagnetic system available—one on $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ [16] and the other on the analogous $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ [18]. From Mössbauer spectroscopy of $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ under applied magnetic fields of 0 and 7 T, Ovanesyan *et al* [16] postulated that this compound is a ferromagnet rather than a ferrimagnet. They held a canted spin structure responsible for the uncompensated magnetization observed in

this compound. However, none of these reports provides much information about the low-temperature spin structure and the nature of magnetic interactions in these compounds. In light of this, we have attempted to visualize the interlayer magnetic interactions and lattice-spin structure of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ with the help of Mössbauer spectroscopy under high magnetic field in order to complement our earlier observations obtained from direct magnetic [7] and heat capacity studies [8], which is described in the present paper.

2. Experimental details

The polycrystalline material of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ used for the present study is of the same batch as was used earlier for magnetic [7] and heat capacity studies [8]. 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 1–5 T 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 [19].

3. Results and discussion

3.1. Mössbauer spectra

The ^{57}Fe Mössbauer spectrum of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ recorded at 100 K under zero magnetic field is presented in figure 1(a). The experimental spectrum was fitted to Lorentzian lines with isomer shift (δ) and quadrupole splitting (ΔE_Q). A well-resolved quadrupole doublet was observed, which is expected for this compound at this temperature, where the thermal energy is still stronger than the magnetic interaction between the high-spin Mn^{II} and Fe^{III} spins and the fluctuation rate of the Fe^{III} spin is faster than the Larmor precession frequency so that the local magnetic field averages out to zero. One more quadrupole doublet of much lower intensity was required for better fitting of the spectrum. The isomer shift (δ) with respect to α -iron and quadrupole splitting (ΔE_Q) values determined for these doublets are summarized in table 1, along with those reported earlier for $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ at other temperatures and some analogous compounds. The estimated δ and ΔE_Q values are consistent with those observed earlier for high-spin Fe^{III} in this class of materials. The doublets observed here call for the existence of two different high-spin Fe^{III} spin sites in this compound.

The Mössbauer spectrum of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ obtained at 4.2 K in the magnetically ordered region ($T_N = 27$ K) under zero and applied magnetic fields of 1, 3 and 5 T are shown in figures 1(b)–(e). On lowering the temperature down to 4.2 K below the magnetic transition temperature, the zero-field spectrum appears as sextets. The presence of these sextets would seem to indicate the presence of long-range magnetic order in this complex. The spectra were fitted to two sextets and the adjustable parameters for a given component in the spectral fits were the isomer shift (δ), quadrupole splitting (ΔE_Q), hyperfine field B_n and the line width. Let us denote these two sub-spectra due to two different high-spin Fe^{III} spin sites as Fe_A^{III} - and Fe_B^{III} - sextets for discussion. The area ratio of the Fe_A^{III} - (gray) and Fe_B^{III} - (deep gray) sextets under zero field were obtained as 3:1, with approximate relative line intensities of 3:2:1:1:2:3 in each case, is expected for measurement in zero applied field. On application of an external magnetic field of 1 T at 4.2 K, the intensity of the Fe_B^{III} -sextet increases at the expense of that of the Fe_A^{III} -sextet. Under a magnetic field of 3 T, the intensity of the Fe_B^{III} -sextet increases

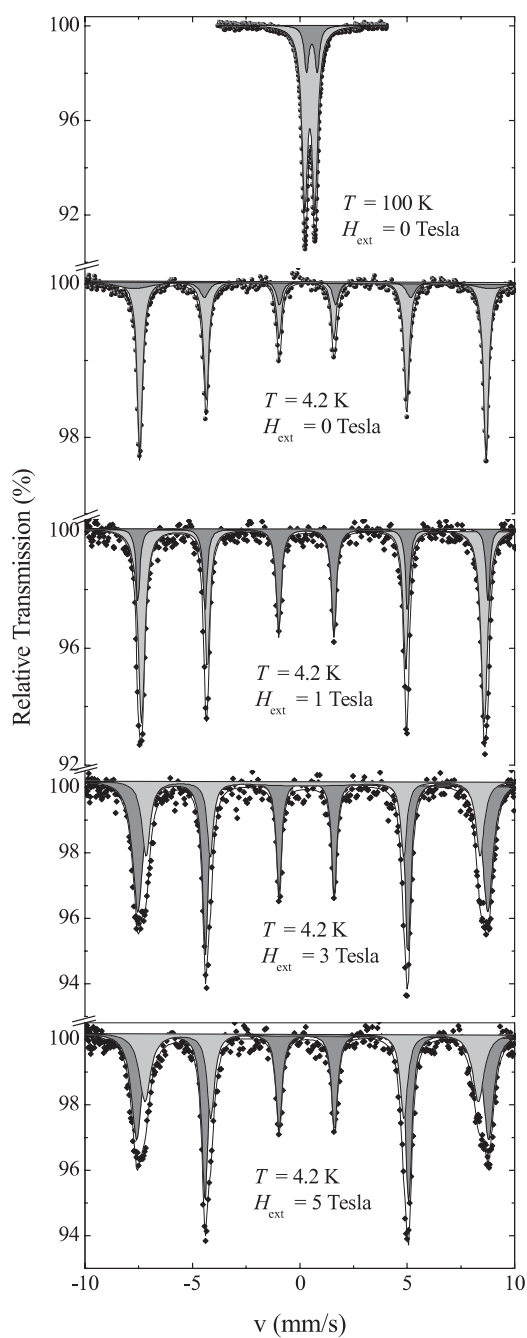


Figure 1. Mössbauer spectra of $\{N(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ at 100 and 4.2 K under different external applied magnetic field conditions. ($\text{Fe}_\text{A}^{\text{III}}$ -sextet: gray; $\text{Fe}_\text{B}^{\text{III}}$ -sextet: deep gray.)

rapidly, whereas for a 5 T magnetic field the intensities of both sextets remain almost the same as those observed under 3 T. The hyperfine parameters estimated from the best-fitted spectra are presented in table 1, along with the previously reported hyperfine parameters for the present

Table 1. Hyperfine parameters of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ obtained from Mössbauer spectra under zero and external magnetic fields at 100 and 4.2 K, along with those of some related materials. (Note: H_{ext} —external magnetic field; B_n —internal magnetic field; δ —isomer shift (with respect to α -iron); ΔE_Q —quadrupole splitting.)

Material	T (K)	H_{ext} (T)	Sites	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	B_n (T)	Area (%)
$\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$	100	0	Fe _A ^{III}	0.47	0.47	—	82
			Fe _B ^{III}	0.56	0.49	—	18
	4.2	0	Fe _A ^{III}	0.46	0.30	50.0	75
			Fe _B ^{III}	0.47	0.22	51.5	25
	4.2	1	Fe _A ^{III}	0.46	0.30	50.5	65
			Fe _B ^{III}	0.46	0.30	49.5	35
	4.2	3	Fe _A ^{III}	0.48	0.28	50.5	32
			Fe _B ^{III}	0.46	0.28	48.2	68
	4.2	5	Fe _A ^{III}	0.45	0.20	50.8	36
			Fe _B ^{III}	0.46	0.26	48.1	64
$\{N(n-C_4H_9)_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ [18]	78	0	Fe ^{III}	0.49	0.62	—	—
	4.2	0	Fe ^{III}	0.50	—	50.2	—
$\{N(n-C_4H_9)_4[Fe^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ [9]	4.2	0	Fe _A ^{III}	0.50	0.34	54.1	—
			Fe _B ^{III}	0.51	0.60	53.7	—
			Fe _C ^{III}	0.52	0.67	54.4	—
	4.2	5	Fe _A ^{III}	0.50	0.34	50.3	—
			Fe _B ^{III}	0.59	0.53	57.7	—
$\{N(n-C_4H_9)_4[Ni^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ [18]	78	0	Fe ^{III}	0.49	0.68	—	—
	4.2	0	Fe ^{III}	0.50	—	50.9	—

compound. The observed δ and ΔE_Q values for Fe^{III} determined at 4.2 K under zero magnetic field are in general agreement with the reported values. Thus, from figure 1, it seems conclusive that the present compound has two Fe^{III} spin sites and the responses of the two Fe^{III} spin sites towards the external magnetic field appear to be different.

3.2. Hyperfine field and magnetic interactions

The saturation value of the hyperfine field B_n for the Fe^{III} high spin under zero external applied magnetic field is 55 T if the Fermi contact field arising from the $S = 5/2$ spin is the only contribution to the effective local magnetic field [20]. The B_n values estimated at 4.2 K under 0, 1, 3 and 5 T external magnetic fields (H_{ext}) are 50.0, 50.5, 50.5 and 50.8 for Fe_A^{III}-sextets and 51.5, 49.5, 48.2 and 48.1 T for Fe_B^{III}-sextets, respectively, which are quite low compared to the expected saturation value for high-spin Fe^{III}. The magnetic interaction between the high-spin Mn^{II} ($S = 5/2$) and Fe^{III} ($S = 5/2$) in the present compound is well known to be antiferromagnetic from both magnetic [7] as well as calorimetric studies [8]. From figure 1, it is clear that there is significant variation in the intensity among the border-line sextets corresponding to the Fe_A^{III}- and Fe_B^{III}-sextets. Under a 3 T applied field, there is a significant change in the intensities of the 1, 2, 5 and 6 lines of the Fe_A^{III}-sextet. A similar change has been observed for the Fe_B^{III}-sextet under a 5 T field. These are the usual signatures of canted spin structure [16]. Under an applied magnetic field of 5 T, the Mössbauer spectrum of an antiferromagnetic single crystal having two Fe^{III} ions coupled antiferromagnetically may

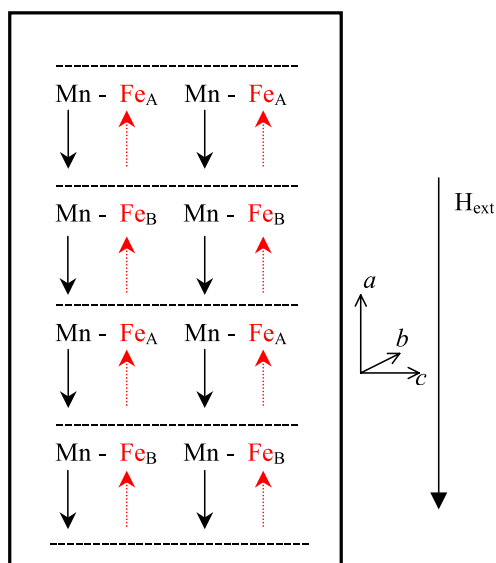


Figure 2. Schematic arrangement of spins at different lattice sites along the c -axis in the lattice of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$. Canting of Fe^{III} spins is not shown. (Solid arrow: Mn^{II} spin, $S = 5/2$; dashed arrow: Fe^{III} spin, $S = 5/2$.)

(This figure is in colour only in the electronic version)

exhibit two sextets, giving rise to B_n values close to (55 ± 5) T for high-spin Fe^{III} ions parallel and antiparallel to the applied magnetic field direction, respectively [9]. Thus, the presently observed Mössbauer spectra under magnetic fields and the B_n values certainly indicate that Fe_A^{III} - and Fe_B^{III} -spins are parallel to each other, and antiparallel to the external applied magnetic field.

From the present studies, it is understood that there exist two different spin sites (Fe_A^{III} and Fe_B^{III}) in this compound. A prediction of different sites of high-spin Mn^{II} is beyond the scope of the present study. Therefore, we presume that Mn^{II} has the same sites only. The application of a magnetic field in the present case has not only resolved the two sites of Fe^{III} spins but also indicated their parallel alignment. Now, taking this point into account and considering the existing intralayer antiferromagnetic interaction between two neighboring Mn^{II} and Fe^{III} sites [7], it may be anticipated that the compound may have two adjacent layers (Mn^{II} -ox- Fe_A^{III} -ox- Mn^{II} -ox- Fe_A^{III} -...) and (Mn^{II} -ox- Fe_B^{III} -ox- Mn^{II} -ox- Fe_B^{III} -...). As the Fe_A^{III} and Fe_B^{III} spins are aligned parallel to each other between the layers, they should be the interlayer nearest neighbors. This will make [Mn^{II} and Fe_A^{III}] and [Mn^{II} and Fe_B^{III}] the interlayer nearest neighbors giving rise to interlayer ferromagnetic interaction. A schematic arrangement of the different spins of the present material below the transition temperature projected in the (110) plane is shown in figure 2.

From a polarized neutron diffraction study of d_{20} - $\{P(C_6D_5)_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ [12] it has been seen that the Mn^{II} and Fe^{III} magnetic ions in the extended molecular network form a two-dimensional honeycomb magnetic lattice and the stacking between the layers is ferromagnetic between the Mn^{II} and Fe^{III} spins. A very weak ferromagnetic moment acting along one of the hexagonals was also hypothesized. But similar interlayer stacking of Mn^{II} and Fe^{III} spins in $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ will lead to an antiparallel alignment of Fe_A^{III} and Fe_B^{III} spins, which is not the case as observed through Mössbauer spectroscopy.

At this point, it has to be noted that the present compound may have a different structure to $d_{20}\text{-}\{\text{P}(\text{C}_6\text{D}_5)_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ as the non-coordinating organic cations often play a crucial role in determining the structure as well as the magnetic properties of the seemingly analogous oxalate compounds [21].

In the calorimetric study of the present material [7] the heat capacity anomaly due to short-range ordering above the magnetic transition temperature was successfully represented by the $S = 5/2$ 2D antiferromagnetic Heisenberg model ($H = -2J\sum S_i \cdot S_j$) for a honeycomb lattice with $J/k_B = -3.3$ K. A spin wave analysis of low-temperature heat capacity data of the present material [7] estimated the interlayer interaction parameter as $J'/k_B = \pm 0.0014$ K; however, that analysis could not ascertain the sign of J' , making us unable to comment on the nature of interlayer interaction (whether ferro- or antiferromagnetic). Thus, the present magnetic-field-dependent Mössbauer study successfully established that there is an interlayer magnetic interaction in $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ and it is ferromagnetic in nature, however small the magnitude may be.

The compound $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ has been characterized to have the $C222_1$ space group, having two anionic and cationic layers each per unit cell [22] in contrast to the space group $P6_3$ in $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ [22] and $R3c$ in $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ [15]. It should be noted that, while for the $R3c$ space group the near neighbors are Mn^{II} and Cr^{III} only, for the $P6_3$ space group the successive layers $\text{Mn}^{\text{II}}\text{-Mn}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{III}}$ are the interlayer contacts. The latter arrangement is in agreement with the layered structure of the title compound (figure 2) proposed through the present Mössbauer spectroscopic study. Thus, as no interlayer magnetic interaction has been seen in $\{\text{N}(n\text{-C}_4\text{H}_9)_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ having $P6_3$ space group, the observations of (i) interlayer magnetic interaction through heat capacity calorimetry and (ii) $\text{Mn}^{\text{II}}\text{-Mn}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{III}}$ as the interlayer contacts (as found in the case of the $P6_3$ space group) through Mössbauer spectroscopy in $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ having the $C222_1$ space group are noteworthy, and requires further investigation on the x-ray crystal structural data of this compound.

3.3. Spin canting

The quadrupole shift values of $\{\text{N}(n\text{-C}_5\text{H}_{11})_4[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_\infty$ are most easily observed in the magnetic spectra (i.e. below T_N) as a difference between S_1 and S_2 , where S_1 and S_2 represent the interval between the lowest-energy and the second lowest-energy peaks, and that between the highest-energy and the second-highest energy peaks in a Zeeman split Mössbauer sextet. The following approximate relation for axial symmetry can be applied to the present case: $S_1 - S_2 = -1/2eV_{zz}Q(3\cos^2\Theta - 1)$, where Θ represents the angle between B_n and the principal axis of V_{zz} [23]. D_3 symmetry is usually observed in $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$ complexes [18, 24, 25], and the principal axis of V_{zz} is supposed to coincide with the D_3 axis in these complexes. The different $S_1\text{-}S_2$ values estimated from the Mössbauer spectra observed under zero as well as applied magnetic fields at 4.2 K for both sextets show that the sign of V_{zz} is positive. The Θ values calculated using the above relation employing the ΔE_Q value estimated at 100 K as the value of $1/2|eV_{zz}Q|$ are plotted in figure 3 as a function of applied magnetic field. With increasing magnetic field, the Θ value for both Fe_B^{III} spin sites initially decreases significantly with respect to Fe_B^{III} and reaches a minimum at 1 T. Beyond this magnetic field, the Θ value increases with increasing magnetic field, attaining a near saturation value beyond 3 T for Fe_A^{III} sites, whereas that for Fe_B^{III} increases steadily beyond 3 T. From this figure it is clear that the two Fe^{III} spin sites respond to the external magnetic field in a dissimilar manner beyond 3 T. Presumably this phenomenon was reflected in the field-

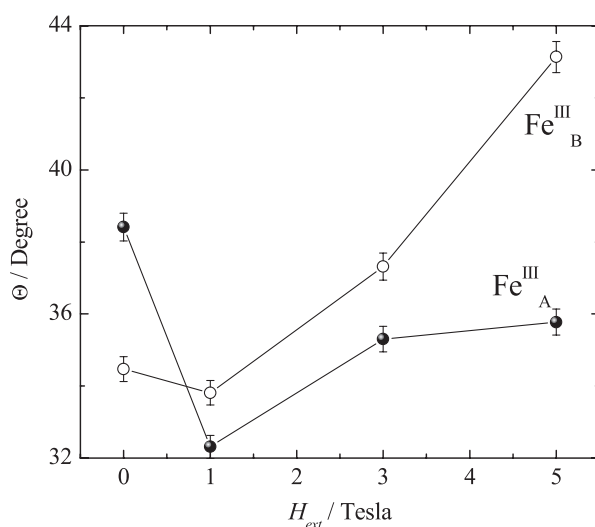


Figure 3. Magnetic field dependence of spin canting angle estimated from Mössbauer spectra of $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ at 4.2 K under different applied magnetic field conditions.

dependent magnetization study of the present compound, and lends support to the hypothesis of a magnetic-field-induced transition in this compound [8]. Magnetic systems containing Mn^{II} or Fe^{III} ions with $S = 5/2$ are well-known examples of spin-canted systems [26–28]. The presence of antisymmetric interaction and/or single-ion anisotropy as a weak perturbation superimposed on the dominant antiferromagnetic spin–spin interaction is the factor responsible for spin canting [29]. For most of the compounds with Mn^{II} ions, the anisotropy in the magnetic ground state is due to a relatively large zero-field splitting, which results in a large single-ion anisotropy. Antiferromagnetic materials having anisotropy ranging from weak to very strong often exhibit spin canting regardless of the nature of the anisotropy. Possible mechanisms for the observed magnetic-field-induced transition in $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ has been discussed earlier [8].

4. Conclusion

The antiferromagnetic material $\{N(n-C_5H_{11})_4[Mn^{II}Fe^{III}(C_2O_4)_3]\}_\infty$ has been studied with the help of Mössbauer spectroscopy under selected applied magnetic fields. Results from this study have clearly resolved the co-existence of different Fe^{III} spin sites in the lattices at low temperatures, and have portrayed the interlayer arrangement of different spins as well as the origin of a canted spin structure. This study has established that there is a ferromagnetic interlayer interaction, which is complementary to the earlier observations from heat capacity studies. The magnetic field dependence of the spin canting angle observed here might be the reason for the field-dependent transition observed in magnetic measurements. Though it is clear that Mössbauer spectroscopy of this material under a few more magnetic fields might have been more helpful to conclude, it is certain that the two Fe^{III} spin sites interact with the applied magnetic field to different extents above 3 T, which reflects the observation of magnetic-field-induced transition at 3 T in this material from magnetic measurements. Thus, the present study completely complements the observations made earlier through magnetic and calorimetric studies.

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