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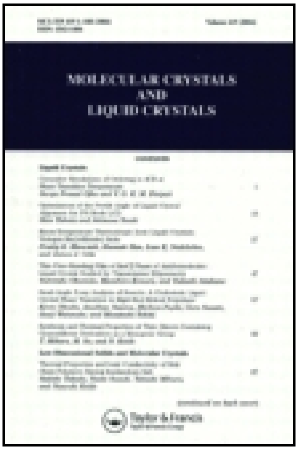

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Structural and Magnetic Properties of Two-Dimensional Oxalate-Bridged Bimetallic Compounds

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Structural and Magnetic Properties of Two-Dimensional Oxalate-Bridged Bimetallic Compounds

NIKOLAY S. OVANESYAN[a], GENA V. SHILOV[a], NATALIA A. SANINA[a], ALEX A. PYALLING[a], LEV O. ATOVMYAN[a] and LÁSZLÓ BOTTYÁN[b]

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Single crystals of $(cat)^+[Mn^{II}M^{III}(C_2O_4)_3]$ ferromagnetic (M^{III}=Cr^{III}, $(cat)^+$ = $(n\text{-}Pr)_4$, n-$Bu(Ph)_3P$), and antiferromagnetic (M^{III}=Fe^{III}, $(cat)^+$= $(n\text{-}Bu)_4N$, $(Ph)_4P$) compounds have been synthesized in order to further elucidate the correlations between their structural and magnetic properties. Single crystal X-ray structural as well as ^{57}Fe Mössbauer studies are reported here. In all these compounds, assigned to a space group $R3c$, Z=6, alternating $[Mn^{II}M^{III}(C_2O_4)_3]_n^{n-}$ 2D honeycomb-like networks, comprise $[M^{III}(C_2O_4)_3]^{3-}$ building units of both kinds of chirality. It has been established that previously reported crystal data for $((n\text{-}Bu)_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$ (space group $P6_3$, Z=2)[1] represent a polymorph structure with similar metallo-oxalate layers containing $[Fe^{III}(C_2O_4)_3]^{3-}$ units of the same kind of chirality (Λ or Δ). An account for twinning effects in crystallization allow us to locate carbon atoms of the $(cat)^+$ in unit cell. Zero- and high-field ^{57}Fe Mössbauer spectroscopy of the polycrystalline compounds as a function of temperature revealed that: (i) $((n\text{-}Pn)_4N)[Mn^{II}e^{III}(C_2O_4)_3]$ is a weak ferromagnet rather than a ferrimagnet, (ii) most of the $\{Mn^{II}Fe^{III}\}$ and $\{Fe^{II}Fe^{III}\}$ compositions are planar (XY) magnets exhibiting unusual magnetic relaxation well below T_c, and (iii) the negative magnetization previously observed[2] in $((n\text{-}Pn)_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$ is certainly a result of strong magnetic anisotropy and an occurrence of a "magnetic compensation point", i.e. a crossing in Fe^{II} and Fe^{III} sub-lattice magnetization curves.

Keywords: two-dimensional magnetism; crystal and magnetic structure; bimetallic oxalates; Mössbauer spectroscopy

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INTRODUCTION

In recent years, the design and synthesis of bimetallic compounds based on the transition metal complexes have attracted a considerable attention in the context of developing new molecule-based ferromagnetic materials of various dimensionalities. A molecular design of such compounds is based on a metallo-complex anion, ML_m, functioning as a polydentate μ_2- or μ_3-coordinating ligand for other transition metal ions, M′. The use of a tri-oxalate chromium(III) complex $[Cr^{III}(C_2O_4)_3]^{3-}$ as a magnetic building block for design of two- or three-dimensional structures has been suggested by H. Okawa *et al.*[3]. This resulted in a new family of ferromagnetic materials of composition $((n\text{-}Bu)_4N)[M^{II}Cr^{III}(C_2O_4)_3]$, where M^{II} = Mn, Fe, Co, Ni and Cu. An analogue series of ferrimagnetic compounds was synthesized on the basis of $[Fe^{III}(C_2O_4)_3]^{3-}$, with M^{II}=Mn, Fe and Ni[4].

The structure of $((n\text{-}Bu)_4N)[Mn^{II}Cr^{III}(C_2O_4)_3]$ compound was the first studied by X-ray diffraction analysis in 1993[5]. Later structural data for $((Ph)_4P)[Mn^{II}Cr^{III}(C_2O_4)_3]$[6] were reported. In both cases the structures were solved within the constraints of the space group *R*3c. The structures consist of $[Mn^{II}Cr^{III}(C_2O_4)_3]_n^{n-}$ 2D anionic layers separated by organic cations. The templating role of organic cation, first outlined by S. Decurtins *et al.*[6], lies in directioning the polycondensation of either achiral 2D or chiral 3D oxalate-bridged framework with the same stoichiometry. All available single crystal data on the 2D $\{Mn^{II}Cr^{III}\}$ network stoichiometries with various quaternary ammonium and phosphonium cations were refined within the *R*3c space group with the unit cell being built of six anionic and six cationic layers. The recent single crystal structure determination of $(n\text{-}Bu)_4N$ and those of $(n\text{-}Pn)_4N$ derivatives with $\{Mn^{II}Fe^{III}\}$ stoichiometry[1,7], however, reveal space groups $P6_3$ and $C222_1$, respectively, with only two anionic and two cationic layers in the unit cell. To clarify this unexpected crystallization behavior we have undertaken structural studies of two $\{Mn^{II}Fe^{III}\}$ compounds with $(n\text{-}Bu)_4N$ and $(Ph)_4P$ cations along with more detailed analysis of previously reported structure data for $\{Mn^{II}Cr^{III}\}$ networks with $(n\text{-}Pr)_4N$, $(n\text{-}Bu)_4N$ and $Ph_3(n\text{-}Bu)P$ cations[8,9].

Furthermore, we report here on ^{57}Fe Mössbauer spectroscopic studies of local structure and magnetic properties of some $\{Mn^{II}Fe^{III}\}$ and $\{Fe^{II}Fe^{III}\}$ polycrystalline powder samples. Based on crystallographic data and high-field Mössbauer measurements we determine the magnetic structure of those compounds and clarify the nature of negative magnetization previously observed[2] in $((n\text{-Pn})_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$ below 30 K. An unusual magnetic relaxational behavior in some {MnFe} and {FeFe} compositions, similar to that reported earlier in ferromagnetic $((n\text{-Bu})_4N)[Fe^{II}Cr^{III}(C_2O_4)_3]$[9,10] is found and interpreted as a manifestation of a non-linear vortex-type spin excitation predicted by D. Kosterlitz and J. Thouless for 2D *XY*-magnets[11].

EXPERIMENTAL

Synthesis of the compounds and results of magnetic susceptibility measurements were published earlier [8,12,13].

The X-ray diffraction data for the crystals of $(cat)[Mn^{II}M^{III}(C_2O_4)_3]$, for M^{III} =Cr, (cat)= $(n\text{-Pr})_4N^+$ (**I**), $Ph_3(n\text{-Bu})P^+$ (**II**), M^{III}=Fe, (cat)= $(n\text{-Bu})_4N^+$ (**III**) and $(Ph)_4P^+$ (**IV**), were collected on a KM-4 four-circle diffractometer (MoK_α radiation, graphite monochromator, $\omega/2\theta$ scan mode, $2° < \theta < 30°$). Subtleties of data collection along with selected crystallographic data have already been reported [9,13].

Mössbauer spectra of iron-containing compounds have been collected using an Oxford CF506 type variable temperature continuous flow helium cryostat and a Janis liquid helium bath cryostat supplied with a 7 T superconducting magnet, respectively. The applied magnetic field was parallel to the gamma ray propagation direction.

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RESULTS AND DISCUSSION

Structural properties

Structures **I** to **IV** were solved by the heavy-atom method within the constraints of the space group $R3c$. The atomic positions in the anionic moieties were refined in the anisotropic approximation, and those of the cationic ones were refined isotropically with constrained bond lengths, the latter due to scarcity of the experimental data and overlapping peaks corresponding to atomic position variations of the disordered organic cation. A decrease in symmetry did not eliminate the disorder.

The atomic coordinates, bond lengths and angles are presented in ref. [9,13].

Crystal structure of compounds **I** to **IV** is similar to those reported earlier[5,6,8,11]. The $(R_4X)^+$ templating cation in assembling the $[M^{II}M^{III}(C_2O_4)_3]_n^{n-}$ extended structural topology leads to a 2D layer compound in which alternating M^{II} and M^{III} centers of opposite chirality are linked by oxalate bridges. The N or P atoms of the cations are situated above the M^{III} atom in a threefold axis (as opposed to the work of Decurtins *et al.*[6], where the $(Ph)_4P$ cation was reported to be above the Mn^{II} atom). Three of the four cationic hydrocarbon chains in structures **I** and **III** as well as the three phenyl rings in **II** and **IV** are arranged as if they 'hovered' over the three oxalate groups of the $[M^{III}(C_2O_4)_3]^{3-}$ fragment. The fourth hydrocarbon chain is placed near the threefold axis threading a honeycomb of the upper anionic layer, thus allowing for a disorder in the chain around this axis. The three further chains or phenyl rings can not disorder due to the interaction with the three oxalate groups of the $[M^{III}(C_2O_4)_3]^{3-}$ anion. In particular, the independent section of the unit cell of compound **IV** contains two $(Ph)_4P$ cations (in a proportion of 3:1). The P atom of one cation lies on the threefold axis and one of the phenyl rings of the catios is disordered around the triple axis. The other cation is in a general position and the corresponding phenyl rings are ordered (see Fig. 1). Despite of the fact that the crystal packing implies a unique arrangement of the organic cation (except for the chain directed along the three-fold axis), an analysis of the Fourier synthesis reveals possibilities of structural disorder. In our opinion, the problem of disorder can be clarified by invoking the data on the synthesis of these compounds as follows.

Since the compounds were synthesized from a *racemic* mixture of the $[M^{III}(C_2O_4)_3]^{3-}$ complexes, it can be expected that the unit cell contains both *Λ* and *Δ* isomers. Actually, in accordance with the space group *R*3c, three of the six anionic layers in the cell incorporate levorotatory $[M^{III}(C_2O_4)_3]$ units, whereas the other three layers incorporate dextrorotatory units. In some cases, the Fourier synthesis allows for the reconstruction of the organic cation turned by ~60° around the three-fold axis. In particular, this can be done for compounds **I** and **III**. In the case of compounds **II** and **IV**, the phenyl ring turned by ~60° around the P-C bond axis can be additionally reconstructed

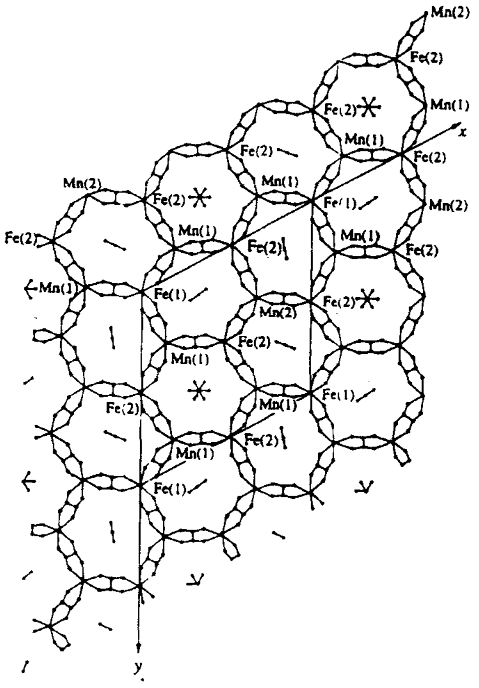

FIGURE 1 A [001] projection of a bilayer fragment in compound $((Ph)_4P)[Mn^{II}M^{III}(C_2O_4)_3]$.

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from the three electron-density peaks. This gives the impression that the crystal contains blocks with different alternation of the chirality in the $[M^{III}(C_2O_4)_3]^{3-}$ fragments in the neighboring layers. Some blocks exhibit a 'Λ - Δ ' alternation, and others a 'Δ - Λ ' alternation. In addition, the samples may contain further types of twins which may be obtained from the above two by a twinning matrix of (0 -1 0, -1 0 0, 0 0 -1) and also, by interchanging the positions of the Mn^{II} and M^{III} ions.

An analysis of the X-ray diffraction data suggests that the crystal of the $((n\text{-Pn})_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$ compound (**V**) described by Carling *et al.*[7] may also be a twin. The crystal structure of this latter compound is somewhat different from those under study. Structures **I** to **IV** relate to the trigonal syngony, whereas compound **V** crystallizes in the orthorhombic system (space group $C222_1$). The disordered organic cation is arranged between the anionic layers in such a way that the N atom and two *n*-Pn chains are placed in a plane between the anionic layers, while the other two chains are nearly perpendicular to those layers. It is noteworthy that the mean Fe-O distance in structure **V** is slightly bigger than the Mn-O distance, although the covalent radius of Fe^{III} is smaller than that of Mn^{II}. The statement of Carling *et al.*[7] that the chiralities of the anionic layers are different, e.g. Mn(Δ) and Fe(Λ) in one layer and Mn(Λ) and Fe(Δ) in the other, is therefore questionable. In our view, with this symmetry, every single layer in **V** should contain either Mn(Δ) and Fe(Λ) or Mn(Λ) and Fe(Δ) isomers. Considering that the reagents contain the racemic mixture of the $[Fe^{III}(C_2O_4)_3]^{3-}$ isomers, one naturally assumes that both chiral forms are present within the same crystal sample, which is, therefore, a *racemic* twin. Obviously, the two components of the twin mutually transform into each other by interchanging the positions of the Mn and Fe atoms in crystal structure **V**.

The alternative way of crystallization of *achiral* layers of oxalate compounds containing the $[Fe^{III}(C_2O_4)_3]^{3-}$ building blocks of unique chirality has been recognized in crystal data of $((n\text{-Bu})_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$. According to Pellaux *et al.*[1], this compound crystallizes in space group $P6_3$ and, like compound **V**, contains only two metal-oxalate layers in the unit cell. It is

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therefore clear by now, that the derived crystal structure of $((n\text{-Bu})_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$ is an isomer variant of the known $R3c$ isomer structure with the same cation. One should mention the distinct packing of layers in the two isomers, which is of importance from the view-point of magnetism of 2D compounds. The interesting feature is that while for the $R3c$ space group the neighboring layers are 'out-of-registry', i.e. near neighbors are M^{II} and M^{III} only, for $P6_3$ space group the successive layers are 'in-registry' (M^{II}-M^{II} and M^{III}-M^{III} interlayer contacts). If interlayer exchange interactions are of any importance, these different kinds of stacking may influence the magnetic ground state.

Magnetic structure and properties

In order to gain more insight into the mechanisms of magnetic ordering in layer magnets local magnetization of Fe^{II} and Fe^{III} sub-lattices were studied in some $Mn^{II}Fe^{III}$ and $Fe^{II}Fe^{III}$ polycrystalline oxalates by ^{57}Fe Mössbauer spectroscopy. Previously, based on the structural data, it was shown that in the ferromagnetic $((n\text{-Bu})_4N)[Fe^{II}Cr^{III}(C_2O_4)_3]$ compound the easy magnetization axis lies in the crystal's basal plane and the main source of the strong magnetic anisotropy is the spin-orbit interaction within the Fe^{II} ion[10]. This property remains valid for all studied layered oxalates containing Fe^{II} ion.

The $((n\text{-Pn})_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$ *compound.* According to the orientation dependence of magnetization measured in the single crystal sample[7] the major component of uncompensated moment is parallel to the *c*-axis. However, the easy magnetization axis of antiferromagnetically (AF) coupled Fe and Mn moments has not been determined since the net magnetization may be associated either with spin canting or with a slight difference in magnitude of collinear Mn^{II} and Fe^{III} moments. The C_2 site symmetry of metal ions located in trigonally flattened octahedra with a small rhombic distortion in the perpendicular direction makes the evaluation of the easy magnetization direction of Fe^{III} moments ambiguous from zero field Mössbauer spectra. For this reason, external magnetic field Mössbauer spectra have been recorded at 4.2 K. It is seen in Fig. 2 that the application of H_{ext} = 7 T parallel to the γ-ray direction results in an increase of the intensity of the second and fifth lines of the Fe^{III} sextet relative to the zero-field spectrum. This strongly suggests that moments of Fe^{III} tend to align normal to the external field direction and hence the net moment originates mainly from spin canting. It should be emphasized, however, that, from the calculated intensity ratio, even at 7 T the uncompensated moment is not fully aligned along the external field direction.

The $((n\text{-}Pn)_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$ *compound.* P. Day *et al.*[2] reported an unprecedented negative magnetization behavior below about 30 K for this mixed-valence ferrimagnet and some related $\{Fe^{II}Fe^{III}\}$ compounds with large organic cations and high Curie temperatures. The authors naturally assumed that the 'negative magnetization' phenomenon was associated with a change of sign of spontaneous magnetization at a so-called "compensation temperature", T_{comp}, at which the two (Fe^{II} and Fe^{III}) sub-lattice magnetizations cancel each

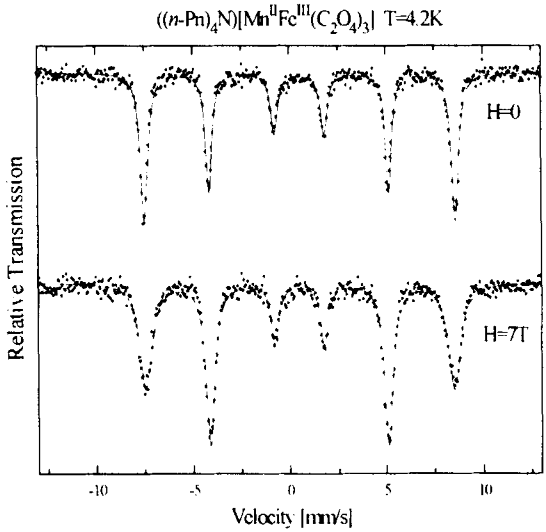

FIGURE 2 Zero-field and external magnetic field Mössbauer spectra at T = 4.2 K of $((n\text{-}Pn)_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$.

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other. Such a situation occurs when the Fe^{III} and Fe^{II} sub-lattice magnetizations have different temperature dependence.

In order to reveal sub-lattice magnetization behavior, temperature dependence of the hyperfine magnetic field was measured for Fe^{III} and Fe^{II} sub-lattices from 4.2 to 39 K. At higher temperatures up to T_C=48 K, spectra exhibit strong magnetic relaxation broadening (see below) which makes the evaluation of hyperfine parameters less straightforward. Note that two different Fe^{II} hyperfine patterns can be resolved in the Mössbauer spectra (with an intensity ratio of 1:1) indicating two structurally and/or magnetically non-equivalent Fe^{II} sites. This might be associated with the close disposition of two available sites for the terminal CH_3 groups of the disordered organic cation. It is seen in the plot of Fig. 3 that the internal field for Fe^{III} falls gradually with temperature, while that for Fe^{II} remains practically unchanged. Since the ground state of Fe^{III} is an orbital singlet (^6A), the internal magnetic field follows the magnetization of the Fe^{III} sub-lattice. On the other hand, this

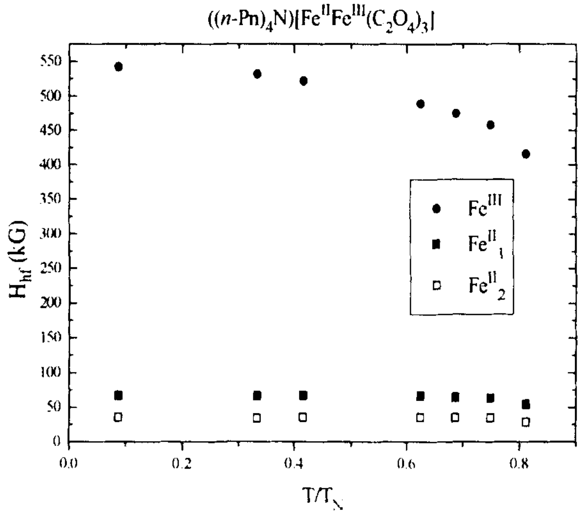

FIGURE 3 Temperature dependence of magnetic hyperfine fields for Fe^{III} and Fe^{II} in $((n\text{-}Pn)_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$.

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proportionality does not hold for Fe^{II}. Despite the singlet ground state of Fe^{II} in a rhombic field, due to spin-orbit interaction, the ground state acquires $\langle L_x \rangle$ and $\langle L_y \rangle$ components of orbital momentum from the low lying orbital levels[10] (at about 300 cm^{-1}). For layer oxalates, the orbital contribution to the internal field (being proportional to $\langle L \rangle$) is comparable with the Fermi-contact term (this latter being proportional to $\langle S \rangle$)[10], and they are generally of opposite sign. Since both $\langle L \rangle$ and $\langle S \rangle$ fall with temperature, the Fe^{II} hyperfine field shows an almost temperature independent behavior and does not reflect the temperature behavior of the Fe^{II} sub-lattice magnetization.

External magnetic field Mössbauer experiments clarified the situation. Exerting a sufficiently high external magnetic field on a strong exchange-coupled magnetic lattice, the Fe^{III} sub-lattice moments tend to align either parallel (below T_{comp}) or antiparallel (above T_{comp}) to the external field direction. As shown in Fig. 4, the application of H_{ext}=7 T results in a *decrease* of magnetic hyperfine splitting at 4.2K for the Fe^{III} component (compared to

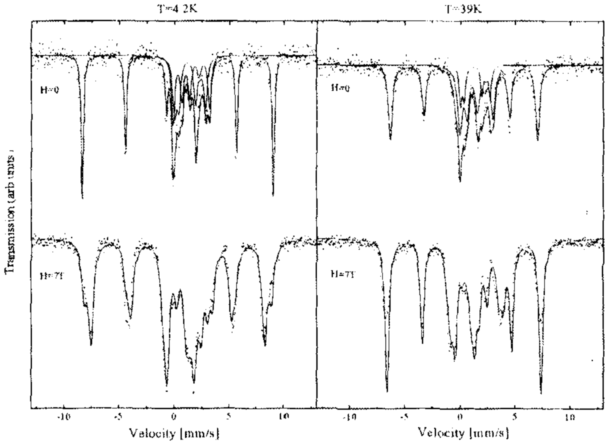

FIGURE 4 Zero-field and external magnetic field Mössbauer spectra at T = 4.2 K (left) and T = 39 K (right) of $((n\text{-}Pn)_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$.

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the zero-field spectrum), while the same field applied to the sample leads to an *increase* of $H_{hf}(Fe^{III})$ at 39 K. The compensation temperature was found around T=36 K, a value about 6 K higher than that derived from SQUID measurements[2] in an external magnetic field of 100 Oe. It should be noted that the rather high external field of 7 T is not sufficient to completely polarize the powder sample (the full alignment of Fe^{III} magnetization would result in a vanishing intensity of the second and fifth lines in the Fe^{III} Mössbauer spectra).

The reported observation of negative magnetization[2] below 30 K means that low field (100 Oe) was insufficient to align the spins even within the crystal's basal plane. Due to the sharp increase in the magnetocrystalline anisotropy constant with decreasing temperature, the effective magnetic anisotropy field at some temperature would overcome the external magnetic field. It is likely that the effect first observed by H. Okawa *et al.*[14] in the $((n\text{-}Bu)_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$ (the compound exhibiting negative magnetization at low fields[2]) was of this type. According to Bahattacharjee *et al.*[14], a minimum of magnetization at about 30 K (H_{ext}=0.5T) is followed by an increase of $\chi(T)$ at lower temperatures. The most striking result is that below 30 K in the zero-field cooled (ZFC) sample χ values are much lower than that in the FC sample.

The $((n\text{-}Bu)_4N)[Mn^{II}Fe^{III}(ox)_3]$ *compound.* Large interlayer separations ranging from 8.2 Å to 14.5 Å as well as the absence of any definite relationship between the interlayer spacing and the T_C (or T_N) values[2,8] makes the bimetallic oxalates excellent model materials for studies of 2D magnetism. In particular, for ferromagnetic $((n\text{-}Bu)_4N)[Fe^{II}Cr^{III}(ox)_3]$ with planar (*XY*-) anisotropy we observed unusual magnetic relaxation behavior below T_C=12 K, as if the long-range magnetic ordering coexisted with rapid spin fluctuations[8]. Similar phenomena were also observed later in {MnFe} and {FeFe} layer oxalates with planar anisotropy. Here we report on the temperature variation of Fe^{III} sub-lattice magnetization for the $((n\text{-}Bu)_4N)[Mn^{II}Fe^{III}(ox)_3]$ compound (T_N=28 K[2]) showing a much higher magnetic hyperfine splitting and a better resolved line pattern than those of Fe^{II} ions. The temperature dependent spectra shown in Fig. 5 demonstrate the main features of magnetic relaxation.

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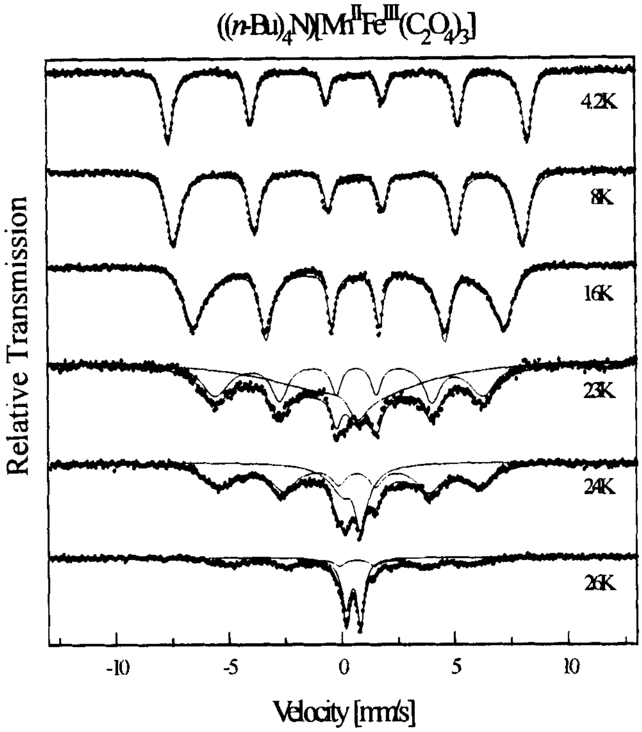

FIGURE 5 Temperature dependence of zero-field Mössbauer spectra of $((n\text{-Bu})_4N)[Mn^{II}Fe^{III}(C_2O_4)_3]$.

Well below the critical temperature i) lines become broader and asymmetric followed by ii) a development of a formally paramagnetic fraction in the ordered state. Magnetic fluctuations with such features are observed in fine magnetic particles (superparamagnets). The present polycrystalline compounds, however, cannot be assigned as superparamagnets, because they are well crystallized and structurally ordered. The unusual magnetic behavior is most likely due to the low dimensionality of magnetic interactions and that of a planar anisotropy as demonstrated below.

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According to D. Kosterlitz and J. Thouless[11], the ideal 2D planar magnet with a continuous symmetry, besides spin-wave excitations, exhibit a specific non-linear excitation in a form of coupled vortex pairs with opposite helicities freely moving (with zero activation energy) in a plane. In real 2D *XY*-systems, owing to the crystal field, the in-plane spin symmetry becomes discontinuous and the spin reorientation requires the overcoming of an energy barrier. It is worth mentioning that the most pronounced relaxation starting even at liquid helium temperature was observed in crystals with high (trigonal) symmetry possessing lower critical temperatures. On the contrary, the rhombic distortion of the hexagonal layer, e.g. as in $((n\text{-Pn})_4N)[Fe^{II}Fe^{III}(C_2O_4)_3]$, creates a preferred direction of magnetization in the basal plane, (Ising-like anisotropy), which, as a consequence, shifts the region of pronounced magnetic relaxation to much higher temperatures. To evaluate the experimental spectra we applied a three-level stochastic relaxation model[15], allowing for anisotropic in-plane spin re-orientations by 120° each. We consider vortex-like excitations as moving intra-layer domain walls which separate the degenerate ground state configurations. The Fe^{III} spins on the boundary of these domain walls fluctuate fast between the three possible orientations. With increasing temperature, the wall density and average wall velocity increase involving more Fe^{III} moments.

At low temperatures, up to 16 K, the spectra are well fitted with a single set of relaxation times. With increasing temperature, as the effectively paramagnetic part appears in the spectra, one should introduce an additional rapidly relaxing component, probably associated with the vortex core. As can be seen in Fig. 5, the applied model fits the experimental spectra quite well. We leave, however, the quantitative results and more detailed discussion for publication elsewhere.

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