Magnetic Studies on the 1-D Antiferromagnetic Chains of enH$_2$Mn(Fe)F$_5$

C. Frommen$^a$, L. Schröder$^a$, U. Bentrup$^b$, W. Massa$^a$, J. Pebler$^a$*

$^a$ Fachbereich Chemie und Wiss. Zentrum für Materialwissenschaften der Philips-Universität, Hans-Meerwein-Str., 35043 Marburg, Germany

$^b$ Institut für Angewandte Chemie Berlin-Adlershof, Rudower Chaussee 5, 12484 Berlin, Germany

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Magnetization, Structure, Exchange and Anisotropy Energy, Mößbauer Effect, Relaxation

Measurements of the $^{57}$Fe Mößbauer effect and of magnetic susceptibilities have been performed on the $^{57}$Fe doped or pure quasi-1-d antiferromagnetic chain compound enH$_2$MnF$_5$ as a function of temperature. Particular attention was paid to the regions very close to the Neél point at $T_N = 14.5(5)$ K. The Mößbauer spectra fitted by the Blume-Tjon model show definite relaxation effects, which are attributed to short-range order with temperature-dependent relaxation times. The soliton model of non-linear excitations was applied. Experimental data confirm the predicted exponential temperature dependence of the thermal excitation of moving domain walls. From the activation energy $E_A/k = 184(5)$ K and the 1-d exchange energy $J/k = -13.6(2)$ K a local anisotropy energy $D/k$ of $-2.4(3)$ K was obtained which is smaller than $D/k = -3.5$ K derived from our single crystal measurements of magnetic susceptibilities. Within the 3-d magnetic ordering the interchain interaction amounts to $J/k = 0.22(4)$ K ($J/J_1 = 15.8 \times 10^{-2}$). A zero-spin reduction $J_3S$ equal to 17% was obtained. 1-d correlations are observed for $T_N < T < J_3(S+1)/k \approx 78$ K, and a crystallographic phase transition at 216 K was indicated in the magnetic properties as well as by DSC and X-ray powder diffraction measurements.

Introduction

In anisotropic chain systems, linear physics involving magnons or spin waves appears to be insufficient to describe their physical quantities, and non-linear physics becomes of dominant importance for the interpretation. Non-linear excitations are solutions of non-linear differential equations, e.g. the sine-Gordon equation, and are commonly referred to as solitons. They are local excitations which connect degenerate ground states.

Solitons in magnetic chains are moving domain walls, which separate spin-up and spin-down regions in a ferromagnet or the two different ordered regions in an antiferromagnet [1–15]. These solitons may be conveniently studied in quasi-1-d ionic compounds with easy-axis anisotropy in which the magnetic moments are arranged in widely separated chains such that the ratio of inter-chain to intra-chain exchange interaction $J'/J$ is very small. A domain wall that passes a Mößbauer ion flips the hyperfine field $H_{hf}$ and the flip rate may become low enough to fall within the Mößbauer frequency window [16–18]. In previous papers we showed that for $^{57}$Fe$^{3+}$ doped fluoromanganates (III) like Rb$_2$Mn$_{0.99}$Fe$_{0.01}$F$_5$ (H$_2$O) [11,12] and (NH$_4$)$_2$Mn$_{0.99}$Fe$_{0.01}$F$_5$ [19] with strong local anisotropy this frequency range covers many decades, typically from $10^3$ up to $10^{11}$ Hz.

In the following study, we present experimental results obtained by Mößbauer spectroscopy for the quasi-1-d magnetic chains of enH$_2$Mn$_{0.99}$Fe$_{0.01}$F$_5$. We discuss in some detail the dynamic and static properties of the non-linear excitations extracted from a series of Fe(III) Mößbauer spectra and measurements of the magnetic susceptibilities of the pure and Fe doped powder, and on a single crystal of enH$_2$MnF$_5$. We pay attention to the relationship between the soliton activation energy, the 1-d exchange energy and the local anisotropy. In so doing our aim is to test how far the magnetic anisotropy can be extracted from dynamic properties of powder samples with the aid of Mößbauer spectroscopy.

* Reprint requests to Prof. Dr. J. Pebler.
Experimental

The compound enH$_2$MnF$_5$ was prepared in an aqueous solution of 20% HF using Mn(OOCCH$_3$)$_3$·2H$_2$O and enH$_2$F$_2$ [20,21]. 1.0 g of manganese(III) acetate dihydrate was dissolved in 20 ml of aqueous HF solution (20%) and mixed with 10 ml of a solution of ethylene-diammonium difluoride, obtained by reaction of 50 ml of absolute ethylenediamine (en) with 100 ml of aqueous HF (20%). The precipitate was filtered and air-dried. Crystals for structure determination and magnetic measurements grew in slow crystallization from a diluted solution.

The $^{57}$Fe sample of enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ for Mössbauer study was prepared in a similar way, using $^{57}$Fe metal for the reaction carried out in aqueous HF. The $^{57}$Fe was dissolved and oxidized in 40% HF using small amounts of 30% aqueous H$_2$O$_2$, thus yielding $^{57}$FeF$_3$(aq). An excess of H$_2$O$_2$ was removed by heating the solution in a platinum crucible and refilling with 40% HF.

enH$_2$FeF$_5$ was obtained by dynamical heating of enH$_2$[FeF$_5$(H$_2$O)] in a Pt crucible (sample weight 200 mg, heating rate 5 K/min, flowing N$_2$, 25 l/h) up to 470 K using a Derivatograph Q-1500 D (MOM Budapest).

DSC investigations have been made with a Perkin-Elmer DSC 7 within the temperature range of 140–300 K.

Magnetic data were obtained from 1.8 to 330 K by using a SQUID magnetometer in a magnetic field from -55 up to 55 kG [22]. Mössbauer measurements were performed from 1.8 to 300 K by using a standard equipment described elsewhere [11] and a 20 mCi $^{57}$Co(Rh) source.

Crystallographic Characterization

enH$_2$MnF$_5$: The structure of enH$_2$MnF$_5$ at room temperature which we reported earlier [23] shows orthorhombic symmetry (space group Cccm, Z = 16, $a = 17.105(1)$ Å, $b = 17.992(1)$ Å, $c = 8.478(1)$ Å). Isolated infinite chains of trans-linked [MnF$_4$F$_2$/2]$_2^-$ octahedra run along the c direction with a mean bridging angle of $\beta$(Mn–F–Mn) = 159.5°. The individual chains are separated by enH$_2^{2+}$ ions. The mean axial and equatorial interatomic Mn–F distances are Mn–F$_{ax}$ = 2.154(1) Å and Mn–F$_{eq}$ = 1.838(1) Å, respectively (Fig. 1). Like the structures of fluoromanganates(III) of the type A$_2$MnF$_5$(H$_2$O) with A = Li, Na, NH$_4$, K, Rb, Cs, and AMnF$_5$(H$_2$O) with A = Sr, Ba, the enH$_2$ compound shows strongly elongated [MnF$_6$] octahedra, similar to the other “strong” Jahn-Teller systems with Cr(II) or Cu(II) [24]. By reasons of stabilization energy the Jahn-Teller elongation points always towards the octahedral axis bearing the weakest bonds [25]. Thus, in the trans chain compounds the weaker bridging bonds along the chain direction undergo an additional remarkable weakening. One observes a ferrodistortive ordering of elongated octahedra [26]. The direction of the elongation indicates the orientation of the half-occupied $d_{z^2}$ orbital stabilized by the elongation.

By this way, antiferromagnetic coupling arises along the chains via $d_{z^2}$–p$_x$–d$_{z^2}$ $\sigma$-super-exchange interactions. Thus, the chain structure of enH$_2$MnF$_5$ is a good model system for studies of exchange and soliton activation energies.

enH$_2$FeF$_5$: In contrast to the Mn(III) compound, enH$_2$FeF$_5$ can be prepared only by thermal decomposition of its monohydrate, and thus only powder samples are available. X-ray powder patterns can be indexed with the following primitive tetragonal unit cell (values and e.s.d.s from Rietveld refinement below)

$$a = 9.0968(2) \text{ Å}$$
$$c = 7.9465(2) \text{ Å}$$

The close relation in size to the unit cell of enH$_2$MnF$_5$ suggested a similar chain structure. An idealized structure model has been established in the space group P4/mcc, a supergroup of Cccm.
Table I. Fractional atomic coordinates and isotropic temperature factors [Å²] (common by groups) for the idealized structure of \( \text{enH}_2\text{Mn(Fe)F}_5 \) in space group P4/mcc.

<table>
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<tr>
<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>1.59(5)</td>
</tr>
<tr>
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<tr>
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<td>0</td>
<td>0</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>x</td>
<td>0.25</td>
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</tr>
<tr>
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<td>8m</td>
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<td>0.0739(9)</td>
<td>0</td>
<td>0.59(25)</td>
</tr>
<tr>
<td>N</td>
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<td>0.6364(14)</td>
<td>0.1413(15)</td>
<td>0</td>
<td>1.54(23)</td>
</tr>
</tbody>
</table>

which is compatible with the systematic extinctions observed. Tentative refinement of this structure by the Rietveld method [27] (Table I, Fig. 2) to \( R_{wp} = 28\% \) and \( R_I = 9.7\% \) confirm in principle the above assumption. This model is based on linear chains (angle Fe–F–Fe 180°) by symmetry, whereas Mössbauer experiments (see below) suggest an angle of about 162°. For a linear bridge a Fe–F distance of 1.987 Å can be calculated from where the above assumption. This model is based on linear chains (angle Fe–F–Fe 180°) by symmetry, whereas Mössbauer experiments (see below) suggest an angle of about 162°. For a linear bridge a Fe–F distance of 1.987 Å can be calculated from

\[
\text{Fe} - \text{F} = -3.5(1) \text{ K} \quad [19]
\]

and for Rb\(_2\)Mn\(_{0.63}\)Fe\(_{0.37}\)F\(_5\) (H\(_2\)O) within the concentration range \( x < 0.5 \) [11–13]. Since Fe(III) solutions (NH\(_4\))\(_2\)MnF\(_5\) (space group Pnma, \( Z = 4 \)) at room temperature are nearly isotropic with two small signals at the \( g \) values \( g_x = 2.002 \) and \( g_z = 1.997 \) [29,11]. The influence of zero-field splitting on the magnetic properties can thus be accounted for by addition of two terms to the isotropic exchange interaction. The Heisenberg Hamiltonian for the single chain in a magnetic field can be written in the form

\[
H = \sum (2JS_iS_{i+1} + D(S^{2}_{iz} - \frac{1}{3}S_i(S_i + 1)) + E(S^{2}_{ix} - S^{2}_{iy}) - g\mu_B\vec{H} \cdot \vec{S}_i)
\]

where \( S \) and \( S_q (= x, y, z) \) are spin operators related to the occupied energy levels. The chain direction is along the \( z \) axis. The first term represents an isotropic Heisenberg exchange interaction between two neighbouring spins on the chain. \( D \) and \( E \) are the axial and orthorhombic crystal field parameters. The single-ion-type anisotropy may arise from the crystal field potential. The orthorhombic term takes into account the anisotropy in the plane perpendicular to the principal axis. It can be shown that \( E << d \) and \( J > D \) for all cases of interest here [11]. Many years ago Kida and Watanabe have determined the zero-field splitting of (NH\(_4\))\(_2\)MnF\(_5\) to be \( D/k = -3.31 \text{ K} \) [30]. They found that the spins are parallel to the chain axis. This uniaxial spin direction was also confirmed for the Mn(III) and Fe(III) ions in the case of the solid solutions (NH\(_4\))\(_2\)Mn\(_{0.98}\)Fe\(_{0.02}\)F\(_5\) with \( D/k = -3.5(1) \text{ K} \) [19] and for Rb\(_2\)Mn\(_{1-x}\)Fe\(_x\)F\(_5\) (H\(_2\)O) within the concentration range \( x < 0.5 \) [11–13]. Since Fe(III)

Fig. 2. Observed and calculated diffraction patterns for \( \text{enH}_2\text{FeF}_5 \) after Rietveld refinement and difference plot.

spectra of the analogous chain compound (NH\(_4\))\(_2\)MnF\(_5\) (space group Pnma, \( Z = 4 \)) at room temperature are nearly isotropic with two small signals at the \( g \) values \( g_x = 2.002 \) and \( g_z = 1.997 \) [29,11]. The influence of zero-field splitting on the magnetic properties can thus be accounted for by addition of two terms to the isotropic exchange interaction. The Heisenberg Hamiltonian for the single chain in a magnetic field can be written in the form

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Magnetic Susceptibilities

Magnetic measurements of the powder susceptibilities of pure enH$_2$MnF$_5$ and a sample doped with 2% Fe show broad maxima in the $\chi$ versus $T$ curve at 78 and 79 K, respectively, which are undoubtedly due to short-range antiferromagnetic interaction within the linear chains (Fig. 3-4). Assuming $S = 2$ and $g = 2$ we have fitted Fisher’s expression for the magnetic susceptibility of a chain to our data by adjusting $J$ [31,32]:

$$\chi(T) = \frac{N g^2 \mu_B^2 S(S+1)}{3kT} \frac{(1 + u)}{(1 - u)}$$

where $u = \coth K - K^{-1}$ and $K = \frac{2JS(S+1)}{kT}$

The best fit was obtained for enH$_2$MnF$_5$ with $g = 2.0$, $J/k = -13.6(2)$ K (see Fig. 5) for temperatures below 200 K. For $T > T(\chi_{max}) = 78$ K the spin correlations vanish and the compounds behave like normal paramagnets with a Curie-Weiss susceptibility (Fig. 3). Near $T = 215$ K we observed a change of the magnetic susceptibility. From the least squares fits of the Curie-Weiss law we have calculated for enH$_2$MnF$_5$ and enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ the effective magnetic moments $\mu_e$ to be 5.40(3) and 5.35(5) $\mu_B$, respectively and the Curie-Weiss temperatures listed in Table I which are compared with data of previous measurements obtained for analogous chain structures [11,19]. For completeness we show in Fig. 6 the 1-d magnetic susceptibility for enH$_2$FeF$_5$. From the least squares fits of eq.(2) we obtained the results listed in Table II.

Fig. 3. Experimental data of magnetic susceptibilities as a function of temperature for enH$_2$MnF$_5$.

Fig. 4. Inverse magnetic susceptibilities as a function of temperature for enH$_2$MnF$_5$.

Fig. 5. Fit of Fisher’s expression for the magnetic susceptibility values of a chain to experimental data of enH$_2$MnF$_5$ with $J/k = -13.6(2)$ K and $g = 2.0$. 

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has 3d$^5$ configuration, the single-ion anisotropy of Fe(III) is negligible. But as Mn(III) is a 3d$^4$ ion, it exhibits strong anisotropic properties, which are transmitted via Mn–Fe exchange to the Fe atoms, and their spins become polarized in the same direction as the Mn spins [11]. We propose that a similar interaction exists in enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$. 

### Magnetic Studies on the 1-D Antiferromagnetic Chains of enH$_2$Mn(Fe)F$_5$

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### Table II. Data of Curie-Weiss temperatures, $T(\chi_{\text{max}})$, intra-chain exchange energies $J/k$, and Néel temperatures $T_N$.

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<tbody>
<tr>
<td>$\text{enH}_2\text{MnF}_5$</td>
<td>-214(5)/190(5)</td>
<td>78(3)</td>
<td>-13.6(2)</td>
<td>14.5(5)</td>
</tr>
<tr>
<td>$\text{enH}<em>2\text{Mn}</em>{0.98}\text{Fe}_{0.02}\text{F}_5$</td>
<td>-214(5)/193(5)</td>
<td>79(3)</td>
<td>-13.6(2)</td>
<td>14.5(5)</td>
</tr>
<tr>
<td>$\text{enH}_2\text{FeF}_5$</td>
<td>-347(5)</td>
<td>120(3)</td>
<td>-14.5(2)</td>
<td>12.0(5)</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{MnF}_5$ [19,26]</td>
<td>-153(5)</td>
<td>65(2)</td>
<td>-10.6(2)</td>
<td>8.0(5)</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{MnF}_5(\text{H}_2\text{O})$ [11,26]</td>
<td>-428(5)</td>
<td>128(2)</td>
<td>-20.8(2)</td>
<td>23.0(7)</td>
</tr>
</tbody>
</table>

Fig. 6. Fit of Fisher’s expression for the magnetic susceptibility values of a chain to experimental data of $\text{enH}_2\text{FeF}_5$ with $J/k = -14.5(2)$ K and $g = 2.0$.

The magnetic susceptibilities of a single crystal (0.7 mg) of $\text{enH}_2\text{MnF}_5$ determined with the measuring field along the a, b and c axes at temperatures between 1.8 and 300 K are shown in Fig. 7. No anisotropy was detectable in the temperature range $T > T(\chi_{\text{max}}) = 78$ K. Below $T(\chi_{\text{max}})$ a small roughly uniaxial anisotropy becomes noticeable and grows with decreasing temperature. Below 20 K $\chi_a$ and $\chi_b$ begin to rise and $\chi_c$ continues to fall.

The approximate tetragonal coordination of $\text{Mn}^{3+}$ ions rules out the orthorhombic component E of the crystal field in eq.(1). Then for a Heisenberg chain with axial anisotropy D the magnetic susceptibility is given by Griffiths [33], Smith et al. [32], and Kida et al. [30] as...
\[ \chi_a = \chi_0 + \frac{4}{45} \{ -1.5 \cos^2 \theta + 0.5 \} \]
\[ D \left\{ \frac{S(S+1)}{kT} \right\}^2 \frac{(1+u)(1+v)}{(1-u)(1-v)} + \frac{2u}{(1-u)^2} \]
\[ \chi_b = \chi_0 + \frac{4}{45} \{ +1.5 \cos^2 \theta - 0.5 \} \]
\[ D \left\{ \frac{S(S+1)}{kT} \right\}^2 \frac{(1+u)(1+v)}{(1-u)(1-v)} + \frac{2u}{(1-u)^2} \]

where we have put \( \chi_a = \chi_b \) and fixed \( \theta = 10^\circ \). \( \chi_0 \) and \( u \) are as defined in eq.(2). From these results, we find that the spins are nearly parallel to the chain direction (c axis) in agreement with the results for \((\text{NH}_4)_2\text{MnF}_5\), \((\text{NH}_4)_2\text{Mn}_{0.98}\text{Fe}_{0.02}\text{F}_5\) and \(\text{Rb}_2\text{MnF}_5(\text{H}_2\text{O})\) [19,11]. The best fit is obtained for the values \( D/k = -3.5(2) \) K and \( J/k = -13.6(2) \) K as discussed above. Near \( T_N = 14.5 \) K the fits become very poor due to the arising of long range ordering. There is a clear evidence of spin canting for \( T < T_N \) derived from single crystal measurements of the magnetization in low magnetic field (see Fig. 8).

**Crystallographic phase transition in enH\(_2\)MnF\(_5\)**

Near 215(5) K an anomaly in the temperature dependence of the magnetic susceptibility occurs for enH\(_2\)MnF\(_5\) (Fig. 3–4). After zerofield cooling we measured the magnetic susceptibility with increasing temperature up to room temperature. After this procedure we cooled down the sample in the same external field. The different branches of magnetic susceptibilities show a hysteresis effect (see Fig. 9) which may be an evidence for a crystallographic phase transition of the first order for the enH\(_2\)MnF\(_5\) compound.

This was confirmed by DSC (differential scanning calorimetry) measurements and X-ray powder diffraction experiments with the film-lift technique.

**DSC measurements**

As Fig. 10 shows, DSC measurements in the low temperature region clearly reveal a reversible phase transition at 216 K (heating) and 207 K (cooling), respectively. The occurrence of a hysteresis...
sis points at a first order mechanism as suggested above. A slight difference has been observed between the behaviour of an assembly of crystals only, and that of a powdered sample. The latter obviously underwent activation by powdering. The phase transition area slightly shifts towards lower temperatures. The thermo-analytical data are summarized in Table III. No phase transition has been observed between 140 and 300 K for enH$_2$FeF$_5$.

**Low temperature X-ray powder investigations**

Film lift Guinier records between 230 and 200 K also showed the phase transition at about 215 K (cooling). It is a special feature of the transition that many reflections, including $\text{e.g. } 2 \overline{2} 0, 2 \overline{2} 2,$ and $0 \overline{0} 4,$ remain practically unchanged in angle positions and show no splitting (Fig. 11). Thus, a group/subgroup transition to a monoclinic crystal class (‘translationengleich’) may probably be excluded. Few reflections disappear at the transition temperature and several new ones appear as expected for a first order transition. It is therefore not surprising that an indexing of the low temperature powder diagram with triplicate cell axes, as expected for a transition to an isomorphous subgroup (‘klassen-gleich’), was also not successful.

Complete and very good indexing could be achieved, however, using a primitive orthorhombic cell with duplicate b axis. The refined lattice constants are as follows:

<table>
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<tr>
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<th>HT form at 232 K</th>
<th>TT form at 222 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1706.3(7) pm</td>
<td>1710.6(11) pm</td>
</tr>
<tr>
<td>$b$</td>
<td>1796.4(8) pm</td>
<td>1794.7(12) pm</td>
</tr>
<tr>
<td>$c$</td>
<td>847.4(4) pm</td>
<td>845.9(3) pm</td>
</tr>
</tbody>
</table>

There are 8 space groups compatible with the possible extinction rules: Pccm(49), Pccb(54), Pncm(53), Pncb(50), Pcm(53), Pcnb(60), Pnmm(58), Pnmm(58). In view of this ambiguity, of the principal uncertainty of indexing with very large lattice constants, and of the already quite complicate structure of the R.T. phase, it is impossible to extract information on details of the low temperature structure. Nevertheless, the relative constancy of the original size of the cell (neglecting the doubling) rules out any significant change in geometry and packing of the chains. A discussion of the magnetic interactions on the basis of the R.T. structure appears to be not obsolete. The small shrinking along the c axis, the chain direction, is within the expected limits for the usual reduction of bond lengths with decreasing temperature. Thus, the Mn–F–Mn bridge angle can be assumed constant within a few degrees. We suppose that the transition is caused by a rearrangement of H bonds between the enH$_2$ cations and the anionic chains.

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**Table III. DSC data of enH$_2$MnF$_5$.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample wt. (mg)</th>
<th>Scanning rate (K/min)</th>
<th>Peak temp. (K)</th>
<th>Onset temp. (K)</th>
<th>Enthalpy (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>enH$_2$MnF$_5$</td>
<td>20.69</td>
<td>10.0</td>
<td>217.9</td>
<td>216.4</td>
<td>508.7 (heating)</td>
</tr>
<tr>
<td>crystals</td>
<td></td>
<td></td>
<td>210.1</td>
<td>212.1</td>
<td>-534.1 (cooling)</td>
</tr>
<tr>
<td>enH$_2$MnF$_5$</td>
<td>32.18</td>
<td>10.0</td>
<td>215.8</td>
<td>213.4</td>
<td>510.8 (heating)</td>
</tr>
<tr>
<td>powder</td>
<td></td>
<td></td>
<td>207.6</td>
<td>210.4</td>
<td>-568.0 (cooling)</td>
</tr>
<tr>
<td>enH$_2$MnF$_5$</td>
<td>32.18</td>
<td>15.0</td>
<td>216.5</td>
<td>213.8</td>
<td>510.8 (heating)</td>
</tr>
<tr>
<td>powder</td>
<td></td>
<td></td>
<td>206.5</td>
<td>209.7</td>
<td>-557.4 (cooling)</td>
</tr>
</tbody>
</table>

---

Fig. 11. Diffraction diagrams of enH$_2$MnF$_5$ above (at 223 K) and below the phase transition (at 213 K), from the Guinier film record.
$^{57}$Fe Mössbauer Effect

The temperature dependence of the Mössbauer spectra for a powder sample of enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ is shown in Fig. 12. The spectra were analyzed by fitting symmetric Lorentzian lines. All spectra above 35 K were essentially the same. There is some slight temperature-independent asymmetry over this range that we attribute to sample texture. The two lines have unequal intensities, the lower energy one being the more intense. It can be explained by non-random orientation of crystallites in the absorber, since sample-crystals readily cleave in planes parallel to the chain directions. From the intensity difference we concluded that the lower-energy line is the $|\pm 1/2 \rightarrow \pm 1/2|$ line and that the quadrupole splitting for Fe$^{3+}$ in enH$_2$MnF$_5$ is positive in agreement with the results for (NH$_4$)$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ [19] and Rb$_2$Mn$_{1-x}$Fe$_x$(H$_2$O) [11,12].

At lower temperatures between 30 and 19 K an additional temperature-dependent asymmetry of the absorption lines was observed. As the temperature was further decreased, the spectra exhibited magnetic hyperfine splitting corresponding to antiferromagnetic ordering. Somewhere between 19 and 17 K the quadrupole doublets of the paramagnetic phases disappeared. The transition to the magnetically split phase was observed by the strong broadening of the lines and by the apparent coexistence of contributions from the paramagnetic and magnetically ordered phase. Below 10 K the line widths returned to normal. In addition to the pure combined hyperfine pattern a remaining paramagnetic part was observed toward lowest temperatures.

As mentioned above the coordination around Mn$^{3+}$ is very nearly axially symmetric. The site symmetry at the Mössbauer nucleus contains a fourfold rotation axis D$_{4h}$, coinciding with the V$_{zz}$ direction. Therefore, for all further discussions we have fixed $r_j = 0$. Below T < T$_N$ the spectra were fitted with a general Hamiltonian of the form

$$H = -g\mu_N\sigma(\theta, \phi) + \frac{eQV_{zz}}{4I(I+1)} \left[ 3 I_z^2 - I^2 + \frac{\eta}{2} (I_z^2 - I^2) \right]$$

(4)

where $\theta$ and $\phi$ are the angles of H$_{hf}$ with respect to the EFG principal axis system. The analysis of the 4.2 K spectra showed that the main axes of the nearly axial symmetric EFG tensors are tilted by an angle $\theta \approx 10(1)^\circ$ with respect to the hyperfine field directions. Assuming for enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ an orientation of V$_{zz}$ parallel to the bridging (Mn,Fe)–F bonds, i.e. a mean angle of 10.1$^\circ$ and with respect to the c axis, we obtain the magnetic hyperfine field directions at a mean angle of about 0(2)$^\circ$ with the c axis, and the angle $\phi$ is indefinite. This means that the moments in enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ nearly lie within the chain, confirming the results of the magnetic studies on a single crystal of enH$_2$MnF$_5$. It is interesting to note that the analysis of the 4.2 K spectrum of enH$_2$FeF$_5$ shows that the main axis of the EFG tensor has an angle $\theta = 81(1)^\circ$ with respect to the hyperfine field direction H. Assuming again that...
the site symmetry at the Mössbauer nucleus contains a fourfold rotation axis D$_{4h}$, coinciding with the V$_{zz}$ direction, we can estimate a Fe–F–Fe bridging angle of 162° for enH$_2$FeF$_5$ and an orientation of the magnetic moments perpendicular to the chain direction. These different spin orientations were also confirmed for the analogous compounds (NH$_4$)$_2$MnF$_5$ and (NH$_4$)$_2$FeF$_5$ [19].

The isomer shift IS = 0.422(8) mm/s (relative to Fe metal) at 4.2 K for enH$_2$Mn$_{0.99}$Fe$_{0.02}$F$_5$ is characteristic for Fe$^{3+}$ and was also observed in the analogous (NH$_4$)$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ and (NH$_4$)$_2$FeF$_5$ chain structures [19,34,35,36]. The quadrupole splitting is $\Delta E^Q = 0.5(c^2QV_{zz})^{1/2} = 0.991(8)$ mm/s at 300 K, which is large for a 3$^6$S state. This might be due to the isolated chain structure. The positive values of the quadrupole splittings show that the octahedra are distorted in such a way that four fluorine anions are closer to the iron ion, and two others more remote, in agreement with the interatomic distances.

Three-dimensional magnetic ordering in enH$_2$Mn$_{0.99}$Fe$_{0.02}$F$_5$ is becoming apparent in the magnetically split low-temperature spectra. The magnitude of the magnetic hyperfine fields H$_{hf}$ at 4.2 K is typical for antiferromagnetic Fe$^{3+}$ fluorine chain compounds (Table IV). The magnetic hyperfine field is reduced in accord with the spinwave theory (zero-spin reduction), to H$_{hf}$(T = 0) = 1.068(5) mm/s at 300 K, which is large for a 3$^6$S state. This might be due to the isolated chain structure. The positive values of the quadrupole splittings show that the octahedra are distorted in such a way that four fluorine anions are closer to the iron ion, and two others more remote, in agreement with the interatomic distances.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$_{hf}$[mm/s] (T = 4.2 K)</th>
<th>$\Delta E^Q$ [mm/s] (T = 300 K)</th>
<th>2$\epsilon$[mm/s] (T &lt; T$_N$)</th>
<th>$\theta_u$[°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>enH$<em>2$Mn$</em>{0.98}$Fe$_{0.02}$F$_5$</td>
<td>532(3)</td>
<td>991(5)</td>
<td>946(8)</td>
<td>10(1)</td>
</tr>
<tr>
<td>enH$_2$FeF$_5$</td>
<td>427(3)</td>
<td>1068(5)</td>
<td>-498(8)</td>
<td>81(2)</td>
</tr>
<tr>
<td>(NH$<em>4$)$<em>2$Mn$</em>{0.98}$Fe$</em>{0.02}$F$_5$</td>
<td>525(3)</td>
<td>720(3)</td>
<td>627(8)</td>
<td>17(1)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$FeF$_5$</td>
<td>419/390(3)</td>
<td>1121(5)</td>
<td>-495(8)</td>
<td>78(2)</td>
</tr>
</tbody>
</table>

The origin of the broadened asymmetric spectra in the region near the critical point must be attributed to non-linear excitations of domain walls as demonstrated previously [11–14,19]. This effect masks the transition usually observed near the critical point and prohibits an accurate determination of the ordering temperature by Mössbauer spectroscopy. The possible occurrence of slow spin-spin relaxation may be excluded as explained in [11].

Just above and below T$_N$ = 14.5 K we observe an unusual (non-Brillouin) behaviour in the temperature dependence of the internal fields. As observed in Rb$_2$Mn$_{0.99}$Fe$_{0.01}$F$_5$ (H$_2$O) and (NH$_4$)$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ [11,12] and in numerous high-spin Fe(II) chain compounds with strong anisotropy [17,18], the transition from the paramagnetic state to the magnetically ordered state is accompanied by slow and fast relaxation phenomena below and above T$_N$, respectively, which may be attributed to non-linear excitations of domain walls as demonstrated previously [11–14,19]. This effect masks the transition usually observed near the critical point and prohibits an accurate determination of the ordering temperature by Mössbauer spectroscopy. The possible occurrence of slow spin-spin relaxation may be excluded as explained in [11].

The detailed theoretical analysis of domain wall dynamics and solitons in magnetic chains [9,16,17] shows that in a certain range above the critical temperature the density of π domain walls and their motion determines the spin autocorrelation function $<S(0)S(t)>$, which is obtained by measuring the fluctuating hyperfine field H$_{hf}(t)$ = S(t).

As a second test the Mössbauer spectra of enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ could be fitted successfully by adopting the Blume and Tjon relaxation model [37,38], in which it is assumed that the hyperfine field jumps stochastically between the two possible values +H$_{hf}$ and -H$_{hf}$. From the resolved spectra, clusters with different relaxation frequencies must be present in the temperature range near 18 K. Between 4.2 and 13.5 K, there appears - as mentioned above - an additional central asymmetric doublet due to faster relaxation of the magnetic
spins. It is worth noting that these spins fluctuate perpendicularly to the chain (c axis). As may be seen from Fig. 12, the fits reproduce the observed spectra remarkably well. The resulting values for $G_w$ are plotted in Fig. 13 on a logarithmic scale versus the inverse temperature.

Knowing that the solitons are moving above $T_N$, one would like to investigate what the soliton dynamics look like. It is thus of interest to compare the experimental data with the predictions from the classical soliton theory. In this case $G_w$ would be proportional to both the soliton density $n_s$ and the average soliton velocity $v_s$, according to [17]:

$$G_w \propto n_s v_s \propto \exp(-E_s/kT) \quad (5)$$

where $E_s$ means the creation energy of the solitons. In Fig. 13 we compare the spin-flip rate for enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ with the flip rate for (NH$_4$)$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ [19] and Rb$_2$Mn$_{0.99}$Fe$_{0.01}$F$_5$(H$_2$O) [11] with the parameters $E_A = 184(5) \text{ K}$, $E_A = 166 \text{ K}$ and $E_A = 234 \text{ K}$, respectively, characteristic for an activated soliton process [16,17].

The trend of activation energy as derived from Mössbauer experiments is quite convincing. We propose that the decrease of activation energy $E_A$ with decreasing exchange energy $J/k$ may be understood from the Sine-Gordon theory [15,17]

$$E_s = 4S^2(\bar{D}J) \frac{1}{2}. \quad (6)$$

Assuming that the domain wall theory is also valid in our case of a random system, and inserting in eq.(6) the experimental values of $J/k$, $E_A = 2E_s$ – as derived for Mössbauer experiments [40] – and the average spin of the solid solutions $S \approx 2$, we can estimate the anisotropy constants $D = E_A^2/(8S^2)^2J$ to be equal to $D/k = -2.4(3) \text{ K}$ for enH$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$. The sign of the anisotropy energy $D$ – as defined in eq.(1) – is negative, since the magnetic moments are aligned along the chain directions (see above). The anisotropy constant is smaller than the values $D/k = -3.5(2) \text{ K}$ derived from magnetic susceptibility measurements on single crystals of enH$_2$MnF$_5$, (NH$_4$)$_2$Mn$_{0.98}$Fe$_{0.02}$F$_5$ [19], and Li$_2$MnF$_5$ [41].

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