Magnetisation and Mössbauer study of triazole

 $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ weberites ($M = Fe, Co, Mn, Zn, Ga, V$)

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A series of triazole fluoride weberites $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ is obtained by hydrothermal synthesis. All phases are found to be isostructural with $ZnAlF_5(Htaz)$ by powder X-ray diffraction. Weberite structures are prone to induce the magnetic frustration of antiferromagnetic interactions originating from the cationic topology of HTB layers. The (nD) magnetic properties of (0D) Co-Ga, (1D) Zn-Fe, (3D) Fe-Ga, Mn-Fe, Co-Fe and Co-V couples, are thus reported. Co^{2+} or Fe^{2+} magnetic anisotropy induces a negative magnetisation below T_N and compensation temperatures for Mn-Fe and Co-Fe couples. All iron 3D magnetic phases exhibit high Néel temperatures, between 81 K and 102 K, and large $|\theta_p/T_N|$ ratios, signalling strong magnetic frustration. Their cation site occupancies and the deduced (de)protonation states of the amine are accurately determined by ^{57}Fe Mössbauer spectrometry. In addition, this spectroscopy evidences a subtle effect of the atmosphere that surrounds the samples: the magnetic ordering temperatures T_N decrease significantly when the samples are cooled under vacuum with respect to samples that are cooled at ambient pressure. This novel phenomenon, that is highlighted for all studied (3D) triazole iron weberites, is reversible, and thus opens promising perspectives for understanding the underlying mechanism.

Introduction

Geometrically frustrated magnetic systems generate unusual and potentially useful properties in magnets based on triangular or kagome lattices. This concept of frustration, initially introduced theoretically by Toulouse in 1977,^{1,2} has been successfully applied to numerous inorganic transition metal compounds.^{3,4} Transition metal fluorides, for instance, have been intensively investigated: most frequently, they exhibit antiferromagnetic superexchange interactions that cannot be satisfied simultaneously in a triangular array of interacting corner-sharing MF_n polyhedra. Numerous divalent and/or trivalent metal cations were considered in pyrochlore, Hexagonal Tungsten Bronze (HTB) or weberite-type structures. A wealth of intriguing magnetic behaviours resulted. Depending on the nature of the single-ion anisotropy of magnetic cations, and on the strength of superexchange interactions, magnetic frustration can be relieved in various ways. The tetrahedral or planar 120° arrangements of magnetic moments in pyrochlore

FeF_3 ⁵ or HTB type $(H_2O)_{0.33}FeF_3$,⁶ respectively, and the idle spin behaviour of Fe^{2+} in $Fe_3F_8(H_2O)_2$ ⁷ are examples of magnetic energy minimization. Recently, research into Metal Organic Frameworks (MOFs) has given a strong impetus to the study of organic magnets with corner-sharing triangles of paramagnetic cations.⁸ Besides their main properties of interest, e.g., gas storage or separation, ion exchange, controlled drug delivery, these MOF compounds and, more generally hybrid organic-inorganic materials, may give rise to new exotic magnetic properties. Giant negative magnetisation for mixed valence $Fe^{2+}-Fe^{3+}$ compounds,^{9,10} quantum spin liquid (QSL) ground states for $S = 1/2$ systems^{11,12} and spin crossover phenomena¹³ have already been evidenced and further theoretical and applied extensions are expected.

MOFs are a class of hybrid networks in which organic linkers form ionic-covalent bonds with metal cations. With paramagnetic cations, the strength of magnetic interactions is depends upon a number of important factors: the nature of the metal cations, the network dimensionality (D), the nature of the ligands (N, O, F), the connection mode of the organic ligands with metal cations and also, the nature of solvated species. Currently, 3D MOFs with strong magnetic interactions remain rare. Among them, $Co_5(OH)_2(OAc)_8 \cdot 2H_2O$,¹⁴ a family of porous formates $M_3(HCOO)_6 \cdot S$ ($M = Fe$,¹⁵ Mn ,¹⁶ Co ,¹⁷ Ni ,¹⁸ $S = \text{solvent}$)¹⁹ and $Co(OH)(HCOO)$,²⁰ which display spin glass behaviour, have been reported. For the cited compounds, long range magnetic order is only observed at low temperatures, i.e. below 30 K.

Recently, we reported the synthesis and the crystal structure of a new mixed valence iron fluoride,

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$(\text{Fe}_{0.96}^{2+}\text{Fe}_{0.04}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.96}(\text{taz})_{0.04}$,²¹ isostructural with $\text{Zn}^{2+}\text{Al}^{3+}\text{F}_5(\text{Htaz})$,²² in which Htaz is 1,2,4-triazole. The unit cell is orthorhombic (*Imma* space group) with lattice constants: $a = 9.1552(3)$ Å, $b = 7.4896(2)$ Å, $c = 9.4644(3)$ Å for $(\text{Fe}_{0.96}^{2+}\text{Fe}_{0.04}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.96}(\text{taz})_{0.04}$. The structure is closely related to that of weberite-type $\text{Na}_2\text{NiFeF}_7$ ²³ or $\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$.²⁴ Two water molecules at a distance apart of $d = 4.02$ Å in $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ are replaced by two contiguous nitrogen atoms of triazole ($\mu_{1,2}$) at $d = 1.38$ Å in $(\text{Fe}_{0.96}^{2+}\text{Fe}_{0.04}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.96}(\text{taz})_{0.04}$ (Fig. 1 left); a rotation of the Fe^{2+} octahedra is then induced and the superexchange angle $\text{Fe}^{2+}\text{-F-Fe}^{3+}$ increases from 135° to 146° . The structure consists of a 3D inorganic network with intersecting (101) and (10-1) HTB layers built up from $[010] \infty[\text{M}^{\text{III}}\text{F}_5]$ chains. These chains of corner sharing $\text{M}^{\text{III}}\text{F}_6$ octahedra are further linked by $\text{M}^{\text{II}}\text{N}_2\text{F}_4$ octahedra (Fig. 2 bottom right). In the HTB layers, the triangular cation network is occupied by two M^{3+} cations and one M^{2+} cation; M^{3+} and M^{2+} cations belong to four and two triangles, respectively (Fig. 1 right).

Fig. 1 Crystal structure of $(\text{Fe}_{0.96}\text{Fe}_{0.04})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.96}(\text{taz})_{0.04}$ (left). Fe^{2+} and Fe^{3+} cation connectivity (right).

The magnetic connectivity is strongly dependent on the nature of the transition metal (Fig. 2). With only divalent paramagnetic cations in the $\text{M}^{\text{II}}\text{F}_4\text{N}_2$ isolated octahedra, the magnetic phase is 0D. Otherwise, with only trivalent paramagnetic cations in $\infty[\text{M}^{\text{III}}\text{F}_5]$ infinite chains, the magnetic phase is one dimensional (1D). When both cations are paramagnetic, the magnetic connectivity is 3D. As a consequence, compounds with paramagnetic M^{3+} and M^{2+} cations should exhibit a frustration of 3D antiferromagnetic interactions.²⁵

In this article, the $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ series is extended by taking one or two cations from the following: $\text{M}^{2+} = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and $\text{M}^{3+} = \text{Al}^{3+}$, Ti^{3+} , V^{3+} , Mn^{3+} , Fe^{3+} , Ga^{3+} . Three new compounds have been synthesised for the first time, so the number of known weberite-type $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ compounds has been increased to ten. The magnetic properties of $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ with $\text{Co}^{2+}\text{Ga}^{3+}$, $\text{Zn}_{0.94}\text{Fe}_{0.06}^{3+}$, $\text{Fe}_{0.99}\text{Fe}_{0.01}^{3+}\text{Ga}_{0.01}^{3+}$, $\text{Mn}_{0.94}\text{Fe}_{0.06}^{3+}$, $\text{Mn}_{0.83}\text{Fe}_{0.12}^{2+}\text{Fe}_{0.05}^{3+}$, $\text{Co}_{0.93}\text{Fe}_{0.07}^{3+}$ and $\text{Co}^{2+}\text{V}^{3+}$, are reported; the

iron-containing phases are discussed in the light of the results of Mössbauer spectrometry. A detailed study of $(\text{Fe}_{0.96}\text{Fe}_{0.04})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.96}(\text{taz})_{0.04}$ is scheduled in a forthcoming paper and, consequently, this compound is only mentioned for comparison here.

Fig. 2 Magnetic connectivity in $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ compounds: 0D or 1D with M^{2+} (yellow octahedra) or M^{3+} (green octahedra) paramagnetic cations, respectively, and 3D when both cations are paramagnetic. The dotted circle in the bottom right figure shows a frustrated M-M-M triangle.

Results

Synthesis and characterisation of the $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ isostructural weberites phases

Twenty-three couples of M^{2+} and M^{3+} cations were tested: (Mn, Fe)-(V, Mn, Fe, Ga), (Co, Zn)-(Ti, V, Mn, Fe, Ga), Cu-(Ti, V, Mn, Fe) and Ni-Fe. Apart from the previously known $\text{Fe}^{2+}\text{-Fe}^{3+}$, $\text{Zn}^{2+}\text{-Fe}^{3+}$, $\text{Co}^{2+}\text{-Fe}^{3+}$, $\text{Mn}^{2+}\text{-Fe}^{3+}$, $\text{Fe}^{2+}\text{-Ga}^{3+}$ couples,²¹ three couples led to new $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ compounds: $\text{Co}^{2+}\text{-Ga}^{3+}$, $\text{Zn}^{2+}\text{-V}^{3+}$, $\text{Co}^{2+}\text{-V}^{3+}$.

All the X-ray powder diffraction patterns can be indexed in the orthorhombic system with *Imma* space group (Supplementary Information, Fig. S1). The values of cell parameters and volumes are reported in Table S1; it is observed that the evolutions of the a cell parameters and of the cell volumes are consistent with the variation of the sum of M^{2+} and M^{3+} ionic radii (Fig. 3 and Fig. S2). Small amounts of unknown impurities were detected in $\text{Co}^{2+}\text{Ga}^{3+}\text{F}_5(\text{Htaz})$, $\text{Zn}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$, $\text{Co}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$ and $(\text{Zn}_{0.94}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$. At the opposite, $(\text{Mn}_{0.94}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ is contaminated with a significant amount of MnF_2 .

Fe^{3+} species. It is important to emphasise that both the isomer shift and quadrupolar splitting values of the minor components are fairly consistent with those observed for the corresponding $\text{MFeF}_5(\text{H}_2\text{O})_2$ weberites.^{31–33} However, as previously mentioned, the presence of such hydrates is ruled out by infrared spectroscopy. This minor component could also correspond to the Fe^{3+} sites that are perturbed by the substitution on the M^{2+} sites. For the second set of compounds ($\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$, $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$ and $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$), the spectra result from the presence of two main contributions attributed to HS Fe^{3+} and HS Fe^{2+} species. Similarly to the first set, a second Fe^{3+} component allows us to better describe the experimental spectra, contrarily to the Fe^{2+} component, for which the data are accurately described with a single quadrupolar component. It must be noted that the values of the isomer shift, δ , and quadrupole splitting, ΔE_Q , of the main components are very similar to that found for $\text{Fe}_3\text{F}_{10}(\text{H}_2\text{amtaz})_2$.³⁴ In this 2D phase, Fe^{2+} and Fe^{3+} cations adopt the same $\text{Fe}^{\text{II}}\text{F}_4\text{N}_2$ and $\text{Fe}^{\text{III}}\text{F}_6$ environments as in the $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ phases.

The 77 K Mössbauer spectra show the onset of a 3D magnetic order in the $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$, $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$, $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ phases, as previously observed in $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ phase (Fig. 5 left). In a first approach, the spectra can be fitted with two Zeeman components characteristic of Fe^{3+} and Fe^{2+} in the $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$ and $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ phases. One sextet characteristic of Fe^{3+} is used for $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$ and $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ compounds. One quadrupolar doublet must be added for these last phases, as in the $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ phase and its intensity is related to the proportion of cations that remain paramagnetic.

Fig. 5 ^{57}Fe Mössbauer spectra of $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ phases recorded under helium gas at 1 bar (left) and vacuum and cooling (right), both series at 77 K (green curve represents Fe^{2+} component while blue and red ones are concerned by Fe^{3+} components).

A surprising and significant modification of the magnetic properties is noted for the samples that are left under vacuum

from RT to 77 K. A disappearance of the magnetic sextet occurs for the $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$, $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ and $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ phases, while the paramagnetic fraction is strongly increased for the $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$ phase. Such features observed at 77 K suggest clearly a significant decrease of the magnetic ordering temperature when the powdered samples are under vacuum. On the contrary, the quadrupolar hyperfine structures at 300 K (Fig. 4) are rather similar and the lack of resolution does not allow for an estimation of systematic differences in the proportions of each component (Table S5).

Mössbauer spectrometry was performed on $(\text{Zn}_{0.94}^{2+}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ at 11 K without and under a 8 T magnetic field applied parallelly to the γ -beam (Fig. 6). Both spectra can be well described with two magnetic components only. The values of the hyperfine fields refined from the zero-field spectrum are 46.7(5) T and 42.6(5) T. The in-field spectrum allows to estimate the effective fields B_{eff} and the θ angles for both sites; B_{eff} corresponds to the vectorial sum of the hyperfine field B_{hf} and the applied field B_{app} and θ is the angle defined by the directions of the effective field and the γ -beam direction. The large intensities of intermediate lines (2, 5) of the in-field spectrum clearly suggest that the Fe^{3+} magnetic moments are almost perpendicular to the external field ($\theta = 75^\circ$). This feature indicates that $(\text{Zn}_{0.94}^{2+}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ behaves as an antiferromagnet, but a small canting of the spins cannot be *a priori* excluded. In addition, it is important to emphasize that (i) both 11 K spectra confirm the proportions of the Fe species previously estimated at 300 K and 77 K and (ii) that the values of hyperfine fields, 46.4(5) T and 42.6(5) T, established from the in-field spectrum are also in perfect agreement with that obtained from the zero-field spectrum. Further in-field Mössbauer experiments at low temperature on all other iron phases were also performed. The results will be reported in a forthcoming publication,³⁵ devoted to the influence of magnetic cation anisotropy.

Fig. 6 Zero-field and in-field ^{57}Fe Mössbauer spectra of $(\text{Zn}_{0.94}^{2+}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ at 11 K and their decomposition into main and minor Fe^{3+} components, represented as red and blue curves, respectively.

Magnetisation measurements

Temperature (T) or field (H) dependent magnetisation (M) data were collected for several $(M_x^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ phases with different magnetic dimensionality: 0D $Co^{2+}Ga^{3+}$, 1D $Zn_{0.94}^{2+}Fe_{1.06}^{3+}$ and 3D $Fe_{0.99}^{2+}Fe_{0.40}^{3+}Ga_{0.61}^{3+}$, $Mn_{0.94}^{2+}Fe_{1.06}^{3+}$, $Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$, $Co_{0.93}^{2+}Fe_{1.07}^{3+}$, $Co^{2+}V^{3+}$. The temperature dependences of zero field cooled (ZFC) and field cooled (FC) susceptibilities, $\chi(T)$, inverse susceptibilities, $1/\chi(T)$, deduced from magnetisation measurements, along with isothermal magnetisation curves, $M(H)$, are presented in Fig. 7-12.

0D magnetic phase $Co^{2+}Ga^{3+}F_5(Htaz)$

The molar Curie constant, obtained from the linear part of the inverse susceptibility curve above 100 K (Fig. 7 upper inset), is $C_M = 3.51 \text{ emu.K.mol}^{-1}$. The resulting value of the effective magnetic moment of Co^{2+} , $\mu \approx 5.3 \mu_B$, is consistent with high-spin $S = 3/2$ $Co(II)$ ions in an octahedral ligand field having a formal $^4T_{1g}$ ground term.³⁶ Because the local ground state is orbitally degenerate, it is not possible to interpret the negative Weiss temperature, $\theta_p = -29 \text{ K}$, in terms of antiferromagnetic interactions. No magnetic order occurs down to approximately 10 K but there is a sharp susceptibility maximum at $\sim 5 \text{ K}$ which could signal the onset of magnetic order.

Fig. 7 ZFC and FC susceptibilities of $Co^{2+}Ga^{3+}F_5(Htaz)$ at 0.1 T. The upper inset shows the inverse susceptibility ($\text{emu}^{-1}.\text{mol.Oe}$) and the lower inset a low temperature enlargement of the $\chi(T)$ curve below 20 K.

1D magnetic phase: $(Zn_{0.94}^{2+}Fe_{0.06}^{3+})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$

As can be seen in Fig. 8a, the susceptibility curve shows a very broad maximum centered at $\sim 80 \text{ K}$. This feature is expected for a non-frustrated 1D antiferromagnetic compound; for this system, the broad susceptibility maximum is due to short-ranged 1D antiferromagnetic correlations. Because the temperature at which the susceptibility maximum occurs is quite high, $T(\chi_{\max}) \approx 80 \text{ K}$, the value of the mean antiferromagnetic interaction should also be high. As a consequence, our data did not allow us to reach the Curie-Weiss regime which should be observed for temperatures higher than 300 K. Thus we could not determine the Curie constant and the Weiss temperature. Below $T_N = 27 \text{ K}$, the ZFC and FC curves separate and this onset of a 3D magnetic order is associated with a parasitic ferrimagnetic component. This component

corresponds to a remnant magnetisation of $\sim 0.015 \mu_B.\text{mol}^{-1}$ at 2 K (Fig. 8b).

Fig. 8 (a) ZFC and FC susceptibilities of $(Zn_{0.94}^{2+}Fe_{0.06}^{3+})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$ at 0.1 T. The upper inset shows the inverse susceptibility ($\text{emu}^{-1}.\text{mol.Oe}$) and the lower inset a low temperature enlargement. (b) Magnetisation vs field loop at 2 K and enlargement at low field in inset.

3D magnetic phases with Mn^{2+} , Fe^{2+} or Co^{2+} and V^{3+} or Fe^{3+}

In comparison to $Co^{2+}Ga^{3+}F_5(Htaz)$, $Fe^{2+}Ga^{3+}F_5(Htaz)$ could also be viewed as a 0D magnetic phase. However, our Mössbauer results indicate a chemical composition, $(Fe_{0.99}^{2+}Fe_{0.01}^{3+})(Fe_{0.39}^{3+}Ga_{0.61}^{3+})F_5(Htaz)_{0.99}(taz)_{0.01}$, for which both Fe^{3+} and Ga^{3+} cations occupy the M^{3+} sites; Therefore, this compound can be considered as a 3D magnetic phase. The inverse susceptibilities, $1/\chi(T)$, of $Fe_{0.99}^{2+}Fe_{0.40}^{3+}Ga_{0.61}^{3+}$, $Mn_{0.94}^{2+}Fe_{1.06}^{3+}$, $Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$, $Co_{0.93}^{2+}Fe_{1.07}^{3+}$ and $Co^{2+}V^{3+}$ samples obey Curie-Weiss laws above 170 K, 250 K, 225 K, 150 K and 50 K, respectively. The values of molar Curie constants, C_M , and the Weiss temperatures, θ_p , are listed in Table 1. For $(Mn_{0.94}^{2+}Fe_{0.06}^{3+})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$, the presence of the impurity of MnF_2 , antiferromagnetic below $T_N = 67 \text{ K}$ ³⁷ was taken into account; its susceptibility was subtracted from the sample susceptibility for the calculations of C_M in the paramagnetic temperature range 250 K – 300 K. The resulting $8 \times C_M$ values compare well with the sums of

$\mu_{\text{eff}}^2(\text{Fe}^{3+}) = \mu_{\text{eff}}^2(\text{Mn}^{2+}) = 35 \mu_B^2$, $\mu_{\text{eff}}^2(\text{Fe}^{2+}) = 30 \mu_B^2$, $\mu_{\text{eff}}^2(\text{Co}^{2+}) = 28 \mu_B^2$, $\mu_{\text{eff}}^2(\text{V}^{3+}) = 8 \mu_B^2$. Orbital contributions are introduced for high-spin Fe^{2+} and Co^{2+} because these ions have orbitally degenerate ground states in six-fold coordination. The calculated values of $\sum(\mu_i)_{\text{eff}}^2$ are listed in Table 1 and take into account the final compositions of each phase. The negative values of θ_p signify dominant antiferromagnetic interactions in all compounds. All ZFC curves separate from FC curves at low temperature for low magnetic field and small ferrimagnetic components appear, as confirmed by the low temperature magnetisation cycles. The estimated Néel temperatures (Table 1) lie between $T_N \approx 18$ K for $\text{Co}^{2+}\text{V}^{3+}$ and $T_N \approx 102$ K for $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$. In $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$, the Fe^{3+} - Ga^{3+} substitution does not markedly decrease the magnetic ordering temperature but the Weiss temperature is strongly affected. For instance, $T_N \approx 81$ K and $\theta_p = -85$ K for $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$ but $T_N \approx 93$ K and $\theta_p = -375$ K for $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$. It must be noted that the presence of a small amount of $\text{M}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$ impurities is undetectable for iron phases. $\text{MnFeF}_5(\text{H}_2\text{O})_2$, $\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$ and $\text{CoFeF}_5(\text{H}_2\text{O})_2$ are ferrimagnetic with $T_N = 39$ K, $T_N = 48$ K and $T_N = 27$ K, respectively (Table S6).^{32,38}

Fig. 9 (a) ZFC and FC susceptibilities of $(\text{Fe}_{0.99}^{2+}\text{Fe}_{0.01}^{3+})(\text{Fe}_{0.39}^{3+}\text{Ga}_{0.61}^{3+})\text{F}_5(\text{Htaz})_{0.99}(\text{taz})_{0.01}$ at 0.1 T. The inset shows the inverse susceptibility ($\text{emu}^{-1}\text{mol.Oe}$). (b) Magnetisation vs field loops at 5 K and enlargement at low field in inset.

After zero-field cooling down to 2 K, the samples exhibit very different values of the low-temperature magnetisation measured in a 0.1 T field. It is small for $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$ (Fig. 9a). It is also small for $(\text{Mn}_{0.94}^{2+}\text{Fe}_{0.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ which contains isotropic Mn^{2+} and Fe^{3+} cations (Fig. 10a) and both ZFC and FC curves superimpose when measured in a 1 T field (Fig. 10a). It is either positive or negative for $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$ (Fig. 10b) and $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ (Fig. 11a) samples; it can be assumed that this effect depends on the orientation, positive or negative, of the small remnant field of the superconducting magnet. When negative at 2 K, the sample magnetisation returns to positive values above $T^* = 64$ K for $(\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.95}(\text{taz})_{0.05}$ and $T^* = 57$ K for $(\text{Co}_{0.93}^{2+}\text{Fe}_{0.07}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$. After field-cooling in 0.1 T field down to 2 K, the sample ZFC magnetisation of $(\text{Co}_{0.93}^{2+}\text{Fe}_{0.07}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$ is negative at 2 K but returns to positive values above $T^* = 57$ K (Fig. 11a). When the applied field is increased to 1 T and 5 T, the differences between the ZFC and FC magnetisation values are less and less pronounced and the magnetisation at low temperature is no longer negative. A similar effect is found for $(\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.95}(\text{taz})_{0.05}$ (Fig. 10b) under a 1 T magnetic field.

The magnetisation versus field loops of the $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$ (Fig. 10c), $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ (Fig. 11c) and $\text{Co}^{2+}\text{V}^{3+}$ (Fig. 12b) samples exhibit a S shape. The values of remnant magnetisations, σ_r , at zero field, deduced from the magnetisation cycles are given in Table 2 together with those of the coercive fields, H_c . Remnant magnetisations vary between $0.522 \mu_B\text{mol}^{-1}$ at 2 K and $0.402 \mu_B\text{mol}^{-1}$ at 10 K for $\text{Co}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$, $0.152 \mu_B\text{mol}^{-1}$ at 5 K and $0.037 \mu_B\text{mol}^{-1}$ at 70 K for $(\text{Co}_{0.93}^{2+}\text{Fe}_{0.07}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$. When the applied field decreases from high fields to $H = 0$ T, the variation of the magnetisation is smooth (almost linear) for $(\text{Co}_{0.93}^{2+}\text{Fe}_{0.07}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$ and $\text{Co}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$, while the variation is sharp when the field direction changes. The reversion of the magnetic domains is not progressively achieved for $\text{Co}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$ and occurs in steps (Fig. 12b lower inset). It must be noted that the cycle of $(\text{Co}_{0.93}^{2+}\text{Fe}_{0.07}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$ is not symmetrical and a shift of H_c occurs for decreasing or increasing fields, -0.277 T and $+0.180$ T, respectively (Fig. 11c lower inset).

Fig. 10 ZFC and FC susceptibilities at 0.1 or 1 T of (a) $(\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.94}(\text{taz})_{0.06}$ and (b) $(\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+})\text{Fe}^{3+}\text{F}_5(\text{Htaz})_{0.95}(\text{taz})_{0.05}$ for various magnetic histories. The upper insets show the inverse susceptibility. Magnetisation vs field loops at 5 K of (c) $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$ and (d) $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$ (enlargements at low field in insets).

Fig. 11 ZFC and FC susceptibilities of $(\text{Co}_{0.93}\text{Fe}_{0.07})\text{FeF}_5(\text{Htaz})_{0.93}(\text{taz})_{0.07}$ measured in (a) 0.1 T. The upper inset shows the inverse susceptibility and the lower inset a low temperature enlargement. (b) 1 T and 5 T (inset) fields. (c) Magnetisation vs field loops at 5 K and 70 K (enlargements at low field in insets).

Fig. 12 (a) ZFC and FC susceptibilities of $\text{Co}^{2+}\text{V}^{3+}\text{F}_5(\text{Htaz})$ measured in 0.1 T field. The upper inset shows the inverse susceptibility and the lower inset a low temperature enlargement. (b) Magnetisation vs field loops at 2 K and 10 K (enlargements at low field in insets).

Table 1 Magnetic parameters extracted from the temperature dependence of magnetisation at 0.1 T or 1 T for the $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ magnetic phases. For the 1D $Zn_{0.94}^{2+}Fe_{1.06}^{3+}$ phase, Curie-Weiss parameters could not be determined from our data. * μ_{eff}^2 is calculated from $4S(S+1)+L(L+1)$.

	Magnetic connectivity	T_N (K)	T^* (K)	θ_P (K)	$ \theta_P /T_N$	C_M (emu.K.mol ⁻¹)	μ_{eff}^2 / μ_B^2		
							observed	calculated spin only	calculated* spin + Orbital
$Co^{2+}Ga^{3+}$	0D			−29(2)		3.51(4)	28.1(3)	15.0	28.1
$Zn_{0.94}^{2+}Fe_{1.06}^{3+}$	1D	27							
$Fe_{0.99}^{2+}Fe_{0.40}^{3+}Ga_{0.61}^{3+}$	3D	81		−95(5)	1.2	4.75(2)	38.0(2)	37.8	43.7
$Mn_{0.94}^{2+}Fe_{1.06}^{3+}$	3D	100		−335(5)	3.4	8.47(1)	67.8(1)	70.0	
$Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$	3D	102	64	−265(5)	2.6	8.90(1)	71.2(1)	68.7	69.4
$Co_{0.93}^{2+}Fe_{1.07}^{3+}$	3D	82	57	−440(5)	5.4	10.8(2)	86.1(2)	51.4	63.6
$Co^{2+}V^{3+}$	3D	18		−54(3)	3.0	4.33(5)	34.7(4)	23.0	36.1

Table 2 Extrapolated remnant magnetisation, σ_r , and coercive field, H_c , for the $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ magnetic phases.

	T (K)	σ_r (H=0) (μ_B .mol ⁻¹)	H_c (T)
$Zn_{0.94}^{2+}Fe_{1.06}^{3+}$	2	0.006	0.430
$Fe_{0.99}^{2+}Fe_{0.40}^{3+}Ga_{0.61}^{3+}$	5	0.359	0.350
$Mn_{0.94}^{2+}Fe_{1.06}^{3+}$	5	0.105	0.200
$Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$	5	0.285	0.600
$Co_{0.93}^{2+}Fe_{1.07}^{3+}$	5	0.152	−0.277 and 0.180
	70	0.037	0.182
$Co^{2+}V^{3+}$	2	0.522	0.275
	10	0.402	0.35

Discussion

All $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ phases obtained by solvothermal synthesis, are isostructural to $(Fe_{0.96}^{2+}Fe_{0.04}^{3+})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$ and their crystal structures are confirmed from X-ray powder diffraction data. The evidence for cation substitutions in the iron-containing phases is assessed by Mössbauer spectrometry and the results are consistent with the evolution of the unit cell volumes due to the variation of cation radii. This consistency is particularly well illustrated for the series of $Mn_{0.94}^{2+}Fe_{1.06}^{3+}$, $Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$ and $Fe_{0.96}^{2+}Fe_{1.04}^{3+}$ phases.

Indeed, room temperature Mössbauer spectra show that the Fe^{3+} component is not unique but must be fitted with an

additional minor Fe^{3+} component. We assume that the substitution on one M^{2+} site implies the perturbation of four Fe^{3+} sites (Fig. 1 top right). The substitution of M^{2+} by M^{3+} implies that the amine is not necessarily neutral and thus, we propose a formulation that takes the deprotonated state of the amine into account and the correlated substitution of M^{2+} cations by Fe^{3+} cations. The corresponding formulations $(M_{1-x}^{2+}M_x^{3+})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ are listed in Table 3. M^{2+} and M^{3+} sub-lattice magnetisations differ for $Mn_{0.83}^{2+}Fe_{0.12}^{2+}Fe_{1.05}^{3+}$ and $Co_{0.93}^{2+}Fe_{1.07}^{3+}$ samples and the compensation temperatures are found at $T^* = 64$ K and $T^* = 57$ K, respectively (Table 1). Similar behaviour is observed for $(Fe_{0.96}^{2+}Fe_{0.04}^{3+})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$ at $T^* = 35$ K, and discussed in a follow-up publication.³⁵ These features imply that the anisotropy fields of Fe^{2+} and Co^{2+} are large and govern the magnetisation. This magnetisation depends strongly on the thermal history of the sample and on the magnetic field—that is applied below T_N . A discussion of the magnetic properties, including the evolution of the magnitude and orientation of the magnetic moments with the temperature, is scheduled in the previously-mentioned follow-up publication.³⁵ It will be based on the results of low temperature Mössbauer experiments on all iron containing phases and a neutron diffraction study of $(Fe_{0.96}^{2+}Fe_{0.04}^{3+})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$.

Table 3 Phase compositions deduced from the contents of Fe²⁺ and minor or main Fe³⁺ components estimated from room temperature Mössbauer spectrometry results (issued from reference 21 for Fe_{0.96}²⁺Fe_{1.04}³⁺).

	Composition	Fe ²⁺	Minor / Main Fe ³⁺ component
Zn _{0.94} ²⁺ Fe _{1.06} ³⁺	(Zn _{0.94} ²⁺ Fe _{0.06} ³⁺)Fe ³⁺ F ₅ (Htaz) _{0.94} (taz) _{0.06}	—	0.20/0.80
Fe _{0.99} ²⁺ Fe _{0.40} ³⁺ Ga _{0.61} ³⁺	(Fe _{0.99} ²⁺ Fe _{0.01} ³⁺)(Fe _{0.39} ³⁺ Ga _{0.61} ³⁺)F ₅ (Htaz) _{0.99} (taz) _{0.01}	0.72	0.02/0.26
Mn _{0.94} ²⁺ Fe _{1.06} ³⁺	(Mn _{0.94} ²⁺ Fe _{0.06} ³⁺)Fe ³⁺ F ₅ (Htaz) _{0.94} (taz) _{0.06}	—	0.20/0.80
Mn _{0.83} ²⁺ Fe _{0.12} ²⁺ Fe _{1.05} ³⁺	(Mn _{0.83} ²⁺ Fe _{0.12} ²⁺ Fe _{0.05} ³⁺)Fe ³⁺ F ₅ (Htaz) _{0.95} (taz) _{0.05}	0.11	0.14/0.75
Fe _{0.96} ²⁺ Fe _{1.04} ³⁺	(Fe _{0.96} ²⁺ Fe _{0.04} ³⁺)Fe ³⁺ F ₅ (Htaz) _{0.96} (taz) _{0.04}	0.47	0.07/0.46
Co _{0.93} ²⁺ Fe _{1.07} ³⁺	(Co _{0.93} ²⁺ Fe _{0.07} ³⁺)Fe ³⁺ F ₅ (Htaz) _{0.93} (taz) _{0.07}	—	0.22/0.78

In addition to the complexity of the sample compositions, a surprising effect evidenced by Mössbauer spectrometry is that the sample environment (He and ambient atmospheres - vacuum) significantly affects the ensuing magnetic behaviour (Fig. 5). A sizeable decrease of the magnetic ordering temperatures when the samples are left under vacuum occurs and it is reversible when ambient atmosphere is further introduced at room temperature. At 77 K, the isomer shift and quadrupole splitting values of Fe²⁺ and of the main and minor Fe³⁺ components remain almost identical for the vacuum treated and non-treated samples; then, all three octahedral cation environments are not strongly modified. Mössbauer experiments have repeatedly revealed this interesting unexpected result, which to the best of our knowledge, has not previously been observed.

Variations of the magnetic properties were already encountered for slightly different sample compositions of mixed valence iron oxalates with negative magnetisation.³⁹ They were explained by the existence of structural disorder (stacking faults in N(*n*-C₃H₇)₄[Fe²⁺Fe³⁺(C₂O₄)₃]) and non-stoichiometry, which are influenced by the preparation method.⁴⁰ In the case of (M_{1-x}²⁺M_x³⁺)M³⁺F₅(Htaz)_{1-x}(taz)_x phases, stacking faults were not evidenced and it is clear that cation substitution plays the key role in determining the overall magnetic response. In (Mn_{0.94}²⁺Fe_{0.06}³⁺)Fe³⁺F₅(Htaz)_{0.94}(taz)_{0.06}, the substitution of the isotropic Mn²⁺ cation by anisotropic Fe²⁺ or Co²⁺ cations leads to negative magnetisation in (Mn_{0.83}²⁺Fe_{0.12}²⁺Fe_{0.05}³⁺)Fe³⁺F₅(Htaz)_{0.95}(taz)_{0.05}, (Fe_{0.96}²⁺Fe_{0.04}³⁺)Fe³⁺F₅(Htaz)_{0.96}(taz)_{0.04}, and (Co_{0.93}²⁺Fe_{0.07}³⁺)Fe³⁺F₅(Htaz)_{0.93}(taz)_{0.07} in contrast to the substitution by isotropic Fe³⁺ in (Mn_{0.94}²⁺Fe_{0.06}³⁺)Fe³⁺F₅(Htaz)_{0.94}(taz)_{0.06}. The influence of the vacuum is not easily explained and the modification of the structure must be very subtle. It was noted that the presence of a very small amount of hydroxyl OH⁻ groups cannot be excluded. They could be responsible for a reversible local proton exchange with the amine N-H group according to the reaction OH⁻ + Htaz → H₂O + taz⁻, which may also be

influenced by pressure. As a consequence, the magnetic superexchange interactions M²⁺-OH-M³⁺ could locally transform to M²⁺-OH₂-M³⁺ and such a modification could induce the observed decrease in the magnetic transition temperatures. To clarify these assumptions, further Mössbauer experiments have to be performed on hydrated weberites using the same environmental conditions. High-pressure X-ray experiments could also provide relevant information on the evolution of superexchange pathways with the pressure.

Experimental

The starting chemicals were MnF₂, FeF₂ (prepared from a mixture of Fe + 2FeF₃ heated at 850°C during 3 h), CoF₂ (98%, Alfa Aesar), ZnF₂ (99%, Alfa Aesar), VF₃ (99%, Cerac), MnF₃ (99%, Alfa Aesar), FeF₃ (≥ 99.9%, Alfa Aesar), GaF₃, 4% hydrofluoric acid solution (prepared from 40% HF, Riedel De Haen), 1,2,4-triazole (Htaz) (99%, Alfa Aesar) and technical ethanol. MnF₂ were obtained by heating the corresponding chlorides under HF gas. GaF₃ was obtained by thermal decomposition of (NH₄)₃GaF₆.

The FeF₂-FeF₃-Htaz-HF_{aq}-ethanol system was previously investigated for a constant concentration [Fe²⁺]+[Fe³⁺] = 0.15 mol.L⁻¹ and a ratio [Fe²⁺]/[Fe³⁺] = 1 at 160°C during 1h by microwave heating (CEM Mars 5 oven). Similar solvothermal conditions were applied for the following couples: Co-Ga, Fe-Ga, Zn-V, Co-V, Zn-Fe, Co-Fe, Mn-Fe. (Mn_{0.83}²⁺Fe_{0.12}²⁺Fe_{0.05}³⁺)Fe³⁺F₅(Htaz)_{0.95}(taz)_{0.05} was obtained from a mixture of MnF₃ and FeF₂ (MnF₂ does not dissolve in the reacting mixture). All solid products were washed with ethanol and dried at room temperature.

X-ray diffraction patterns were collected on a Panalytical X'Pert Pro diffractometer with CuK_α radiation in the range 10° ≤ 2θ ≤ 100°.

Thermogravimetric experiments were performed with a SETARAM TGA 92 thermo analyzer under humid air atmosphere and a heating rate of 5°C.min⁻¹ from room temperature to 800°C.

Infrared spectra were collected on a FT-IR ALPHA Bruker Optik spectrometer (single reflection diamond) over the range 400–4000 cm^{-1} .

Mössbauer experiments were performed in transmission geometry with a 925 MBq γ -source of $^{57}\text{Co}/\text{Rh}$ mounted on a conventional constant acceleration drive. The spectra were recorded between 300 K and 77 K using both a bath cryostat and a homemade cryofurnace, in which the sample under helium atmosphere and secondary vacuum (10^{-6} Torr), respectively, can be well thermalised (indeed, the instrumental design of the cryofurnace prevents from temperature deviations of the sample)^{41–46}. In-field Mössbauer experiments were carried out using a cryomagnetic device where the applied field is oriented parallel to the γ -beam, the sample located in the main coil and the source in the compensated coil, preventing thus from polarization effects. The spectra were fitted using the MOSFIT program⁴⁷, involving quadrupolar and magnetic components with Lorentzian lines; the isomer shift values are referred to that of α -Fe at RT. The velocity of the source was calibrated using α -Fe as standard at RT.

Magnetisation measurements for $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$: $\text{Co}^{2+}\text{Ga}^{3+}$, $\text{Zn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$, $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$, $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$, $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$, $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ and $\text{Co}^{2+}\text{V}^{3+}$ were obtained using commercial SQUID magnetometers (Quantum Design, MPMS). Data were recorded during warming over the temperature range of 2–300 K after zero-field cooling (ZFC) or field cooling (FC) the sample down to 2 K. The molar diamagnetic contribution was corrected by using Pascal's constants and the contribution of the sample holder was taken into account.

Conclusions

A series of hybrid fluorides $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$, with a dense magnetic array is prepared by solvothermal synthesis. Rietveld refinements confirm that all compounds are isostructural with $\text{M}^{2+}\text{M}^{3+}\text{F}_5(\text{H}_2\text{O})_2$ weberite (*Imma*) but some specific local atomic structural disorder is evidenced from the complex Mössbauer hyperfine structure at ^{57}Fe . High magnetic ordering temperatures are observed and a negative magnetisation is found in three of the reported phases. This specific magnetic behaviour is dependent on:

- (i) the presence of anisotropic Fe^{2+} or Co^{2+} cations in M^{2+} sites, along with a total occupancy of M^{3+} sites by Fe^{3+} ;
- (ii) the magnetic history of the samples below T_N .

The magnetic behavior of $\text{Fe}_{0.99}^{2+}\text{Fe}_{0.40}^{3+}\text{Ga}_{0.61}^{3+}$, $\text{Mn}_{0.94}^{2+}\text{Fe}_{1.06}^{3+}$, $\text{Mn}_{0.83}^{2+}\text{Fe}_{0.12}^{2+}\text{Fe}_{1.05}^{3+}$, $\text{Co}_{0.93}^{2+}\text{Fe}_{1.07}^{3+}$ and $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ phases is now investigated by Mössbauer spectrometry under applied magnetic field at low temperature. The thermal evolution of the magnetic structure of the mixed valence iron phase $\text{Fe}_{0.96}^{2+}\text{Fe}_{1.04}^{3+}$ is also studied by neutron diffraction. All the results will be presented in a forthcoming publication.

Finally, the presented results illustrate the importance of geometrical frustration in the HTB layers of $(\text{M}_{1-x}^{2+}\text{M}_x^{3+})\text{M}^{3+}\text{F}_5(\text{Htaz})_{1-x}(\text{taz})_x$ weberites: the $|\theta_p|/T_N$ values are high when both M^{2+} and M^{3+} sites are fully occupied by paramagnetic cations (maximum frustration) but decrease strongly when these cations are substituted by diamagnetic cations.

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References

- G. Toulouse, *Comm. Phys.*, 1977, **2**, 115.
- G. Toulouse, in *Modern Trends in the Theory of Condensed Matter*, eds. A. Pekalski and J. Przystawa, Springer Berlin / Heidelberg, Lecture Notes in Physics 115, 1980, DOI: doi:10.1007/BFb0120136, pp. 195–203.
- G. Férey, M. Leblanc, R. De Pape and J. Pannetier, in *Inorganic Solid Fluorides*, ed. P. Hagenmuller, Academic Press, London, 1985, ch. 10, pp. 395–415.
- S. T. Bramwell and M. J. P. Gingras, *Science*, 2001, **294**, 1495–1501.
- G. Férey, R. De Pape, M. Leblanc and J. Pannetier, *Rev. Chimie Miner.*, 1986, **23**, 474–484.
- M. Leblanc, R. De Pape, G. Férey and J. Pannetier, *Solid State Commun.*, 1986, **58**, 171–176.
- M. Leblanc, G. Férey, Y. Calage and R. De Pape, *J. Solid State Chem.*, 1984, **53**, 360–368.
- M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353–1379.
- G. Tang, Y. He, F. Liang, S. Li and Y. Huang, *Physica B.*, 2007, **392**, 337–340.
- R. S. Fishman and F. A. Reboredo, *Phys. Rev. Lett.*, 2007, **99**, 217203 1–4.
- F. H. Aidoudi, D. W. Aldous, R. J. Goff, A. M. Z. Slawin, J. P. Attfield, R. E. Morris and P. Lightfoot, *Nature Chemistry*, 2011, **3**, 801–806.
- L. Clark, F. H. Aidoudi, C. Black, K. S. A. Arachchige, A. M. Z. Slawin, R. E. Morris and P. Lightfoot, *Angew. Chemie Int. Edit.*, 2015, **54**, 1–6.
- W.-T. Liu, J.-Y. Li, Z.-P. Ni, X. Bao, Y.-C. Ou, J.-D. Leng, J.-L. Liu and M.-L. Tong, *Crystal Growth Des.*, 2012, **12**, 1482–1488.
- R. Kuhlman, G. L. Schimek and J. W. Kolis, *Inorg. Chem.*, 1999, **38**, 194–196.
- Z. M. Wang, Y. J. Zhang, T. Liu, M. Kurmoo and S. Gao, *Adv. Funct. Mater.*, 2007, **17**, 1523–1536.
- Z. Wang, B. Zhang, H. Fujiwara, H. Kobayashi and M. Kurmoo, *Chem. Commun.*, 2004, 416–417.
- Z. Wang, B. Zhang, M. Kurmoo, M. A. Green, H. Fujiwara, T. Otsuka and H. Kobayashi, *Inorg. Chem.*, 2005, **44**, 1230–1237.
- Z. Wang, B. Zhang, Y. Zhang, M. Kurmoo, T. Liu, S. Gao and H. Kobayashi, *Polyhedron*, 2007, **26**, 2207–2215.
- M. Viertelhaus, P. Adler, R. Clérac, C. E. Anson and A. K. Powell, *Eur. J. Inorg. Chem.*, 2005, **2005**, 692–703.
- Y.-L. Fu, J.-L. Ren, Z.-W. Xu and S. W. Ng, *Acta Crystallogr., Sect. E*, 2005, **61**, m2395–m2396.

- 21 M. Smida, J. Lhoste, V. Pimenta, A. Hémon-Ribaud, L. Jouffret, M. Leblanc, M. Dammak, J.-M. Grenèche and V. Maisonneuve, *Dalton Trans.*, 2013, **42**, 15748–15755.
- 22 A. Cadiau, C. Martineau, M. Leblanc, V. Maisonneuve, A. Hémon-Ribaud, F. Taulelle and K. Adil, *J. Mater. Chem.*, 2011, **21**, 3949–3951.
- 23 R. Haegele, W. Verscharen, D. Babel, J. M. Dance and A. Tressaud, *J. Solid State Chem.*, 1978, **24**, 77–84.
- 24 Y. Lalignant, J. Pannetier, P. Labbe and G. Férey, *J. Solid State Chem.*, 1986, **62**, 274–277.
- 25 L. Néel, *Ann. de Phys.*, 1948, **3**, 137–198.
- 26 V. Ya. Grinshtein, A. A. Strazdin and A. K. Grinvalde, *Khim. Geterotsikl.*, 1970, **6**, 248–258.
- 27 G. Corbel, E. Suard, J. Emery and M. Leblanc, *J. Alloys Comp.*, 2001, **315**, 287–295.
- 28 A. Demourgues, L. Francke, E. Durand and A. Tressaud, *J. Fluorine Chem.*, 2002, **114**, 229–236.
- 29 U. Bentrup, *Thermochim. Acta*, 1996, **284**, 397–406.
- 30 D. Dambournet, A. Demourgues, C. Martineau, E. Durand, J. Majimel, C. Legein, J.-Y. Buzaré, F. Fayon, A. Vimont, H. Leclerc and A. Tressaud, *Chem. Mater.*, 2008, **20**, 7095–7106.
- 31 P. Imbert, G. Jehanno, Y. Macheteau and F. Varret, *J. de Phys.*, 1976, **37**, 969–972.
- 32 Y. Lalignant, Y. Calage, E. Torres Tapia, J.-M. Grenèche, F. Varret and G. Férey, *J. Magn. Magn. Mater.*, 1986, **61**, 283–290.
- 33 J.-M. Grenèche, J. Linares, F. Varret, Y. Lalignant and G. Férey, *J. Magn. Magn. Mater.*, 1988, **73**, 115–122.
- 34 I. Abdi, J. Lhoste, M. Leblanc, V. Maisonneuve, J.-M. Grenèche, G. Viau and A. Ben Ali, *J. Fluorine Chem.*, 2015, **173**, 23–28.
- 35 L. Clark, M. Albino, J. Lhoste, I. Da Silva, M. Leblanc, C. Payen, J.-M. Grenèche, V. Maisonneuve and P. Lightfoot, in preparation.
- 36 F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973.
- 37 W. J. Dehaas, B. H. Schultz, and J. Koolhaas, *Physica*, 1940, **7**, 57–69.
- 38 E. R. Jones Jr. and R. Dawson, *J. Chem. Phys.*, 1979, **71**, 202–205.
- 39 C. J. Nuttall and P. Day, *Chem. Mater.*, 1998, **10**, 3050.
- 40 P. Day, *Chem. Mater.*, 2003, **15**, 2288.
- 41 M. E. Lopez-Herrera, F. Varret, Y. Calage and G. Férey, *J. Magn. Magn. Mater.*, 1984, **44**, 304–312.
- 42 M. Miglierini and J.M. Grenèche, *J. Phys.: Condens. Matter*, 1997, **9**, 2321–2347.
- 43 J. P. Attfield, A. M. T. Bell, L. M. Rodriguez-Martinez, J. M. Grenèche, R. J. Cernik, J. F. Clarke and D. A Perkins, *Nature*, 1998, **396**, 655–658.
- 44 L. K. Varga, F. Mazaleyrat, J. Kovac and J. M. Grenèche, *J. Phys.: Condens. Matter*, 2002, **14**, 1985–2000.
- 45 I. Škorvánek, P. Švec, J. M. Grenèche, J. Kováč, J. Marcin and R. Gerling, *J. Phys.: Condens. Matter*, 2002, **14**, 4717–4736.
- 46 R. Canioni, C. Roch-Marchal, F. Sécheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Férey, J. M. Grenèche, F. Lefebvre, J. S. Chang, Y. K. Hwang, O. Lebedev, S. Turner and G. Van Tendeloo, *J. Mater. Chem.*, 2011, **21**, 1226–1233.
- 47 J. Teillet and F. Varret, unpublished Mosfit program, University du Maine (France).