Cation Distributions and Magnetic Properties of Ferrispinel MgFeMnO$_4$

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Abstract

The crystal structure and magnetic properties of the cubic spinel MgFeMnO$_4$ were
studied using magnetometers, Mössbauer spectroscopy, x-ray/neutron/electron diffraction techniques, and muon spin rotation spectroscopy in the temperature range between 1.5 and 500 K. The crystal structure is successfully refined using a typical cubic spinel structure described by the space group $Fd\bar{3}m$. Cations within tetrahedral $A$ and octahedral $B$ sites of the spinel were found to be in a disordered state. Finally, ferrimagnetic ordering is observed below $T_C = 394.2$ K with a collinear spin arrangement, i.e. spins at the $A$ sites and the $B$ sites are anti-parallel.

Introduction

The long-established spinel magnesium oxide family ($\text{MgM}_2\text{O}_4$ where $M$ is a transition metal atom) has been the subject of interest in diverse research fields, e.g., catalyst, humidity sensor or microwave devices.$^{1-4}$ Recently, much attention has been drawn to series of Mg materials, following the development of high-energy-density rechargeable magnesium batteries.$^{5-7}$ The main fundamental interest of studying the spinel magnesium oxide is that various magnetic properties like paramagnetism, ferrimagnetism, superparamagnetism and spin glass behaviour have been reported for these classes of materials. These magnetic properties play an essential role in the application of magnetic resonance imaging, data storage and drugs delivery.$^{4,8}$

Spinels have the general formula $AB_2O_4$, and most of them are reported to have a cubic structure with space group $Fd\bar{3}m$. The structure consists of tetrahedrally coordinated $A$ site cations at $8a$ (1/8, 1/8, 1/8), octahedrally coordinated $B$ sites cations at $16d$ (1/2, 1/2, 1/2), and O atoms on the body diagonals of a cube at $32e$ ($u, u, u$), where $u$ is approximately 1/4. In the case of magnesium oxides, divalent magnesium and trivalent transition metal atoms tend to occupy $A$ and $B$ sites, respectively. However, the cation distribution between the $A$ and $B$ sites, which is known to influence the physical properties of these materials,$^{9,10}$ is a controversial issue.

Recently, $\text{Mg(Mn}_{1-x}\text{Fe}_x\text{)}_2\text{O}_4$ has been synthesized and characterized by electrochemical
measurements. The parent compounds, MgMn$_2$O$_4$ and MgFe$_2$O$_4$, crystallize in different space groups and display very different magnetic properties. This was the main motivation for studying the solid solution of these two compounds. MgFe$_2$O$_4$ crystallizes in the typical cubic spinel structure, with a slight Mg/Fe disorder between the A and B sites. The magnetic ground state of MgFe$_2$O$_4$ has been reported to be a ferrimagnet below $T_C = 363 \sim 493$ K (here $T_C$ is strongly dependent on the cation distribution.). On the other hand, MgMn$_2$O$_4$ is known to form a distorted tetragonal phase (SG: $I4_1/amd$), due to the Jahn-Teller effect. Typically this compound shows a perfect cation ordering with the lattice sites being occupied as $A = \text{Mg}^{2+}$ and $B = \text{Mn}^{3+}$. Further, an antiferromagnetic spin order occurs below $T_N = 50$ K. Hans et al. reported in Ref. that more than 20 % of Fe substitution could stabilize the cubic spinel structure of Mg(Mn$_{1-x}$Fe$_x$)$_2$O$_4$. However, no detailed crystal structure and magnetic characterization have been reported so far.

In this article, we show the detailed crystal and magnetic properties of the cubic spinel MgFeMnO$_4$ (i.e. $x = 0.5$). The cationic arrangement of the compound was studied by the combination of x-rays and neutron diffraction methods. In contrast to the x-ray method, the differences in the neutron scattering amplitudes of the constituent atoms have allowed an accurate determination of the cation distribution in MgFeMnO$_4$. These crystallographic studies unveiled that MgFeMnO$_4$ indeed forms a cubic spinel structure with Mg/Fe/Mn disorder. Macroscopic magnetization measurement and Mössbauer spectroscopy show that the magnetic transition temperature is above room temperature (RT). A ferrimagnetic spin ordering is revealed below $T_C = 392$ K by the combination of neutron diffraction and $\mu^+\text{SR}$.

**Experimental methods**

**Materials synthesis**

Stoichiometric amounts of Mn$_2$O$_3$ (Kishida Chemicals, 99% purity), Fe$_2$O$_3$ (Kishida Chemicals, 98% purity) and MgO (99.9%, Wako pure chemical) powders were weighed in a molar
ratio of 1:1:1. The powders were mixed using a planetary ball mill to attain a homogeneous mixture. The powder was pelletized and calcined at 800 °C for 5 h in air.

Quantification of the chemical composition of the as-prepared MgFeMnO$_4$ was assessed using inductively coupled plasma absorption electron spectroscopy (ICP-AES) on a Shimadzu ICPS-8100 instrument.

**X-ray and neutron powder diffraction**

XRD measurements of the as-synthesised powders were performed in Bragg-Brentano mode using a diffractometer (Bruker D2 ADVANCE) at a $2\theta$ range of 5 to 90° (with a step size of 0.01°). The wavelength was set at Cu-K$\alpha$ and measurements were performed at room temperature. Neutron powder diffraction (NPD) was performed on the D2B instrument (ILL, Grenoble) using the selected neutron wavelength $\lambda = 1.595$ Å. Data was collected at two temperatures $T = 300$ and 500 K. The measurement at 500 K was carried out using a dedicated furnace. Symmetry analysis and Rietveld refinements for both x-ray and neutron diffraction patterns were performed with tools from the FULLPROF suite$^{18}$ and the Bilbao Crystallographic Server.$^{19}$

**Electron Microscopy**

The morphologies of the materials were analysed by a field-emission scanning electron microscope (JSM-6510LA). High-resolution transmission electron microscopy (HRTEM) images of pristine MgFeMnO$_4$ were obtained on a TITAN80-300F at an accelerated voltage of 200 kV. Simulations of the HRTEM images were performed with the JEMS 31(PECD) software.

**Magnetization measurements**

Bulk magnetic (DC) susceptibility measurements as a function of temperature were performed with a Quantum Design superconducting quantum interference device magnetometer
upon warming in a temperature range from 5 to 400 K. Data were collected in both zero-field-cooled (ZFC) and field-cooled (FC) protocols using an external magnetic field $H = 100$ Oe. Magnetisation data as a function of field were collected up to ± 10.0 kOe after zero field cooling.

**Mössbauer spectroscopy**

$^{57}$Fe Mössbauer experiments were performed at 298 K using a conventional Mössbauer spectrometer. The cryostat was equipped with a helium refrigerator. About 100 mg of sample was mixed with boron nitride and pressed into pellets (having a diameter of 10 mm) for Mössbauer transmission experiments. α-Fe was used for velocity calibration. The Mössbauer spectra were fitted with the MossWinn program.$^{20,21}$

**Muon spin rotation and relaxation ($\mu^+\text{SR}$) measurements**

$\mu^+\text{SR}$ experiments were performed at a muon beam line using the surface muon spectrometer GPS at the Swiss Muon Source ($\text{S}\mu\text{S}$) of PSI in Switzerland. The temperature scan measurements between $T = 2 – 300$ K are performed using a liquid-He flow-type cryostat. The powder sample ($m \approx 0.5$ g) was placed in an envelope made of very thin Al-coated Mylar tape covering a surface area of $1 \times 1$ cm$^2$. In order to minimise the background signal, the envelope was attached to a fork-type Cu-sample holder using a single layer of the Mylar tape. The sample holder was attached to a stick and inserted into the cryostat. The measurements above room temperature (RT) were carried out using a closed-cycle refrigerator (CCR) cryostat. For such measurement the powder sample was pressed into a pellet that was attached onto a Cu-plate sample holder by Al-coated Mylar tape and secured by a thin Cu-wire.

$\mu^+\text{SR}$ time spectra were subsequently collected using the zero-field (ZF) and weak transverse-field ($\text{wTF} = 50$ Oe) protocols. Here, one of the powers of the $\mu^+\text{SR}$ technique is that magnetic spin order can be studied in true ZF environment. Further details regarding the
experimental techniques and set-ups are provided in Ref.\textsuperscript{22} The musrfit\textsuperscript{23} software package was used to analyse the $\mu^+\text{SR}$ data.

**Results**

**Fundamental Characterization**

Laboratory XRPD was first performed to check the quality of the sample at room temperature. It is known that the stoichiometry of magnesium spinel oxides is sensitive to heat treatments during the synthesis process.\textsuperscript{24} Thus the composition ratio of MgFeMnO$_4$ was carefully examined by using ICP-AES (Supplemental Material Table. S1). The synthesized MgFeMnO$_4$ was confirmed to have the stoichiometric composition within the experimental accuracy. The concentration of Mg was found to be only slightly lower than that of Fe and Mn, probably related to the evaporation of Mg during the heat treatment process. The detailed analysis of laboratory XRPD data will be brought in the next section, together with neutron diffraction results.

The temperature dependence of the DC magnetic susceptibility, $\chi(T)$, for MgFeMnO$_4$ using both ZFC and FC protocols are shown in Figure 1(a). As seen, the ZFC and FC magnetizations bifurcate at $T \approx 370$ K and show a broad peak in the ZFC curve with a maximum at $T_{\text{max}} \approx 330$ K. Such behaviour supports the existence of antiferromagnetic and/or ferrimagnetic spin clusters. When the sample is measured during the FC process, more ferro or ferrimagnetic clusters are aligned along the field direction, which causes a large separation between FC and ZFC.\textsuperscript{25} FC susceptibility reaches its maximum around $T \approx 20$ K and then saturates, which indicates the ferromagnetic behaviour.

The correlations between magnetization and the magnetic field strength ($M$ vs. $H$ plots) at different temperatures are shown in Figure 1(c,d). Hysteresis loops were observed at both $T = 298$ K and $T = 5$ K. $M$ increases steeply at a low fields, then rises relatively slowly and do not fully saturate up until $H = 10$ kOe. The hysteresis curves of MgFeMnO$_4$ show
a soft ferromagnetic behaviour at both temperatures. The coercivity \( (H_C) \) and retentivity values \( (M_r) \) at the two different temperatures are summarized in Table 1. The coercivity is the magnitude of the field that must be applied in the negative direction to bring the magnetization of the sample back to zero. These magnetic properties at RT are very similar to the features of the ferrimagnetic parent compound MgFe\(_2\)O\(_4\). In contrast, the other parent compound MgMn\(_2\)O\(_4\) displayed an antiferromagnetic spin order instead.\(^{26}\)

![Graphs showing magnetic properties](image)

Figure 1: (a) Temperature dependence of the magnetic susceptibility for MgFeMnO\(_4\) recorded in ZFC and FC protocols under an external magnetic field \( H = 100 \text{ Oe} \) (b) and corresponding inverse susceptibility \( 1/\chi(T) \). (c-d) Magnetization v.s magnetic field curves recorded at \( T = 298 \text{ K} \) and \( T = 5 \text{ K} \).

Figure 2 shows the Mössbauer spectrum of MgFeMnO\(_4\) recorded at RT. The sextet splitting of the Mössbauer spectrum indicates that MgFeMnO\(_4\) is in a magnetically ordered state.
with Fe$^{3+}$ at RT. This result is consistent with the magnetic transition temperature ($\sim$ 370 K) observed by magnetization measurement. The spectrum shows a somewhat broad shape, which is probably due to the small grain size of the synthesised sample (50 to 200 nm, which was extracted from SEM measurements, image is shown in Figure S1). Additional broadening may stem from a broad magnetic hyperfine distribution as also observed in MgFe$_2$O$_4$.$^{14}$ However, as De GRAVE et al. mentioned in Ref,$^{14}$ it is impossible to determine the Fe$^{3+}$ cation distribution among A and B sites of a spinel lattice from only zero field spectra.

The magnetism of spinel ferrites is known to be strongly related to the cation distribution between the A and B sites. For instance, Osmond et al. claimed that the disorder of

Table 1: The saturation magnetization ($M_s$), coercivity ($H_C$), retentivity ($M_r$) and squareness ratio/remanence ratio ($r$) of MgFeMnO$_4$ at $T = 5$ K and $T = 298$ K. The coercive field ($H_C$) is defined as $H_C = (|H_C^+| + |H_C^-|)/2$ ($|(H_C^- - H_C^+)/2$), where the coercivity at the positive ($H_C^+$) and negative ($H_C^-$) fields has been determined by linear interpolation of the data points nearest to zero magnetization. The exchange bias field ($H_{EB}$) was extracted according to the following relation: $H_{EB} = (|H_C^- + H_C^+|)/2$.

| Magnetic parameters       | 5 K   | 298 K |
|---------------------------|-------|-------|
| Magnetization ($M_s$) ($\mu_B$) | 2.258 | 0.928 |
| Coercivity ($H_C$) (Oe)     | 479.4 | 69.70 |
| Retentivity ($M_r$) ($\mu_B$) | 1.185 | 0.184 |
| Squareness ($r$)            | 0.52  | 0.20  |
| Exchange Bias ($H_{EB}$) (Oe) | 9.740 | 37.23 |
the magnetic cation in both A and B sites induces ferrimagnetic interaction.\textsuperscript{27} In order to investigate the details of cation distribution, a crystal structure analysis was performed by combining both x-ray and neutron powder diffraction.

**Crystal structure determination**

The crystal structure of MgFeMnO\textsubscript{4} was determined using both XRPD and NPD techniques. Here the neutron technique was absolutely necessary due to its higher sensibility to oxygen as well as greater Mn/Fe contrast, in comparison to XRPD. The structural parameter of MgFeMnO\textsubscript{4} started from the reported unit cell and atomic coordinates of cubic spinel MgFe\textsubscript{2}O\textsubscript{4}.\textsuperscript{28,29} The XRPD and NPD patterns of MgFeMnO\textsubscript{4} are indexed perfectly with a cubic crystal structure (space group \textit{Fd\textbar{3}m}, No. 227) with \(a \approx 8.43\ \text{\AA}\). The space group and cell parameters are also confirmed by electron diffraction recorded at RT (see Figure S1 (c,d)).

In order to avoid the influence of magnetic Bragg peaks, the NPD pattern recorded at \(T = 500\ \text{K}\) (i.e. above magnetic transition temperature) was used initially to determine the crystal structure. The crystallographic parameters obtained from the refinement performed on the NPD data (\(T = 300\ \text{K}\) and \(T = 500\ \text{K}\)) and the corresponding interatomic distances are presented in Table 2. Figure 3 shows the obtained XRPD and NPD patterns, along with the calculated patterns. The crystal structure obtained from the calculated patterns is displayed in Figure 4. The values of the lattice parameter of the cubic structure, determined in this study, are 8.4290 \text{\AA}\ at \(T = 500\ \text{K}\) and 8.4116 \text{\AA}\ at \(T = 300\ \text{K}\). The values are comparable to the reported cell parameter of MgFe\textsubscript{2}O\textsubscript{4} studied by synchrotron x-ray diffraction (at 500 K: \(a = 8.437\ \text{\AA}\), at 300 K: \(a = 8.4208\ \text{\AA}\)).\textsuperscript{30}

No impurity phase peaks were observed in either XRPD or NPD patterns, indicating that the synthesized sample is a single phase. The structure is a typical spinel structure and the three cations (Mg, Fe and Mn) are distributed in both tetrahedral and octahedral oxygen environments. The cation distribution was determined by refinements performed step by step. First, the ratio of Mg and Fe/Mn was obtained from the refinement of the laboratory
Figure 3: Rietveld refinements of MgFeMnO$_4$: (a) XRPD data at $T = 300$ K ($R_{\text{Bragg}} = 3.8\%$ and global $\chi^2 = 1.6$), (b) NPD data at $T = 500$ K ($R_{\text{Bragg}} = 2.5\%$ and global $\chi^2 = 3.1$) and (c) NPD data at $T = 300$ K ($R_{\text{Bragg}} = 2.2\%$, $R_{\text{Braggmag}} = 17\%$ and global $\chi^2 = 3.9$). Experimental data: open circles, calculated profile: continuous line, allowed Bragg reflections: vertical marks. The difference between the experimental and calculated profiles is displayed at the bottom of each graph as a blue line. (d) The difference of NPD data between recorded at $T = 300$ K and $T = 500$ K. Black triangles highlight additional Bragg intensities due to the magnetic ordering.

XRPD pattern, and the obtained result was reflected in the first step of NPD pattern fit process. The obtained distributions are that the tetrahedra site is occupied by Mg : Fe : Mn = 33% : 24% : 43% whereas the octahedral site is by Mg : Fe : Mn = 35% : 52% : 13%.

Cation disorder within a spinel ferrite is reported to show to change with temperature.$^{24,30}$ However, the nuclear Bragg peaks at $T = 300$ K and $T = 500$ K of NPD patterns do not show any significant differences, which implies the cation distribution remains similar in this entire temperature range. Indeed, this is consistent with a previous report on MgFe$_2$O$_4$.}$^{30}$
Table 2: Structural parameters of MgFeMnO$_4$ at $T = 500$ K and $T = 300$ K from Rietveld refinement of neutron powder diffraction (NPD) data. The space group is $Fd\bar{3}m$ and cations occupy Wyckoff positions $8a$ [tetrahedral sites ($A$)] and $16d$ (octahedral sites [$B$]). The fractional coordinates of ($A$) and [$B$] positions are $(1/8, 1/8, 1/8)$ and $(1/2, 1/2, 1/2)$, respectively. O atoms occupy Wyckoff position $32e$ with fractional coordinates $(x, x, x)$. The isotropic thermal factors ($B_{iso}$) are given for the different sites.

|                      | $T = 500$ K | $T = 300$ K |
|----------------------|-------------|-------------|
| structural parameters|             |             |
| $a$ (Å)              | 8.4290 (1)  | 8.4116 (1)  |
| $V$ (Å$^3$)          | 598.9 (1)   | 595.2 (1)   |
| $x$                  | 0.2587 (1)  | 0.2587 (1)  |
| $O_{(A)}$ (Mg/Fe/Mn) | 0.325 (2)/0.241 (2)/0.434 (2) | 0.63 (2) |
| $B_{iso(A)}$ (Å$^3$) | 0.81 (2)    | 0.63 (2)    |
| $O_{[B]}$ (Mg/Fe/Mn) | 0.350 (2)/0.518 (2)/0.133 (2) | 0.43 (3) |
| $B_{iso[B]}$ (Å$^3$) | 0.73 (3)    | 0.43 (3)    |
| $B_{iso O}$ (Å$^3$)  | 1.30 (1)    | 1.08 (1)    |
| $\chi^2$ (Å)         | 3.05        | 3.93        |
| $R_{Bragg}$ (Å)       | 2.52        | 2.24        |
| selected interatomic distances (Å) |         |             |
| $A$ - $O$ ($\times$ 4) | 1.951 (1)  | 1.948 (1)  |
| $B$ - $O$ ($\times$ 6) | 2.037 (1)  | 2.033 (1)  |
| $A$ - $A$             | 3.650 (1)   | 3.642 (1)   |
| $B$ - $B$             | 2.980 (1)   | 2.974 (1)   |
| $A$ - $B$             | 3.494 (1)   | 3.487 (1)   |

suggesting that the cation distribution remains unchanged in the temperature range RT to $T = 773$ K. The subsequent magnetic structure determination was therefore performed under the assumption that the cation distribution does not change between $T = 300$ K and $T = 500$ K.

**Magnetic structure determination**

From the magnetic susceptibility curve (Figure 1(a)), either ferromagnetic or ferrimagnetic interactions are expected to govern the magnetic ordering of MgFeMnO$_4$ below the magnetic transition temperature. Comparing the two neutron diffraction patterns recorded above and below the magnetic transition temperature, the appearance of new Bragg peaks [Figure 3(b-d)], clearly reveal the presence of long-range magnetic ordering. There is an enhancement
Figure 4: Crystal structure of the cubic ($Fd\bar{3}m$) spinel structure (a) along (100) with cation-oxygen bonds and (b) polyhedra representation. Tetrahedra $A$ sites and octahedra $B$ site are displayed in green and orange, respectively. The refined cation ratio on each sites of MgFeMnO$_4$ are $A$ (Mg/Fe/Mn = 33/24/43) and $B$ (Mg/Fe/Mn = 35/52/13).

of the intensity of the Bragg peaks indexed (1 1 1), (2 2 0), (2 2 2), (4 0 0), (3 3 1) and (5 3 1) due to the magnetic contributions with decreasing of temperature (highlighted by black triangles in Figure 3(d)). All the magnetic Bragg peaks can be indexed with a commensurate propagation vector $k = (0 0 0)$. This means that the magnetic unit cell is the same as the crystallographic unit cell having identical symmetry relations. Therefore, the nuclear and magnetic contributions to the Bragg reflections occur at the same scattering angles (i.e. nuclear and magnetic contributions of Bragg reflections are overlapping).

Each structural model was refined to convergence and the best result was selected based on agreement factors and stability of the refinement. The occupancy of cations on tetrahedral and octahedral sites obtained from the earlier refinements were kept fixed and all other parameters were varied freely. Figure 3(c) shows a the neutron diffraction pattern comprising both nuclear and magnetic contributions. The solid line is the resulting refinement based on two phase analysis, showing a satisfactory agreement between the observed and calculated profiles. Since there is no magnetic Bragg peak observed at the position of (2 0 0) (the indexation is in Figure 3(c) in red), the spin orientation can be estimated to have only one
magnetic component (i.e. as described in Figure 5). The resulting magnetic structure at $T = 300$ K is with magnetic moments of $A = 1.57 (5)$ and $B = 1.22 (4) \mu_B$. The spins of $A$ and $B$ sites are found to aligned in a collinear fashion but anti-parallel suggesting that the magnetic structure is ferrimagnetic. The resulting ferrimagnetic spin structure of MgFeMnO$_4$ is shown schematically in Figure 5.

![Figure 5: Proposed spin structure model of MgFeMnO$_4$ at 300 K. (a) projection along (100) and (b) (010) As an example, the magnetic component is aligned in $\pm m_y$. In (b) the moments are along $b$ and symbolized by + or - signs depending on their direction.](image)

**Muon spin relaxation ($\mu^+\text{SR}$)**

We also performed positive muon spin rotation/relaxation ($\mu^+\text{SR}$) measurements of MgFeMnO$_4$ under zero-field (ZF) and weak transverse field (wTF) at temperatures between 2 and 470 K. The wTF-$\mu^+\text{SR}$ spectrum was fitted using a combination of a slowly relaxing precessing signal, due to the externally applied magnetic field wTF = 50 Oe and a non-precessing relaxing (‘tail’) signal:

$$A_0 P_{TF}(t) = A_{TF} \cos(2\pi \omega_{TF} t + \phi_{TF}) \cdot \exp(-\lambda_{TF} t)$$
+ \ A_{\text{tail}} \cdot \exp (-\lambda_{\text{tail}}t) \quad (1)

where $P_{\text{TF}}(t)$ is the muon spin polarisation function, $A_0$ is the initial asymmetry, $A_{\text{TF}}$ and $A_{\text{tail}}$ are the asymmetries of the related polarisation components, $2\pi\omega_{\text{TF}}$ is the angular frequency of the Larmor precession under the applied transverse field, $\lambda_{\text{TF}}$ and $\lambda_{\text{tail}}$ are the exponential relaxation rates for the two components and $\phi_{\text{TF}}$ is the initial phase of the precessing signal. In particular, $A_{\text{TF}}$ is the fraction of muons sensing the applied $w_{\text{TF}} = 50$ Oe, while $A_{\text{tail}}$ is the fraction of muons coupled to the internal field that is parallel to the initial muon spin. Note that the experimental set-up was changed at 300 K from low-temperature cryostat to high-temperature CCR. The time spectrum was collected at 300 K using both set-up as an overlap point. The $w_{\text{TF}}$-signal shown in Figure 6(b) was measured using CCR.

There is no precessing signal ($A_{\text{TF}} = 0$) at 300 K when one uses the cryostat but $A_{\text{TF}} = 0.06$ was observed when the set-up was changed to the CCR. The additional $A_{\text{TF}} = 0.06$ stems from muons hitting the Cu sample holder, a courtesy of the CCR.

Since the applied field is weak relative to the internal field (when the sample is magnetically ordered), the fraction of normalized asymmetry approximately corresponds to the paramagnetic fraction of the sample. Therefore, the temperature dependence of $A_{\text{TF}}(T)$ can be considered as the evolution of the magnetic state in the sample. By plotting $A_{\text{TF}}$ versus $T$ (see Figure 6(c)), the trend of the asymmetry can be fitted with a sigmoid function and the transition temperature $T_C = 394.2 \ (12)$ K defined as the middle point of the fitting curve, where the normalized, $A_{\text{TF}}/A_0 = N_{\text{ATF}}$, is equal to 0.5. This value of $T_C$ is in excellent agreement with other experimental results mentioned previously. From the $w_{\text{TF}}$ spectra collected below $T_C$ it is clear that the entire volume of the sample enters into a long-range magnetic order (since $A_{\text{TF}} = 0$ at low temperatures as shown in Figure 6(a)). This is a clear indication that the investigated sample is homogeneous and of high quality. The unique possibility to accurately determine the magnetically ordered volume fraction of a sample is another powerful capability of the $\mu^+\text{SR}$ technique.
Figure 6: (a) \(\mu^+\)SR time spectra of MgFeMnO\(_4\) at \(T = 2\) K (in cryostat) and (b) temperature dependence \(\mu^+\)SR time spectra (at 300, 380, 400, 420 and 470 K in CCR) under a weak-transverse field (wTF) of 50 Oe, and the corresponding fits using Eq. 1 (solid lines). For clarity, \(A_0\) is the initial asymmetry and PTF(t) is the muon spin polarisation function. (c) Temperature dependence of the normalized wTF asymmetry \(A_{TF}\) of MgFeMnO\(_4\), obtained from fits of the wTF \(\mu^+\)SR time spectra. The sigmoid fit (red solid line) indicated the magnetic transition temperature (\(T_C\)) at 394.2 K.

Figure 7(a) shows ZF-\(\mu^+\)SR time spectra recorded at lowest experimental temperature, \(T = 2\) K. It is apparent that no oscillation signal is present even in the shortest time range at \(T = 2\) K [see inset of Figure 7(a)]. In fact, no oscillatory signal was observed in the entire experimental temperature range (\(T = 2 - 470\) K, see also Figure 7(b,c)). Consequently, the ZF spectra were fitted by three exponentially relaxing non-oscillatory components. Here one of such signal is due to the paramagnetic (PM) background signal which was observed in the high temperature wTF CCR measurements (i.e. such component was only used for the data recorded above 300 K, where \(A_{PM}\) was fixed to 0.0284). The resulting ZF fit function
is described by:

$$A_0 P_{ZF}(t) = A_{\text{fast}} \cdot \exp(-\lambda_{\text{fast}} t) + A_{\text{tail}} \cdot \exp(-\lambda_{\text{tail}} t) + A_{\text{PM}} \cdot \exp(-\lambda_{\text{PM}} t)$$  \hspace{1cm} (2)$$

where $A_0$ is the initial asymmetry, $A_{\text{fast}}$, $A_{\text{tail}}$ and $A_{\text{PM}}$ are the asymmetries associated with each signal. $\lambda_{\text{fast}}$, $\lambda_{\text{tail}}$ and $\lambda_{\text{PM}}$ are the exponential relaxation rates of each signal. It is clearly shown in Figure 7 that both short ($t < 0.2 \mu s$) and long ($t$ up to $8 \mu s$) time spectra were well fitted using Eq. 2. At $T = 2$ K ($A_{\text{PM}} = 0$), $A_{\text{tail}}$ is about 0.08, which is coherent with the expected 1/3 powder average tail component (local field oriented parallel to the muon spin). This further supports the wTF results showing that the volume fraction of the magnetic phase is effectively 100% below $T_C$. $A_{\text{fast}}$ on the other hand corresponds to internal field components that are perpendicular to the initial muon spin (on average 2/3 of the local fields).

The fitting parameters of ZF-$\mu^+$SR time spectra above 300 K are summarized in Figure 8. It is noted that the paramagnetic signal from the high temperature set-up is from the Cu-sample holder. The previous $\mu^+$SR study on Cu-metal shows that a small relaxation rate ($\lambda_{\text{PM}} \sim 0.025$) observed at 300 K and it decreases by increasing the temperature.\textsuperscript{31} Since $A_{\text{PM}}$ is small, it is difficult from the data to discern such small relaxation, which as stated decreases with temperature. Thus, we set $\lambda_{\text{PM}} = 0$, which is a good approximation for our purposes.

In the temperature dependence of $\lambda_{\text{tail}}$, a maximum is observed at $T_{\text{max}} = 400$ K. Such maximum occurs close to the inflection point of $A_{\text{tail}}$, and is considered to be due to a critical slowing down of magnetic moments accompanied by the magnetic order. Such magnetic ordering temperature is in good agreement with the one determined by wTF-$\mu^+$SR time spectra, i.e. $T_C = 394.2$ K. This suggests that in the entire temperature range, the depo-
Figure 7: (a) ZF-$\mu^+$SR time spectra of MgFeMnO$_4$ at $T = 2$ K shown for the full time domain. The inset shows the shorter time domain to emphasize the absence of clear oscillations and a missing asymmetry fraction. Temperature-dependent ZF-$\mu^+$SR spectra for MgFeMnO$_4$(b) in the long time domain up to 8 $\mu$s and (c) in an early time domain up to 0.2 $\mu$s. Each spectrum is offset along the y-axis by 0.1, for clarity of display. Solid lines show the best fits using Eq. 2.

Larizations occurs much faster than the time resolution of the current measurement. Such situation is often observed in ZF-signals for either systems with very large magnetic moments and/or ferro/ferrimagnetic materials.$^{32-34}$ Since the magnetic moments of each magnetic site of MgFeMnO$_4$ are maximum $\sim 1.6 \mu_B$, the latter scenario is more reasonable. This is in perfect agreement with the current NPD results that reveal a collinear ferrimagnetic ordering.
Figure 8: Temperature dependencies of the ZF-$\mu^+$SR parameters for MgFeMnO$_4$; (a) the asymmetries ($A_{\text{tail}}$ and $A_{\text{fast}}$), (b) the relaxation rate of tail component ($\lambda_{\text{tail}}$), (c) the relaxation rate of fast component ($\lambda_{\text{fast}}$). The data were obtained by fitting the ZF-$\mu^+$SR spectra using Eq. 2 above 300 K.

Discussion

Cation distribution

In this study an accurate cation distribution of MgFeMnO$_4$ was determined by combining x-ray and neutron powder diffraction. Disorder between the tetrahedral and octahedral sites in spinel oxides is known to create "anti-site defects", resulting in physical and electrochemical properties, which are favourable for battery and other applications.\textsuperscript{16,35} Mg\textsuperscript{2+} is migrated to only the tetrahedral A site in MgMn$_2$O$_4$.\textsuperscript{15-17} On the other hand, MgFe$_2$O$_4$ shows a certain degree of anti-site effect (10 - 30 % of Mg in the octahedral site\textsuperscript{30}). In the current case of MgFeMnO$_4$, the mixture of manganese and iron in spinel oxide clearly increases the anti-site defects. The same effect was observed in Mg(Mn$_{2-x}$Co$_x$)O$_4$.\textsuperscript{16} Moreover, in case of Mg(Mn$_{2-x}$Co$_x$)O$_4$, Zhao \textit{et al.} claimed that the anti-site effect plays a critical role to improve the electrochemical performance.\textsuperscript{16} Our current results, together with the previously reported electrochemical performance studies,\textsuperscript{6} also support the critical role of the anti-site effects for
the improved electrochemical behaviour.

**Magnetic structure**

The present system is composed of two types of magnetic ions, i.e. Mn and Fe. Here, Mn is generally known to be in a divalent state at the tetrahedral sites, whereas Fe and Mn in the octahedral sites usually poses a trivalent state. The trivalent state of Fe$^{3+}$ is confirmed by Mössbauer spectroscopy (Figure 2). The theoretical ordered magnetic moment values are $5.9 \mu_B$ for Fe$^{3+}$ and Mn$^{2+}$, $4.9 \mu_B$ for Mn$^{3+}$. Consequently, the values for each sublattice moments are $A = 3.86$ and $B = 3.70 \mu_B$ obtained by applying the cation distributions from the Rietveld refinement of the presented diffraction data. Clearly, the experimental (NPD) values for both $A$ and $B$ site magnetic moments ($A = 1.57 (5)$ and $B = 1.22 (4) \mu_B$) are well below theoretical expectations, losing $59.3$ % and $67.0$ % of moment value, respectively. The concentration of diamagnetic ions in the $B$ site is more than that in the $A$ site. As a result, the system becomes magnetically inhomogeneous and frustrated, causing a perturbation to the usual collinear ferrimagnetic ordering of spins. It should also be mentioned at this point that the geometrical frustration of $B$ site due to pyrochlore lattice of corner sharing tetrahedra may have some additional contribution to the strong disorder in the $B$ site.

**Conclusion**

Accurate studies of crystal structure of the mangnesium spinel MgFeMnO$_4$ have been performed combining by electron, x-ray and neutron diffraction techniques. The crystal structure has been confirmed to be a typical cubic spinel structure (SG: $Fd\overline{3}m$ with $a = 8.429$ Å at 500 K). Three cations (Mg, Fe and Mn) are distributed over tetragonal $A$ and octahedral $B$ sites and the crystal structure is unaffected by the onset of the magnetic order. The precise magnetic transition temperature is determined as 394.2 (12) K by wTF-$\mu^+$SR measurements spectra, and the collinear ferrimagnetic spin structure has been investigated by neutron pow-
der diffraction. In the ferrimagnetic phase below the transition temperature, no clear muon spin oscillation has been observed in the ZF-$\mu^+$SR time spectra. This ZF-$\mu^+$SR result further supports the ferrimagnetic spin ordering determined by NPD. The magnetic properties of MgFeMnO$_4$ are more similar to the ferrimagnetic MgFe$_2$O$_4$ than the antiferromagnetic MgMn$_2$O$_4$.

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MgFeMnO$_4$ crystallizes in the typical cubic spinel structure with cation disordering between the tetrahedra $A$ sites and the octahedra $B$ sites. Combining the different techniques, magnetization vs. temperature and field, Mössbauer spectroscopy measurements, high-resolution neutron powder diffraction studies and $\mu$+SR measurement reveal that (i) accurate crystal structure of MgFeMnO$_4$ at 300 and 500 K and (ii) a collinear ferrimagnetic spin ordering below $T_C = 394.2$ K.