Correlation between polyhedral distortions and phase transitions in spinel FeMn$_2$O$_4$†

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Abstract

Spinel compounds AB$_2$X$_4$ consist of both tetrahedral (AX$_4$) and octahedral (BX$_6$) environments with the former forming a diamond lattice and the latter a geometrically frustrated pyrochlore lattice. Exploring the fascinating properties and their correlations with structural features is critical in understanding these materials. FeMn$_2$O$_4$ has been

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reported to exhibit one structural transition and two successive magnetic transitions. Here, we report the polyhedral distortions and their correlations to the structural and two magnetic transitions in FeMn$_2$O$_4$ by employing the high-resolution neutron powder diffraction. The cation distribution is determined to be $(\text{Mn}^{2+}_{0.9}\text{Fe}^{3+}_{0.1})_A(\text{Mn}^{3+}\text{Fe}^{3+}_{0.9}\text{Mn}^{2+}_{0.1})_B\text{O}_4$.

While a large trigonal distortion is found even in the high-temperature cubic phase, the first-order cubic-tetragonal structural transition associated with the elongation of both tetrahedra and octahedra along the $c$ axis occurs at $T_S \approx 750$ K, driven by the Jahn-Teller effect of the orbital active B-site Mn$^{3+}$ cation. A strong magnetoelastic coupling is unveiled at $T_{N1} \approx 400$ K as manifested by the appearance of Néel-type collinear ferrimagnetic order, an anomaly in both tetrahedral and octahedral distortions, as well as an anomalous decrease of the lattice constant $c$ and a weak anomaly of $a$. Upon cooling below $T_{N2} \approx 65$ K, it evolves to a noncollinear ferrimagnetic order with a canting of half B-site Mn$^{3+}$/Fe$^{3+}$ spins in the pyrochlore lattice, which is a unique magnetic order among spinels. The canting angle between A-site and B2-site moments is $\sim 25^\circ$, but the B1-site moment stays antiparallel to the A-site moment even at 10 K. Such a noncollinear order induces modifications of the O-B-O bond angles in the octahedra without affecting much the bond lengths of the tetrahedra/octahedra. We demonstrate the distinct roles of the A-site and B-site magnetic cations in the structural and magnetic properties of FeMn$_2$O$_4$. Our study indicates that FeMn$_2$O$_4$ is a wonderful platform to unveil interesting magnetic order and to investigate their correlations to polyhedral distortions and lattice.

Introduction

Spinel compounds AB$_2$X$_4$ (X=O, S, Se or Te) are known to exhibit a variety of interesting physical properties such as multiferroicity, excellent electrochemical activity as cathode material for Li-ion batteries, colossal magnetoresistivity, topological semimetallic state, etc. These properties are largely related to their unique crystal structure consisting of both AX$_4$ tetrahedra and BX$_6$ octahedra. The A-site cations form a diamond lattice, while the
B-site cations form a pyrochlore lattice which is geometrically frustrated. The interplay between lattice, orbital and spins degrees of freedom is a key in understanding the physical properties in these compounds. The system is even more interesting when both A and B sites are occupied by magnetic cations in spinel oxides, for instance MnV$_2$O$_4$ and FeV$_2$O$_4$. In these materials, a Néel type collinear ferrimagnetic (CFI) order is frequently observed at higher temperatures, but transformed to a noncollinear ferrimagnetic (NCFI) order at lower temperatures. A common ground-state magnetic structure is a triangular arrangement of Yafet-Kittel type FI order due to the competing magnetic interactions. For this magnetic structure, the B-site spins in the pyrochlore lattice are canted relative to the A-site moment direction. The net moment from the B-site spins is antiparallel to that of the A-site spins, with uncompensated moments. It is of great interest to explore new type of magnetic ground state and to investigate the correlations between the magnetic order and tetrahedral/octahedral distortions in spinel oxides.

FeMn$_2$O$_4$ is one of the spinel oxides involving distinct magnetic cations at the A and B sites. It has been well documented that Mn$^{2+}$ cations mainly occupy the tetrahedral A site, whereas Mn$^{3+}$ and Fe$^{3+}$ cations share the octahedral B site, based on Mössbauer, x-ray absorption spectroscopy and magnetic circular dichroism measurements. In this sense, FeMn$_2$O$_4$ should be written as Mn$_A$(MnFe)$_B$O$_4$. FeMn$_2$O$_4$ shows a cubic-to-tetragonal structural transition at $\sim$ 520-600 K, depending strongly on the composition and/or a shift of the cation distribution. In contrast, the two magnetic transition temperatures have been reported to be less sensitive to the sample preparation conditions, with $T_{N1}$ $\sim$ 373-390 K and $T_{N2}$ $\sim$ 50-75 K, respectively. According to an early neutron diffraction experiment, two noncollinear FI orders were proposed at $T_{N1}$ and $T_{N2}$. However, the noncollinear FI order in the high temperature region ($T_{N2} < T < T_{N1}$) is unusual. Furthermore, the proposed ground-state magnetic structure in $T < T_{N2}$ was very complicated with a low magnetic space group $C2'\overline{1}m'$ derived from a monoclinic structure: 1). The A-site moment does not point to any high symmetry axis but an angle 172° to the [100]$_T$ direction in the tetragonal notation;
2). The octahedral B site is divided into 4 magnetic sublattices with different canting angles. All these features in the proposed magnetic structure as the ground state are surprising given that the crystal structure has a much higher tetragonal symmetry of $I4_1/amd$.\textsuperscript{13,14,17} Note that only a couple of low-$Q$ nuclear or magnetic peaks were collected in that experiment.\textsuperscript{13} leaving the possibility that there are other possible magnetic structures to be considered. In addition, it remains an open yet very important question if there exists a correlation between magnetism, lattice and distortions of tetrahedra and/or octahedra in FeMn$_2$O$_4$.

Here, we report the crystal and magnetic structures, and their correlations with the polyhedral distortions as determined by high-resolution neutron diffraction technique with a large $Q$ coverage. We find that there is a large trigonal distortion existing even in the cubic phase. When cooling down, a first-order cubic-tetragonal transition at $T_S$ is induced by the elongation of both tetrahedra and octahedra along the $c_T$ axis. A collinear FI order with moment along the $a_T$ axis is found in $T_{N2} < T < T_{N1}$, which is associated with an anomalous suppression of tetrahedral elongation, an enhanced octahedral distortion, and anomalies in lattice constants. All these results indicate the existence of a strong magnetoelastic coupling at $T_{N1}$. With further cooling below $T_{N2}$, the magnetic structure evolves to an unusual noncollinear FI order, where only half B-site spins are canted. The magnetic space group is $Imma$\textsuperscript{t} involving only two magnetic sublattices at the B site. Such magnetic transformation at $T_{N2}$ induces anomalies in the O-B-O bond angles in the octahedra. We demonstrate that the A-site Mn$^{2+}$, B-site Fe$^{3+}$ and Mn$^{3+}$ magnetic cations play distinct roles in the structural and magnetic phase transitions in FeMn$_2$O$_4$. We further shed light on the origin of the structural and magnetic ordering processes and its connection to competing interactions.
Results

First-order nature of the structural transition at $T_S$

To identify the structural transition temperature $T_S$ and reveal the nature of the transition, neutron diffraction patterns were collected upon warming from 500 K to 773 K, followed by a cooling process at a ramping rate of 1.5 K/min. Neutron diffraction plots of the temperature versus $d$ spacing are displayed in Fig. 1 (a) and (b) for warming and cooling processes, respectively. Clear peak splitting occurs on many nuclear Bragg peak positions, such as (400) and (440), confirming the existence of the cubic-tetragonal structural transition reported previously.\cite{13,14,17} Notably, there is a huge thermal hysteresis for the structural transition temperature with $T_S \approx 750$ K upon warming and $\approx 625$ K when cooling down, revealing the first-order nature of the structural transition. Furthermore, the neutron patterns taken at the same temperature 500 K after the warming and cooling processes show clear difference, for instance some of the Bragg peak positions did not reproduce upon temperature cycling. This indicates that the crystal structure was not completely restored after a single temperature cycle we performed, further supporting a strongly first order structural phase transition.

![Figure 1: Temperature versus $d$ spacing of the neutron diffraction contour plots for (a) warming and (b) cooling processes with a ramping rate of 1.5 K/min.](image1)

The high resolution neutron diffraction patterns at 773 K and at 500 K are shown in Fig. 2(a-b), respectively. The Rietveld analysis on such neutron data over a large $Q$ coverage
up to $\approx 11.8^{-1}$ allows us to obtain accurate structural parameters including the thermal parameters, site occupancy and inversion between A and B sites. The results are summarized in Table I. At 773 K, we find that FeMn$_2$O$_4$ crystallizes the cubic structure with the space group $Fd-3m$, as illustrated in the Fig. 2(c). We confirmed the previous reports$^{15,16}$ that the Mn$^{2+}$ ions occupy the A site (i.e., in the tetrahedral environment), whereas the Mn$^{3+}$ and Fe$^{3+}$ ions occupy the B site (i.e., in the octahedral environment) randomly without site ordering. Due to the difference in the neutron scattering lengths of Mn and Fe, we are able to determine that there is $\approx 10\%$ of Fe$^{3+}$ on the A site, with the corresponding $\approx 10\%$ Mn$^{2+}$ on the B site in our sample. Thus, the cation distribution of our FeMn$_2$O$_4$ should be rewritten as $(Mn^{2+}_{0.9}Fe^{3+}_{0.1})_A(Mn^{3+}_{0.9}Fe^{3+}_{0.1})_B$O$_4$. At 500 K (below $T_S$), Rietveld analysis on neutron data in Fig. 2(b) confirms the tetragonal structure with the space group $I4_1/amd$ with a clear lattice distortion (see Fig. 2(d)), consistent with the previous reports.$^{13,14}$ The refined atomic positions, lattice constants, site occupancy and thermal parameters at 773 K and 500 K are summarized in Table 1 and 2, respectively.

Table 1: Refined atomic positions, isotropic temperature factors, occupancy, O-A-O bond angles in AO$_4$, O-B-O bond angles in BO$_6$, the tetrahedral distortion parameter $D_T$ and the octahedral distortion parameter $D_O$ from modeling high resolution powder neutron diffraction data of FeMn$_2$O$_4$ at 773 K. Analysis of the nuclear Bragg reflections lead to the space group selection of $Fd-3m$ (No. 227) and indexed unit cell constants of $a = 8.562(3)\ \text{Å}$.

| atom | site | x   | y   | z   | $B$   | occupancy | $\angle$ O-A-O (°) | $\angle$ O-B-O (°) | $D_T$ | $D_O$ |
|------|------|-----|-----|-----|-------|-----------|----------------------|----------------------|-------|-------|
| Mn   | 8a   | 0.125 | 0.125 | 0.125 | 1.675(5) | 0.9       | 109.47               | 96.34, 83.66         | 1     | 1     |
| Fe   | 8a   | 0.125 | 0.125 | 0.125 | 1.675(5) | 0.1       |                      |                      |       |       |
| Fe   | 16d  | 0.5  | 0.5  | 0.5  | 1.602(6) | 0.45      |                      |                      |       |       |
| Mn   | 16d  | 0.5  | 0.5  | 0.5  | 1.602(6) | 0.55      |                      |                      |       |       |
| O    | 32e  | 0.262(4) | 0.262(4) | 0.262(4) | 1.870(9) | 0.5       |                      |                      |       |       |

**Intrinsic trigonal distortion of the BO$_6$ octahedron**

Figure 3(a-d) shows the geometrical information of the AO$_4$ (A=Mn$^{2+}$/Fe$^{3+}$) tetrahedra and BO$_6$ (B=Mn$^{3+}$/Fe$^{3+}$/Mn$^{2+}$) octahedra, and their projections in the (HHL) plane in the cubic notation. In the cubic structure at 773 K, all O-A-O bond angles in AO$_4$ tetrahedra are the same $\approx 109.47^\circ$, forming a perfect tetrahedron. All O-O bond lengths
Figure 2: (a). Rietveld refinement fits to high resolution neutron diffraction patterns at (a) 773 K and (b) 500 K, and the corresponding graphic representations of the crystal structures in (c) and (d).

Table 2: Refined atomic positions, isotropic temperature factors, occupancy, O-A-O bond angles in AO$_4$, O-B-O bond angles in BO$_6$, the tetrahedral distortion parameter D$_T$ and the octahedral distortion parameter D$_O$ from modeling high resolution powder neutron diffraction data of FeMn$_2$O$_4$ at 500 K. Analysis of the nuclear Bragg reflections lead to the space group selection of $I4_1/amd$ (No. 141) and indexed unit cell constants of $a_T = 5.921(4)\,\text{Å}$, $c_T = 8.900(3)\,\text{Å}$.

| atom | site | x   | y    | z    | $B$             | occupancy | $\angle$ O-A-O ($^\circ$) | $\angle$ O-B-O ($^\circ$) | $D_T$ | $D_O$ |
|------|------|-----|------|------|-----------------|-----------|---------------------------|---------------------------|-------|-------|
| Mn   | 4a   | 0   | 0.25 | 0.875| 1.212(5)       | 0.9       | 110.88, 106.69, 96.35, 83.65 | 96.01, 83.99             | 1.027 | 1.068 |
| Fe   | 4a   | 0   | 0.25 | 0.875| 1.212(5)       | 0.1       |                           |                           |       |       |
| Fe   | 8d   | 0   | 0.5  | 0.5  | 0.952(7)       | 0.45      |                           |                           |       |       |
| Mn   | 8d   | 0   | 0.5  | 0.5  | 0.952(7)       | 0.55      |                           |                           |       |       |
| O    | 16e  | 0   | 0.474(6) | 0.261(4) | 1.245(8)       | 0.5       |                           |                           |       |       |
within the tetrahedron are the same. For the BO$_6$ octahedron, the O-B-O angle deviates significantly from 90°, with one 83.66° and another 96.34°. This can also be seen from the projection of BO$_6$ octahedra in Fig. 3(c), reflected by a noncollinear ...O-B-O-B-O... chain due to the stretching of octahedra in < 111 > direction. Such a trigonal distortion is closely

Figure 3: Geometrical representation of the AO$_4$ (A=Mn$^{2+}$/Fe$^{3+}$) tetrahedron and BO$_6$ (B=Mn$^{3+}$, Fe$^{3+}$ or Mn$^{2+}$) octahedron, and their projections in the (HHL) plane at (a,c) 700 K and (b,d) 500 K. The thick open arrows in (a) illustrates the trigonal distortion of one octahedron at 773 K. The thin arrows in (b) indicate the evolution of the bond lengths in one tetrahedron and octahedron at 500 K.

associated with the oxygen position within the cubic $Fd-3m$ space group. Our results indicate that the trigonal distortion is already present in the cubic phase of FeMn$_2$O$_4$. The angular separation for FeMn$_2$O$_4$ is 96.34 – 83.66 ≈12.6° at 773 K is comparable to MnV$_2$O$_4$ (12.9°)[16] and FeV$_2$O$_4$ (10.7°)[13] Such a trigonal distortion in the cubic phase only modifies the O-B-O bond angles, but does not change the O-B bond lengths (2.037 Å at 773 K). Note that the trigonal distortion extends to $T < T_S$ as shown in Fig. 3(b) and (d), indicating that
this is an intrinsic structural feature in FeMn₂O₄.

**Magnetic structure determination in** \( T_{N2} < T < T_{N1} \) **and** \( T < T_{N2} \)

To identify the magnetic transition temperatures, the 2θ scans of the (111) and (200) magnetic peaks at different temperatures were measured at the constant-wavelength triple-axis spectrometer HB1A. The representative results are shown in Fig. 4(a-b). The temperature dependence of the integrated intensity and linewidth of these two peaks are displayed in Fig. 4(c-d). The rapid increase of the integrated intensity of the (111) peak below \( T_{N1} \) indicates a high-temperature magnetic transition. The pure magnetic peak (200) emerges below the low-temperature magnetic transition temperature \( T_{N2} \approx 65 \text{ K} \). Both \( T_{N1} \) and \( T_{N2} \) are consistent with those observed from magnetization measurements.\(^{12}\) Below \( T_{N1} \) and \( T_{N2} \), the magnetic peaks (111) and (200) are resolution limited indicative of long-range magnetic or-
orders in $T_{N2} < T < T_{N1}$ and $T < T_{N2}$. There is no obvious increase of the linewidth for (111) peak above $T_{N1}$, indicating that there is no short-range magnetic order above $T_{N1}$. Note that in addition to (111) and (200) peaks, we have observed magnetic contribution on nuclear peak positions such as (202), (220), (222), (313), and (331), etc. All the magnetic reflections can be indexed on the chemical unit cell in these two temperature regions. Therefore, the magnetic propagation vector is $\mathbf{k} = (0,0,0)$.

![Graphical representation of magnetic structures](image)

Figure 5: Rietveld refinement fits to high resolution neutron diffraction patterns at (a) 297 K and (b) 10 K and the corresponding graphic representations of the determined magnetic structures in (c) and (d).

The Rietveld analysis on high-resolution neutron diffraction patterns, shown in Fig. 5(a), over a large $Q$ region in $T_{N2} < T < T_{N1}$, reveals a collinear FI order with the ordered moment along the tetragonal $a_T$ axis, as illustrated in Fig. 5(b). The ordered moments at the B1 and B2 sites are the same. Both are antiparallel to those at the A site with
the different moment, thus forming a Néel-type collinear FI order. At 297 K, the ordered moment of the \((Mn^{2+}/Fe^{3+})_A\) site is \(3.08(4) \mu_B\), whereas the ordered moment at the B site \((Mn^{3+}, Fe^{3+} \text{ and } Mn^{2+})\) is \(-1.61(3) \mu_B\). The net ordered moment is \(-0.14(5) \mu_B/\text{f.u.}\) \((3.08 - 2 \times 1.61 = -0.14)\) along the \(a_T\) axis.

In \(T < T_{N2}\), a noncollinear magnetic structure involving a spin canting at the B2 site is found to fit well the neutron data. The Rietveld refinement on the POWGEN data at 10 K is shown in Fig. 5(c). Compared to the magnetic structure in \(T_{N2} < T < T_{N1}\), the main difference in \(T < T_{N2}\) is that a moment component along the +/- \(c_T\) axis at the B2 site appears, leading to a spin canting in the \(a_Tc_T\) plane and a noncollinear FI order, as illustrated in Fig. 5(d). The projection of the canted spins along the \(c_T\) axis shows an antiferromagnetic arrangement and is directly responsible for the emergence of the pure magnetic peak (200). In both \(T_{N2} < T < T_{N1}\) and \(T < T_{N2}\), the magnetic space group is the same, \(Immm\) (No.74.559). For this magnetic space group, there are two magnetic sublattices at the B site (namely B1 and the B2 sites), in addition to one magnetic sublattice at the A site. The moments at the A site and the B1 site \((0 0 0.5)\) are constrained to point along the \(a_T\) axis, whereas the moment at the B2 site \((0.25 0.75 0.75)\) is constrained in the \(a_Tc_T\) plane, as shown in Table III. At 10 K, \(m_a(A)\) and \(m_a(B1)\) are \(4.65(5)\) and \(-2.89(6) \mu_B\), respectively. The moment at the B2 site is \((-2.76(3),0,-1.31(7)) \mu_B\), yielding a spin canting angle of \(25^\circ\). The global net ordered moment at 10 K is \(\approx 1 \mu_B/\text{f.u.}\) along the \(a_T\) axis.

It is worthwhile pointing out that although B-site is divided into two magnetic sublattices in this NCFI order, the crystal structure can be described by its parent space group \(I4_1/amd\) that retains down to the lowest investigated temperature 10 K. The structural and magnetic parameters at 10 K are listed in Table III. To the best of our knowledge, the ground-state magnetic structure of FeMn2O4 is unique among all the reported spinel oxides in that only half of the B-site spins are canted but other half of the B-site spins are not.
Table 3: Refined structural and magnetic parameters from modeling high resolution powder neutron diffraction data of FeMn$_2$O$_4$ at 10 K. The magnetic space group is determined to be $Immm\tilde{a}t$ (No. 74.559) with parent space group $I4_1/amd$ and indexed unit cell constants of $a_T = 5.8945(2)$Å and $c_T = 8.8855(3)$Å.

| label | spin valence | x     | y     | z     | multiplicity | $B$      | symmetry constrains on M | $M_x$ | $M_y$ | $M_z$ | $M$     |
|-------|--------------|-------|-------|-------|--------------|---------|--------------------------|-------|-------|-------|---------|
| Mn1   | Mn$^{2+}$    | 0     | 0.75  | 0.125 | 4            | 0.320(6) | $m_x,0,0$                | 4.65(5)| 0     | 0     | 4.65(5) |
| Fe1   | Fe$^{2+}$    | 0     | 0.75  | 0.125 | 4            | 0.320(6) | $m_x,0,0$                | 4.65(5)| 0     | 0     | 4.65(5) |
| Fe2_1 | Fe$^{3+}$    | 0     | 0     | 0.5   | 4            | 0.266(4) | $m_x,0,0$                | -2.89(6)| 0     | 0     | 2.89(6) |
| Fe2_2 | Fe$^{3+}$    | 0.25  | 0.75  | 0.75  | 4            | 0.266(4) | $m_x,0,0$                | -2.76(3)| 0     | -1.31(7)| 3.05(9) |
| Mn2_1 | Mn$^{2+}$    | 0     | 0     | 0.5   | 4            | 0.266(4) | $m_x,0,0$                | -2.89(6)| 0     | 0     | 2.89(6) |
| Mn2_2 | Mn$^{2+}$    | 0.25  | 0.75  | 0.75  | 4            | 0.266(4) | $m_x,0,0$                | -2.76(3)| 0     | -1.31(7)| 3.05(9) |
| Mn3_1 | Mn$^{3+}$    | 0     | 0     | 0.5   | 4            | 0.266(4) | $m_x,0,0$                | -2.89(6)| 0     | 0     | 2.89(6) |
| Mn3_2 | Mn$^{3+}$    | 0.25  | 0.75  | 0.75  | 4            | 0.266(4) | $m_x,0,0$                | -2.76(3)| 0     | -1.31(7)| 3.05(9) |
| O1_1  | O$^{2-}$     | 0     | 0.474(4)| 0.261(5)| 8            | 0.642(7) |                         |       |       |       |         |
| O1_2  | O$^{2-}$     | 0.775(8)| 0.75  | 0.511(6)| 8            | 0.642(7) |                         |       |       |       |         |

Correlation between polyhedral distortions and structural transition at $T_S$

To characterize polyhedral elongation/suppression, we examined the average bond lengths, angles and polyhedral distortion parameters based on the Rietveld analysis on the neutron data. The distortion parameter of the AO$_4$ tetrahedron $D_T$ is defined as the ratio of the O-O bond length along the $<101>$ direction to that along the $<110>$ direction, whereas the distortion parameter of the BO$_6$ octahedron $D_O$ is characterized by the ratio of the B-O bond length along the $<001>$ direction to that along the $<100>$ direction. The temperature dependence of the bond lengths and angles in tetrahedra AO$_4$ and octahedra BO$_6$ is displayed in Fig. 6 and 7 respectively. The temperature dependence of the distortion parameters $D_T$ and $D_O$ is shown in Fig. 8 (a). In the cubic phase, both $D_T$ and $D_O$ are 1 despite the existence of trigonal distortion of the octahedron with split O-B-O bond angles. Upon cooling below $T_S$, the O-O bond length in the tetrahedron increases along the $<101>$ direction but decreases along the $<110>$ direction (see Fig. 3(b) and 6(a)), leading to an elongated tetrahedron along the $c$ axis. Correspondingly, the tetrahedral distortion parameter $D_T$ is found to increase from 1 at 773 K to 1.027 at 500 K. Below $T_S$, one O-A-O bond angle within the tetrahedron at 773 K splits into two, for instance 110.88° and 106.69° at 500 K (see Fig. 7(a)).
Figure 6: Temperature dependence of the O-O bond lengths in tetrahedra AO₄ along (a) <101> and (b) <110>, and the B-O bond lengths in octahedra BO₆ along (a) <001> and (b) <100>.

As for the octahedron, the B-O bond length is elongated significantly along the <001> direction but shortened along the <100> direction (see Fig. 7(b) and 8(b)), yielding a large octahedral distortion parameter of 1.068 at 500 K. Below $T_S$, one O-B-O angle (96.34° at 773 K) in the octahedron splits into two ones (96.35° and 96.01° at 500 K), whereas another O-B-O angle (83.66° at 773 K) changes into 83.65° and 83.99° at 500 K (see Fig. 7(b)). The elongated tetrahedra and octahedra along the $c$ axis lead to the cubic-tetragonal structural
transition with elongated lattice constant $c = c_T$ and shortened lattice constant $a = \sqrt{2}a_T$, i.e., $c > a$. The bond lengths, angles and the polyhedral distortion parameters at 773 and 500 K are also added in Table I and II, respectively. Our results reveal a correlation between the cubic-tetragonal structural transition and the elongations of both tetrahedra and octahedra.

Figure 7: Temperature dependence of (a) O-A-O bond angles in tetrahedra AO$_4$ and (b) O-B-O bond angles in octahedra BO$_6$. 

Figure 7: Temperature dependence of (a) O-A-O bond angles in tetrahedra AO$_4$ and (b) O-B-O bond angles in octahedra BO$_6$. 
Correlation between polyhedral distortion and magnetic orders

Fig. 8(b-d) shows the temperature dependence of the lattice constants, ordered moments at different magnetic sites and spin canting angle, respectively. Below $T_{N1}$, an anomalous decrease of the O-O bond length along the $<101>$ direction in tetrahedron AO$_4$ is observed while the O-O bond length along the $<110>$ direction continues to decrease (see Fig. 6(a)), which leads to a decrease of $D_T$ indicative of a suppression of the tetrahedral elongation in Fig. 8(a). Note that compared to the ideal tetrahedron in the cubic phase in $T > T_S$, the tetrahedra is still elongated in this temperature region. In contrast, we find an additional increase of the B-O bond lengths along the $<001>$ direction below $T_{N1}$, without clear anomaly in the B-O bond lengths along the $<100>$ direction (see Fig. 6(b)). This results in an increase of $D_O$, i.e., an enhancement of the octahedral elongation below $T_{N1}$ (see Fig. 8(a)). There are no clear anomalies in the O-A-O and O-B-O bond angles at $T_{N1}$ (see Fig. 7). As shown in Fig. 8(c), the collinear FI order is established at $T_{N1}$ and the ordered moments along the $a_T$ axis at the A and B sites increase upon cooling. All these results indicate that the formation of the collinear FI order drives both tetrahedral and octahedral distortions, mainly on the changes of the bond lengths rather than bond angles at $T_{N1}$. The tetrahedral and octahedral distortions lead to an anomalous decrease of the lattice constant $c$ below $T_{N1}$ and a weak anomaly in $a$ at $T_{N1}$. The concurrent collinear FI order, and the anomalies in polyhedral distortions and lattice constants at $T_{N1}$ indicate a strong magnetoelastic coupling.

Upon further cooling below $T_{N2}$, a collinear FI order to noncollinear FI one with the spin canting to the $c_T$ axis at the B2 site occurs. At $T_{N2}$, a weak anomaly in the O-O bond lengths along both the $<101>$ and $<110>$ directions is observed with similar temperature dependence. Thus, no clear anomaly in $D_T$ can be seen at $T_{N2}$ in Fig. 8(a). There is no anomaly in the O-A-O bond lengths in the tetrahedron at $T_{N2}$ either (see Fig. 7(a)). As for octahedral BO$_6$, one does not find anomalies in the B-O bond lengths along the $<001>$, $<100>$, or $D_O$. Interestingly, we find clear anomalies in the O-B-O bond angles in the octahedron at $T_{N2}$ (see Fig. 7(b)), i.e., an anomalous decrease of the two low
Figure 8: Temperature dependence of (a) tetrahedral and octahedral distortions, (b) lattice constants in cubic notation, (c) the ordered moments at the A, B1 and B2 sites, and (d) the spin canting angle at the B2 site, one half of the B site in pyrochlore lattice. The inset of the (b) shows the zoomed figure for the lattice constant $c$. 
O-B-O angles near 83.6° and 84.3° with the corresponding increase of the two high O-B-O angles ∼ 95.7° and 96.4°. Therefore, the CFI-NCFI transition at $T_{N2}$ mainly induces changes of the O-B-O bond angles in the octahedron without a clear effect on the bond lengths in tetrahedron/octahedron, the O-A-O bond angles in tetrahedron and lattice constants.

## Discussion

### Roles of the A-site Mn$^{2+}$, B-site Fe$^{3+}$ and/or Mn$^{3+}$ in the structure and magnetic properties

Given that there is only ∼10% inversion, we simplify the cation distribution of FeMn$_2$O$_4$ to $(Mn^{2+})_A(Mn^{3+}Fe^{3+})_B$O$_4$ to reveal the roles of the dominant A-site Mn$^{2+}$, B-site Fe$^{3+}$ and Mn$^{3+}$ in the structure and magnetic properties, by comparing with other related spinel oxides.

**Roles of B-site Fe$^{3+}$ cation**

Compared to Mn$_3$O$_4$ with cation distribution of $(Mn^{2+})_A(Mn^{3+}Mn^{3+})_B$O$_4$, FeMn$_2$O$_4$ with cation distribution $(Mn^{2+})_A(Mn^{3+}Fe^{3+})_B$O$_4$ can be viewed as the resultant compound by replacing 1/2 of the B-site Mn$^{3+}$ by Fe$^{3+}$ in Mn$_3$O$_4$. Given that Fe$^{3+}$ $(t_{2g}^3e_g^2)$ is not orbitally active, the existence of only 1/2 of the B-site orbitally active Mn$^{3+}$ $(t_{2g}^3e_{g1})$ weakens the Jahn-Teller (JT) effect compared to Mn$_3$O$_4$, resulting in a significantly reduced cubic-tetragonal structural transition temperature by ∼ 1433-750=683 K. It also helps understand a smaller lattice distortion $c/a \approx 1.06$ in FeMn$_2$O$_4$ as compared to $c/a \approx 1.16$ in Mn$_3$O$_4$. The magnetic properties change dramatically although both compounds belong to the same tetragonal space group. Mn$_3$O$_4$ exhibits three magnetic transitions. A FI order occurs at ∼ 43 K, followed by an incommensurate spiral order below ∼ 39 K. Below ∼ 33 K, it shows a noncollinear ferrimagnetic order. As discussed above, FeMn$_2$O$_4$ shows two magnetic transitions. The ground-state magnetic structures are distinct between these two compounds, as illustrated in Fig. 9(a-b,e-f). In Mn$_3$O$_4$ with the magnetic space group $Pb'c'n$, there are
two magnetic sublattices at the B site. While the moment of the A-site Mn$^{2+}$ points to the $b$ axis, the Mn$^{3+}$ spins at both the B1 (0 0 0.5) and B2 (0.25 0.75 0.75) sites are canted, with slightly different moment sizes (3.64 $\mu_B$ at the B1 site and 3.25 $\mu_B$ at the B2 site) and canting angles. The component on the $c$ axis for the B2-site Mn$^{3+}$ spins is aligned antiparallelly, which leads to a magnetic unit cell doubled compared to the chemical unit cell, i.e., $k_1=(0,1/2,0)$. The spin ordering of the B-site Mn$^{3+}$ in the pyrochlore sublattice is displayed in the Fig. 9(f). In FeMn$_2$O$_4$, the A-site Mn$^{2+}$ moment points to the $a_T$ axis, equivalent to the $b_T$ axis in Mn$_3$O$_4$ due to the tetragonal symmetry. In contrast, only the B2-site moment is canted to the $c_T$ axis in FeMn$_2$O$_4$, with the magnetic unit cell identical to the chemical unit cell. The B-site spin ordering in the pyrochlore sublattice of FeMn$_2$O$_4$ is shown in Fig. 9(e).

Figure 9: Comparison of the magnetic structures and magnetic space groups of (a) FeMn$_2$O$_4$, (b) Mn$_3$O$_4$, (c) MnV$_2$O$_4$ and (d) FeV$_2$O$_4$. The bottom panel shows the corresponding spin order in the B-site pyrochlore lattice only. Within the pyrochlore lattice, there are two magnetic sublattices B1 and B2 in FeMn$_2$O$_4$ and Mn$_3$O$_4$, whereas there is only one magnetic site in MnV$_2$O$_4$ and FeV$_2$O$_4$. The main magnetic interactions in the pyrochlore lattice are also labeled.
Roles of B-site $\text{Fe}^{3+}/\text{Mn}^{3+}$ cations

To understand the roles of the B-site cations, we compare $\text{FeMn}_2\text{O}_4 (\text{Mn}^{2+})_A (\text{Mn}^{3+}\text{Fe}^{3+})_B \text{O}_4$ with $\text{MnV}_2\text{O}_4 (\text{Mn}^{2+})_A (\text{V}^{3+})_B \text{O}_4$. $\text{MnV}_2\text{O}_4$ exhibits a collinear FI transition with net moment along the tetragonal $c_T$ axis near 60 K. At a slightly lower temperature, 58 K, a noncollinear FI order occurs with a net moment along the $c_T$ axis, accompanied by a simultaneous cubic-tetragonal structural transition to a space group $I4_1/a$. The structural transition is driven by the orbitally active $\text{V}^{3+} (t^2_2 e^0_g)$ with the $t^2_2$ degeneracy that induces a contraction of the VO$_6$ octahedron along the $c_T$ axis yielding $c < a$. In sharp contrast, $\text{Mn}^{3+} (t^3_2 e^1_g)$ involving the $e^1_g$ degeneracy in $\text{FeMn}_2\text{O}_4$ gives rise to the elongation of the octahedron along the $c_T$ axis with $c > a$. The distinct orbital freedom between these two compounds results in different moment directions via spin-orbit coupling, i.e., along the $c_T$ axis in $\text{MnV}_2\text{O}_4$ and the $a_T$ axis in $\text{FeMn}_2\text{O}_4$. In addition, the noncollinear FI order of $\text{MnV}_2\text{O}_4$ below $T_N$ is very different from $\text{FeMn}_2\text{O}_4$. The magnetic space group of $\text{MnV}_2\text{O}_4$ is $I4_1/a$ where there is only one magnetic B site with the moment canted to the same angle of 65.12° relative to the A-site moment despite the B-site spin canting directions are different as illustrated in Fig. (c) and (g).

Roles of A-site $\text{Mn}^{2+}$ cation

In $\text{Mn}_3\text{O}_4$, $\text{MnV}_2\text{O}_4$, and $\text{FeMn}_2\text{O}_4$, what is in common is $\text{Mn}^{2+}$ at the A site. The ordered moment for $\text{Mn}^{2+}$ in these three compounds is $\approx 4.5 \mu_B$, indicating that it is in the high spin state $(t^3_2 e^2_g)$. Thus, the A-site $\text{Mn}^{2+}$ is not an orbitally active cation and should not contribute to the structural transition in these compounds. However, the A-site $\text{Mn}^{2+}$ is necessary for forming both collinear FI and noncollinear FI orders via the antiferromagnetic interactions $J_{AB}$ with the B-site moment. The strength of $J_{AB}$ and the moment direction of $\text{Mn}^{2+}$ depend on the B-site cations. As characterized by the magnitude of $T_{N1}$, $J_{AB}$ is weak in $\text{Mn}_3\text{O}_4 (T_{N1} = 43K)$ and $\text{MnV}_2\text{O}_4 (T_{N1} = 60K)$, but is much stronger in $\text{FeMn}_2\text{O}_4$ due to the presence of $\text{Fe}^{3+}$ at the B site. The moment direction of $\text{Mn}^{2+}$ points to the $c_T$ axis in $\text{MnV}_2\text{O}_4$, whereas it points to in-plane $a_T$ (or $b_T$) direction in $\text{Mn}_3\text{O}_4$ and $\text{FeMn}_2\text{O}_4$. 

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As discussed above, this is related to the difference between $t_{2g}^2$ degenerate V$^{3+}$ and $e_g^1$ degenerate Mn$^{3+}$. It should be noted that there is a negligible change in the A-site Mn$^{2+}$ moment below/above $T_{N2}$ in all these three compounds since the magnetic transition mainly occurs in the B-site pyrochlore lattice.

**Important roles of cation distributions in spinel oxides**

At a first glance, the only difference between FeV$_2$O$_4$ and FeMn$_2$O$_4$ is V vs Mn. However, the structural and magnetic transitions of FeMn$_2$O$_4$ are very different from those of FeV$_2$O$_4$. In FeV$_2$O$_4$, there exist three successive structural transitions: cubic-tetragonal ($c < a$) transition at $T_S = 138$ K, a tetragonal-orthorhombic transition at $T_{N1} = 111$ K, and an orthorhombic-tetragonal ($c > a$) transition at $T_{N2} = 56$ K. The latter two structural transitions are accompanied with PM-CFI and CFI-NCFI transitions, respectively, with the net moments along the $c$ axis. The differences in structures and magnetic transitions are due to completely different cation distributions in these two compounds, leading to distinct orbital and spin degree of freedom. The cation distribution of FeV$_2$O$_4$ is (Fe$^{2+}$)$_A$(V$^{3+}$)$_B$O$_4$, in sharp contrast to (Mn$^{2+}$)$_A$(Mn$^{3+}$Fe$^{3+}$)$_B$O$_4$ in FeMn$_2$O$_4$. There are two orbitally active cations Fe$^{2+}$ ($e_g^3 t_{2g}^3$) at the A site and V$^{3+}$ ($t_{2g}^2 e_g^0$) at the B site, responsible for the rich structural and magnetic transitions in FeV$_2$O$_4$. The JT distortion at the Fe$^{2+}$ site favors the compression of the tetrahedron, leading to cubic-tetragonal transition with $c < a$. The cooperative orbital distortion manifested by an elongated FeO$_4$ and compressed VO$_6$ induces the low-T tetragonal structure with $c > a$. The orthorhombic structure in $T_{N2} < T < T_{N1}$ is the necessary intermediate regime between the switch of these two types of tetragonality. The net moments in both the CFI and NCFI regions point to the $c$ axis, with the magnetic space group $I4_1/am'd'$. In $T < T_{N2}$, all the V spins at the B site are canted, forming the “two-in-two-out" ice-rule spin order in the pyrochlore lattice, with the same canting angle $\sim 55^\circ$ relative to the moment direction of the A-site Fe moment (see Fig. 9 (d) and (h). All of these results reinforce the importance of cation distribution to understand the crystal and magnetic structures of the spinel oxides.
Ordering processes and magnetic interactions

The polyhedral distortion, structural and magnetic ordering processes in FeMn$_2$O$_4$ are summarized in Fig. 10. In the cubic structure ($Fd - 3m$), while the AO$_4$ shows a perfect tetrahedron, the BO$_6$ shows a large trigonal distortion along the $< 111 >$ direction. The effect of the trigonal distortion of VO$_6$ octahedra has been reported to vary in different vanadium spinels involving the $t^2_{2g}$ degeneracy. It has a negligible effect on the degenerate $t^2_{2g}$ orbitals in ZnV$_2$O$_4$. However, the trigonal distortion lifts the degenerate $t^2_{2g}$ orbitals and lowers the cubic symmetry from $Fd - 3m$ to $F4 - 3m$ in MgV$_2$O$_4$. In MnV$_2$O$_4$, the trigonal distortion splits the $t^2_{2g}$ orbitals into a singlet and a doublet separated by an energy gap and reduces site symmetry from cubic $O_h$ to $D_{3d}$. The effect of the trigonal distortion on the orbitals in the cubic phase of FeMn$_2$O$_4$ is unknown and requires further investigation.

Upon cooling to $T_S$, the highest energy term that comes into play is the JT effect of orbitally active Mn$^{3+}$(t$^3_{2g}$e$^1_g$) at the B site responsible for the cubic-tetragonal structural transition. The $e^1_g$ orbital degeneracy is lifted by the elongated octahedra along the $c$ axis, leading to the $d_{z^2}$ and $d_{x^2-y^2}$ singlets to host one electron. The distortion of the oxygen atoms also results in an elongation of tetrahedra along the $c$ axis. The elongated tetrahedra and octahedra along the $c$ axis results in cubic-tetragonal structural transition with elongated lattice constant $c$ and shortened lattice constant $a$ yielding $c > a$ ($c/a \approx 1.06$ at 500 K) in FeMn$_2$O$_4$, showing the strong orbit-lattice coupling at $T_S$. With cooling below $T_S$, both tetrahedral and octahedral distortion parameters $D_T$ and $D_O$ increase rapidly from 1 at 773 K to 1.027 and 1.068 at 500 K, respectively, indicating the enhancement of the elongations of both tetrahedron and octahedron.

As the temperature decreases to $T_{N1}$, the antiferromagnetic interaction $J_{AB}$ between the nearest-neighbor A and B spins, the second energy term, comes into play and leads to the antiparallel alignments of the A-site and B-site spins to form the Néel-type ferrimagnetic order. Such a magnetic transition has a strong effect on the polyhedral distortions via the spin-orbit coupling, yielding a further enhancement of the octahedral elongation and a
Figure 10: Sequence of the polyhedral distortions, structural and magnetic ordering processes in FeMn$_2$O$_4$. In the top panel, the thick open arrows indicate the trigonal distortion to the $<111>$ direction and the thin arrows illustrate the evolution of the bond lengths in different temperature regions. The dashed stealth arrows in $T < T_{N2}$ show representative and enlarged O-B-O bond angles near 95.7° and 96.4° (the correspondingly reduced O-B-O bond angles are not illustrated for clarity). The thick open arrows in the bottom panel show the change of the unit cell.

The suppression of the tetrahedral elongation upon cooling below $T_{N1}$. The magnetic interaction $J_{AB}$ also induces a decrease of the lattice constant $c$ and a slope change in $a$ upon cooling, which is closely associated with its effect on the octahedral and tetrahedral distortions. All of these results indicate a strong magnetoelastic coupling at $T_{N1}$.

With further decreasing the temperature to $T_{N2}$, the important energy terms are the AFM interactions within the B-site moments in the pyrochlore lattice, which come into play and induce the spin canting. The spin canting transition at $T_{N2}$ only induces modifications on the O-B-O bond angles by suppressing two low O-B-O angles in the octahedron and enlarging two high O-B-O angles without affecting the bond lengths of tetrahedron or octahedron or...
lattice constants. In Mn$_3$O$_4$, MnV$_2$O$_4$, and FeV$_2$O$_4$, two magnetic interactions within the pyrochlore lattice were found to be important: $J_{BB}$ in the $a_Tb_T$ plane and $J_{BB'}$ out of the $a_Tb_T$ plane as illustrated in Fig. 9(f-h). $J_{BB'}$ is very weak in Mn$_3$O$_4$ and FeV$_2$O$_4$ due to the $c$-axis elongation of the BO$_6$ octahedra, but is large and comparable to $J_{BB}$ in MnV$_2$O$_4$ related to the compressed BO$_6$ octahedra along the $c$ axis. The unique feature in the NCFI order of FeMn$_2$O$_4$ is that only the B2-site spins are canted while the B1-site moment direction remains unchanged. This suggests that besides $J_{BB'}$ out of the $a_Tb_T$ plane, there are probably two types of $J_{BB}$ in the $a_Tb_T$ plane, i.e., weak $J_{B1B1}$ and strong $J_{B2B2}$, as illustrated in Fig. 9(e). The competition of strong AFM $J_{B2B2}$ and AFM $J_{AB}$ induces a spin canting in the B2 site. But a small $J_{B1B1}$ cannot drive a spin canting within B1 sublattice. Due to the $c$-axis elongation of BO$_6$ octahedra, $J_{B1B2}$ should be weak as overlapping of the neighboring orbitals of (Fe$^{3+}$/Mn$^{3+}$)$_B$ spins is expected to be weak. Further theoretical calculations and the inelastic neutron scattering experiments are required to obtain the quantitative magnetic exchange couplings and to explore the microscopic origin of different magnetic interactions $J_{B1B1}$ and $J_{B2B2}$ in this compound.

Conclusions

In summary, we report the crystal structures, magnetic structures and their correlations with the polyhedral distortions in FeMn$_2$O$_4$ spinel. A first-order structural transition from cubic to tetragonal with a large thermal hysteresis (120 K) is found at high temperature ($T_S \approx 750$ K for the warming process). A large intrinsic trigonal distortion exists even in the cubic phase and extends to the tetragonal phase, which however does not contribute to the structural transition. Instead, the structural transition results from the elongation of both tetrahedra and octahedra driven by orbitally active Mn$^{3+}$ at the B site. This indicates the existence of the orbital-lattice coupling at $T_S$. Remarkably, we find the anomalies in polyhedral distortion and lattice constants driven by the collinear FI order with moment
along the $a_T$ axis, reflecting a strong magnetoelastic coupling at $T_{N1} \approx 400$ K. Such magnetoelastic coupling does not affect the bond angles in tetrahedra or octahedra. With further cooling to $T_{N2} \approx 65$ K, a noncollinear FI order with spin canting at only half of the B sites is found, which drives the anomalies in the O-B-O bond angles in the octahedra without affecting much the bond lengths of both tetrahedra and octahedra. Such a unique non-collinear magnetic ground state in the spinel family indicates that the magnetic couplings in the pyrochlore lattice can be distinct. The novel magnetic state and the interplay of spin, lattice and orbital degree of freedom presented here should motivate further experimental and theoretical work on FeMn$_2$O$_4$, its derivatives and more broadly other spinels.

**Experimental**

High quality polycrystalline samples were obtained by pulverizing the single crystals reported previously.$^{17}$ High resolution neutron diffraction patterns at different temperatures were collected at the time-of-flight neutron diffractometer POWGEN in Spallation Neutron Source (SNS), located at Oak Ridge National Laboratory (ORNL). A POWGEN sample changer (PAC) and vacuum furnace were used as the sample environments to cover the temperature regions of 10-300 K and 300-1473 K, respectively. The neutron bank with center wavelength of 0.8 Å was used to cover a wide $Q$ region of 0.9-11.8 Å$^{-1}$. To track the temperature dependence of the integrated intensity and linewidth of the low-$Q$ nuclear or magnetic peaks, we collected neutron data at the Fixed-Incident-Energy Triple-Axis Spectrometer HB1A in High Flux Isotope Reactor (HFIR) at ORNL, taking advantage of the simple peak profile function in the data collected at HB1A. A constant-wavelength neutron beam with $\lambda = 2.36$ Å was used for data collection. A cryofurnace (JANIS) was employed to cover the temperature region between 5 K and 700 K. Rietveld refinement on the neutron data was performed by the FullProf package.$^{27}$ The symmetry-allowed magnetic structures were analyzed via the Bilbao Crystallographic Server.$^{28}$ To facilitate discussion, the cubic notation will be used
to index the nuclear and magnetic peaks as well as bond length directions unless otherwise noted.

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