Magnetic and structure transition of $\text{Mn}_{3-x}\text{Fe}_x\text{O}_4$ solid solutions under high-pressure and high-temperature conditions

Takamitsu Yamanaka$^{1,2}$ · Naohisa Hirao$^3$ · Yuki Nakamoto$^4$ · Takashi Mikouchi$^5$ · Takanori Hattori$^6$ · Kazuki Komatsu$^7$ · Ho-kwang Mao$^2$

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Abstract
Magnetic and structure transitions of $\text{Mn}_{3-x}\text{Fe}_x\text{O}_4$ solid solutions under extreme conditions are clarified by neutron time-of-flight scattering diffraction and X-ray Mössbauer measurement. The ferrimagnetic-to-paramagnetic transition temperature (100 °C) of $\text{Mn}_2\text{Fe}_2\text{O}_4$ spinel is different from the tetragonal-to-cubic structure transition temperature (180 °C). The structure transition temperature decreases with increasing pressure. The transition is not coupled with the magnetic transition. Synchrotron X-ray Mössbauer experiments have revealed the pressure effects on the distribution of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ at the tetrahedral and octahedral sites in the spinel structure. Ferrimagnetic $\text{MnFe}_2\text{O}_4$ and $\text{Mn}_2\text{Fe}_2\text{O}_4$ spinels show sextet spectral features with hyperfine structure elicited by internal magnetic fields. Cubic $\text{MnFe}_2\text{O}_4$ spinel and tetragonal $\text{Mn}_2\text{Fe}_2\text{O}_4$ transform to high-pressure orthorhombic postspinel phase above pressures of 18.4 GPa and 14.0 GPa, respectively. The transition pressure decreases with increasing Mn content. The postspinel phase has a paramagnetic property. $\text{Mn}_2\text{O}_{10}$ dimers of two octahedra are linked via common edge in three dimensional direction. The occupancy of $\text{Fe}^{2+}$ in the tetrahedral site is decreased with increasing pressure, indicating more ordered structure. Consequently, the inverse parameter of the spinel structure is increased with increasing pressure. The magnetic structure refinements clarify the paramagnetic and ferrimagnetic structure of $\text{MnFe}_2\text{O}_4$ and $\text{Mn}_2\text{Fe}_2\text{O}_4$ spinel as a function of pressure. The magnetic moment is ordered between A and B sites with the anti-parallel distribution along the $b$ axis. The nuclear tetragonal structure ($a_N$, $a_N$, $c_N$) has the ferrimagnetic structure but the orthorhombic magnetic structure has the ferrimagnetic structure with the lattice constants ($a_M$, $b_M$, $c_M$). The magnetic moment is ordered between A and B sites with the anti-parallel distribution along the $b_M$ axis.

Keywords Magnetic structure analysis by neutron diffraction · Pressure dependence of the site occupancy · X-ray Mössbauer measurement at high pressure · Magnetic and structure transition under compression · Charge transfer of spinel at high pressure
Introduction

Important information about plate tectonics and geomagnetic reversals has been derived from measurements of remnant magnetization of spinels in basalts. Spinels are also the most fundamental magnetic compounds in industrial applications. Their magnetic properties, charge transfer and electrical resistivity changing under high-pressure conditions are significant research issues of intensive studies. The iron bearing spinels are the most fundamental magnetic compounds in industrial applications (Fei et al. 1999; Lavina et al. 1994; Jackson et al. 2005; Lin et al. 2013).

Numerous investigations have been conducted on the temperature dependence of the cation distribution in Mn$_{3-x}$Fe$_x$O$_4$ spinel solid solution. (Hasting 1956; Rieck et al. 1966). Their phase stabilities and structures under extreme conditions have been studied. (Xu et al. 2004; Kirby et al., 1996; Yamanaka et al. 2001). The Curie temperature of Mn$_3$O$_4$ of about – 250 °C was reported by Boucher et al. (1971); Ole’s, et al. (1976); Chardon et al. (1986).

Curie temperatures in these spinels increase with increasing Fe content: 140 °C in Mn$_3$FeO$_4$ (synthetic ferrite), 290 °C in MnFe$_2$O$_4$ (jacobsite) and 585 °C in Fe$_3$O$_4$ (magnetite) (Nakagiri et al. 1986; Willerd et al. 1999).

In the present experiment, magnetic and structure studies of MnFe$_2$O$_4$ and Mn$_2$FeO$_4$ were conducted using neutron time-of-flight scattering diffraction under high-pressure condition at PLANET J-PARC (Hattori et al. 2015). Our previous Raman spectroscopic studies and synchrotron X-ray powder diffraction studies of various postspinels have proposed orthorhombic phases of CaFe$_2$O$_4$-type (Pmma), CaTi$_2$O$_4$-type (Ccmm) and CaMn$_2$O$_4$-type (Pbcm) structures as high-pressure polymorphs of different spinels (Yamanaka et al. 2008). Transformations of the oxide spinels are summarized in Table 1. These phases further transform to a new phase by martensitic transformation to a maximal isotropic subgroup structure.

X-ray structure analysis of Mn$_{3-x}$Fe$_x$O$_4$ causes an ambiguity, because X-ray atomic scattering factors of Fe (26) and Mn (25) are extremely similar. Neutron diffraction, however, has an effective advantage for the precise diffraction studies of Mn$_{3-x}$Fe$_x$O$_4$ because of the big difference in the coherent scattering lengths of Mn (~ 3.73 fm) and Fe (9.54 fm). X-ray powder diffraction study at high pressures up to 40 GPa has been also performed by synchrotron radiation at Photon Factory using symmetric diamond anvil pressure cell (DAC) in this experiment.

Mössbauer spectroscopy (MS) study is the effective method to investigate the iron electronic properties at high pressure. MS allows distinguishing between ferric and ferrous ions. High and low spin states of Fe and their relative abundance in substances are clarified. MS studies of high-pressure Fe$_3$O$_4$ (h-Fe$_3$O$_4$) at ambient temperature have been carried out by Pasternak et al. (1994). The cation distributions in spinels at ambient conditions were reported by Mössbauer experiments and NMR studies (Yasuoka et al. 1967; Singh et al. 1981). Hyperfine-structure spectra changes of ferrites were reported as a function of pressure (Kobayashi et al. 2006).
The pressure dependence of the site occupancy and their magnetic structures were determined. In the present study, neutron diffraction at high pressure and high temperature has been conducted. The precise cation distribution has been elucidated by use of the significant difference in coherent scattering lengths between Mn and Fe. Furthermore, Fe$^{2+}$ and Fe$^{3+}$ distributions have been clarified by synchrotron X-ray Mössbauer experiments at increasing pressure. We also investigated the electrical resistivity measurement with increasing pressure up to 40 GPa to elucidate the enhancement of electrical conductivity from semiconductor to metal in Mn$_3$Fe$_2$O$_4$ spinel and postspinel with increasing pressure (Yamanaka et al. 2022). The observed enhancement of electrical resistivity with increasing pressure is shown in Supplement file 1.

**Table 1** Transformations of the oxide spinels are summarized in three types. of CaTi$_2$O$_4$, CaFe$_2$O$_4$ and CaMn$_2$O$_4$

| Compound          | Press (GPa) | method | reference                        |
|-------------------|-------------|--------|----------------------------------|
| Cubic spinel-to-postspinel |             |        |                                   |
| ZnFe$_2$O$_4$     | 24.6 GPa    | DAC    | Raman                           |
| ZnFe$_2$O$_4$     | 24.4 GPa    | quenched | XRD | Z. Wang et al (2003a, b)          |
| CoFe$_2$O$_4$     | 32.5 GPa    | DAC    | Raman                           |
| MgFe$_2$O$_4$     | 24.6 GPa    | DAC    | XRD                             |
| Fe$_3$O$_4$       | 24 GPa      | DAC    | XRD                             |
| Fe$_3$O$_4$       | 21.8 GPa    | DAC    | XRD                             |
| Fe$_3$O$_4$       | 2***        | DAC    | XRD                             |
| MgCr$_2$O$_4$     | 14.2 GPa    | DAC    | Raman                           |
| Fe$_2$TiO$_4$     | 16 GPa      | DAC    | XRD                             |
| FeCr$_2$O$_4$     | 12-16 GPa   | quenched | XRD | T. Ishii et al (2014)          |
| Fe$_2$TiO$_4$     | 15 GPa      | quenched | XRD | M. Akaogi (2019)  |
| MnFe$_2$O$_4$     | 18 GPa      | DAC    | XRD                             |
| MnFe$_2$O$_4$     | 18 GPa      | DAC    | NRD                             |
| MgAl$_2$O$_4$     | 25 GPa      | quenched | XRD | M. Akaogi (1999)  |
| Tetragonal spinel-to-postspinel |             |        |                                   |
| Mn$_3$O$_4$       | 7.2 GPa 673 K | quenched | XRD | J. Darul (2013)          |
| Mn$_3$O$_4$       | 10 GPa      | DAC    | XRD                             |
| Mn$_2$FeO        | 13 GPa      | DAC    | NRD                             |
| MgMn$_2$O$_4$     | 30 GPa      | DAC    | XRD                             |
| CoFe$_2$O$_4$     | 32.5 GPa    | DAC    | XRD                             |

Postspinels transform from CaMn$_2$O$_4$ to the CaTi$_2$O$_4$ structure with increasing pressure. The latter phase further transforms to new phase with multisite transformation by maximal isotropic subgroup structure change (Yamanaka et al. 2008).

**Experiment**

Powder samples of MnFe$_2$O$_4$ and Mn$_3$Fe$_2$O$_4$ were prepared by solid–solid reaction at ambient pressure. To prepare the samples used for X-ray Mössbauer experiment, isotope-enriched samples with 30% $^{57}$Fe content were prepared. The sample preparation is detailed in the supplement file 2. Neutron diffraction experiment was executed at BL-11 J-PARC (Japan Proton Accelerator Research Complex, Japan Atomic Energy Agency) under high-pressure using spallation neutron time-of-flight (TOF) facility. We used a Paris–Edinburgh (PE) press (VX4) for the experiments at pressures up to 40 GPa at room temperature (Hattori et al. 2019), and also a large-volume six-axis multi-anvil press ATSUHIME at PLANET J-PARC (Sano-Furukawa et al. 2014) for the experiments at pressures to 10 GPa and high temperatures up to 2000 °C. Incident neutron wavelength is 0.3 Å–5.8 Å and beam size is 15 mm × 15 mm at maximum.
We performed Rietveld analyses of neutron diffraction data to refine the nuclear structure and magnetic structure. The analysis is conducted using the program GSAS (Larson et al. 1994; Toby 2001). The integrated intensity $I_o$ is produced by combination of magnetic scattering factor $F_M(h)$ and nuclear scattering factor $F_N(h)$:

$$I_o = s(h)A(h)L(h)m(h) \{ |F_N(h)|^2 + |F_M(h)|^2 \},$$  

where $s$: scale factor, $A$: absorption, $L$: Lorentz factor and $m$: multiplicity.

The nuclear structure factor $F_N(h)$ for neutron diffraction is expressed by

$$F_N(h_k) = Sg_b T_j \exp\{2\pi i(hx_j + ky_j + lz_j)\},$$

where $T_j$ is the temperature factor of j atom. $\gamma$ indicates the $\gamma$-factor of the nuclear magneton.

$$\gamma = 1.913, b = \text{the scattering length } (b_{\text{Mn}} = -3.73 \text{ fm}, b_{\text{Fe}} = 9.54 \text{ fm}).$$

And magnetic scattering factor $F_M(h)$ is

$$F_M(h_k) = g e^2 / 2mc^2 \sqrt{1 - \cos^2 h} > xf(h_k) Sg_b T_j \exp\{2\pi i(hx_j + ky_j + lz_j)\},$$

where $\mu$ is magnetic moment.

The detailed derivation of the neutron diffraction refinement is presented in the Supplement file 3.

Neutron diffraction experiments cannot provide precise information about the distribution of Fe$^{2+}$ and Fe$^{3+}$ between the A and B sites in the Mn–ferrite spinel and the M1 and M2 sites of the postspinel structure under high pressure. We measured the synchrotron X-ray Mössbauer spectra of the Mn$_{3-x}$Fe$_x$O$_4$ solid solution at SPring-8 BL-10XU (Hirao et al. 2020) under high pressure using micro-beam with the wavelength of 14.4 keV and diamond anvil cell (DAC). A symmetric diamond anvil cell was used to generate high pressure. Ne gas was used as a pressure transmitting media. Rh gasket of 200 µm thick was preindented to 80 µm. High-pressure measurement was performed by ruby-fluorescence scale.

We used the program MossA (Prescher et al. 2012) for the analysis of our Mössbauer spectra and determined the cation distribution as a function of pressure. Deviations from Lorentzian profile shape may have to be fitted using Voigtian (a convolution of Gaussian and Lorentzian functions). The full width half maxim (FWHM) of spectrum is related to the positional disorder of cations.

The isomer shift is referred to the spectrum from zero velocity of the $^{57}$Fe spectrum in Fe$_2$O$_3$. The peak positions of the spectra were detected within an error of less than $\pm 0.05$ mm/sec. The internal magnetic fields of the hyperfine structure spectra were determined with the reference of 26.26 T (330 kOe) of the $^{57}$Fe in Fe$_2$O$_3$ spectrum.

### Result and discussion

#### Pressure effect on the cooperative Jahn–Teller distortion of Mn$_2$FeO$_4$ spinel phase

Mn$_{3-x}$Fe$_x$O$_4$ spinel structure transforms to high-pressure phase of orthorhombic CaMn$_2$O$_4$-type postspinel structure. Present neutron diffraction study reveals the phase diagram of Mn$_{3-x}$Fe$_x$O$_4$ under high pressure at ambient temperature, which is presented in Fig. 1. Structure transition from tetragonal to cubic of Mn$_2$FeO$_4$ spinel under pressure at 20 °C is shown as a function of normalized unit-cell volume. Mn$_2$FeO$_4$ and MnFe$_2$O$_4$ spinel transform to postspinel at different pressures at 14.0 GPa and 18.4 GPa, respectively. Present neutron diffraction patterns of Mn$_2$FeO$_4$ at 2.2 GPa in the heating experiment disclose the tetragonal-to-cubic transition temperature at 180 °C. The cooling experiments show the back transformation from cubic structure to the tetragonal structure at 140 °C. The tetragonal-to-cubic transition is reversible and shows hysteresis, as shown in Fig. 2.

Mn$^{3+}$ (3$d^4$) prefers octahedral configuration in the strong ligand field. In the Mn$_{3-x}$Fe$_x$O$_4$ solid solution, Mn-rich phases present lattice distortion due to the cooperative Jahn–Teller (JT) effects. At ambient pressure, Mn$_2$O$_4$ transforms from tetragonal (I$4_1$/amd $z=4$) to cubic (Fd$_3$m $z=8$)

![Fig. 1 Phase diagram of Mn$_{3-x}$Fe$_x$O$_4$ under high pressure at ambient temperature](image)

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at 1170 °C (McMurdie et al. 1950) with vanishing JT effect. The phase has an elongated structure along the c-axis with $c/a > 1$.

The tetragonal-to-cubic transition temperature of $\text{Mn}_2\text{FeO}_4$ is 160 °C at 3 GPa and 180 °C at 1 GPa by the temperature dependence of $c/a$. These experiments prove the transition temperature decreases with increasing pressure. The $P$–$T$ boundary between the tetragonal and cubic phases has a negative slope. The distortion of the elongation along the c-axis disappears in the cubic $\text{Mn}_2\text{FeO}_4$. The lattice distortion may be reduced with increasing temperature and finally the lattice constant ratio becomes $c/a = 1$, resulting in the transformation to the cubic symmetry ($c = a$).

The two-phase mixtures with postspinel are found in the transition region (Fig. 3). The normalized unit-cell volumes of the three phases of cubic, tetragonal spinel and orthorhombic postspinel are shown in the figure. Both spinels have two-phase mixture regions with high-pressure postspinel phase.

The present transition case from tetragonal-to-cubic phase of $\text{Mn}_2\text{FeO}_4$ is extremely rare for the JT transition under compression. The following spinels: $\text{Fe}_2\text{TiO}_4$ (Yamanaka et al. 2013), $\text{FeCr}_2\text{O}_4$ (Kyono et al. 2011a, b), $\text{ZnMn}_2\text{O}_4$ (Choi et al. 2006), $\text{CuMn}_2\text{O}_4$ (Waskowska et al. 2001), $\text{CuFe}_2\text{O}_4$ (Kyono et al., 2015), $\text{ZnGa}_2\text{O}_4$ (Errando-nea et al. 2009), $\text{NiMn}_2\text{O}_4$ (Åsbrink et al., 1988), transitions from cubic-to-tetragonal spinel show the with increasing pressure. Many of them have the tetragonal distortion with flattened octahedral distortion along the c-axis ($c/a < 1$). The octahedral site of the tetragonal phase of $\text{Mn}_2\text{FeO}_4$ is elongated along the c-axis and the lattice constant ratio $c/a > 1$ according to the crystal field stabilization energy (CFSE). Topological presentation is developed from the JT distortion. Pressure dependence of cooperative JT distortion in $\text{Mn}_2\text{FeO}_4$ is caused by localized orbital electronic states of $\text{Mn}^{3+}$ under extreme conditions.

The result of the structure refinements of cubic $\text{MnFe}_2\text{O}_4$ and tetragonal $\text{Mn}_2\text{FeO}_4$ are presented in Supplement Table 1 and Supplement Table 2. The site occupancies are also presented in these tables. Their bond distances of $\text{A–O}$
and B–O together with AO₄ tetrahedral volume and BO₆ octahedral volume are presented in the tables.

The magnetic interaction is induced by supper exchange mechanism via oxygen. A–O and B–O bond distances and A–O–B bond angle are strongly related for the mechanism.

The compressions of the inter-nucleus distances A–A, A–B and B–B are strongly affected to the supper exchange. The B–B distance is much smaller than the other two A–A and A–B distances (Fig. 4). Then, the super-exchange between the B and the adjacent B cation is easier to gain extremely low resistivity. With compression, B–B shorter distance promotes a higher conduction. The B–B super-exchange model in the corner sharing octahedra is shown in Fig. 5. Super exchange for the electron hopping between Fe²⁺ and Fe³⁺ ion is more possible.

### Cation ordering

MnFe₂O₄ and Mn₂FeO₄ compounds are composed of the mixed-charge elements and their ionic radii are similar. According to the effective ionic radii (Shannon et al. 1969) and cation site preference (Duniz et al. 1957, 1960), positional change of these cations may be possible at high pressure. The distortions of the tetrahedral and octahedral sites make cation exchange possible by compression.

The cation exchange is common at high temperature and thermal atomic vibration is a strong mechanism for the cation positional change. Charge transfer in Fe²⁺, Fe³⁺, Mn²⁺ and Mn³⁺ is often observed in many experiments. Neutron diffraction studies show the change of the site occupancies at the A and B site and A–O and B–O distances at extreme high pressures. The bond distances at the A and B sites of Mn–O and Fe–O were evaluated through neutron diffraction study. The site occupancies have a significant effect on electrical conductivity. The magnetic moments of the A and B sites in the MnFe₂O₄ and Mn₂FeO₄ spinel structures were also clearly observed. The inverse parameter \(i\) of the spinel structure in \((\text{Mn}^{2+} \text{Fe}^{3+}_{1-i})\[\text{Mn}^{3+}_{1-i} \text{Fe}^{2+}_{i} \text{Fe}^{3+}_{2i}\]O₄\) could be precisely defined for MnFe₂O₄. At high pressure, just before the transition pressures of the respective samples, they more closely adopt the normal spinel structure with \(i = 1\). The inverse parameter of MnFe₂O₄ is presented as a function of pressure in Fig. 6.
Mössbauer resonance experiment also shows Fe\textsuperscript{2+} and Fe\textsuperscript{3+} positional change in the A and B site at high pressure. Mössbauer spectra indicate two hyperfine structures of sextet patterns indicating ferrimagnetic moment of the A and B sites of MnFe\textsubscript{2}O\textsubscript{4} cubic spinel at 0.25 GPa and 300 K in Fig. 7. The spectrum of the A site is assigned to Fe\textsuperscript{3+} in the tetrahedral site. The spectrum of the octahedral site (B) site is assigned to mixture of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} in the octahedral site. Intensity spectra ratio of the A and B site is presented.

Mössbauer spectra of MnFe\textsubscript{2}O\textsubscript{4} cubic spinel at 10.0 GPa and 300 K are shown in Fig. 8 and they indicate two hyperfine structures of sextet patterns to the spectra at 0.25 GPa shown in Fig. 5. Internal magnetic field observed from the both sextets at A and B sites are not changed between two pressures, 0.25 and 10.0 GPa.

Under further compression at 17.0 GPa 300 K shown in Fig. 9, Mössbauer spectrum of MnFe\textsubscript{2}O\textsubscript{4} cubic ferrimagnetic phase shows one doublet indicates the Fe\textsuperscript{3+} spectrum at the tetrahedral site One sextet shows the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} spectrum at the octahedral site are shown. The former spectrum proves neither hyperfine structure and nor internal magnetic field.

Mössbauer spectra of MnFe\textsubscript{2}O\textsubscript{4} cubic spinel at 10.0 GPa and 300 K are shown in Fig. 8 and they indicate two hyperfine structures of sextet patterns indicating ferrimagnetic moment of the A and B sites, which is a very similar spectra of the spectra in Fig. 7. Internal magnetic field observed from the both sextets at A and B sites are not changed between two pressures, 0.25 and 10.0 GPa.
the hyperfine structure at the A site is not observed but the spectrum at the B site shows the internal magnetic field.

Neutron diffraction study of MnFe₂O₄ and Mn₂FeO₄ spinels indicates the ferrimagnetic cubic spinel structure at pressures up to 17.4 GPa and 14.0 GPa, respectively. Mössbauer spectra do not show any remarkable change up to 12.5 GPa. However, at 17.0 GPa the spectrum changes from sextet to doublet, proving neither hyperfine structure and nor internal magnetic field and magnetic moment of magnetic ions disappears, as shown in Fig. 9. Peak width of the sextet spectrum becomes broad at 17.0 GPa. The positional disorder of magnetic ions in the octahedral (B) site induces the peak broadening of the large FWHM in the spectrum.

Mössbauer spectra of the orthorhombic postspinel Mn₂FeO₄ at 18.0 GPa and 300 K have two doublets, as shown in Fig. 10. One indicates the sixfold octahedron indicating Fe³⁺ in the octahedral site (M2 site). Another doublet represents Fe²⁺ in the highly distorted eightfold large cation site (M1 site) with good reason of a large quadruple splitting. Two doublets of the Mössbauer spectra of postspinel indicate paramagnetic behavior. The result of Fe²⁺ and Fe³⁺ distributions in the VIIIM₁ and VIIM₂ sites is expressed by the following cation distribution: VIIIM₁[Fe²⁺₀.746,Fe³⁺₀.254]VI (Mn³⁺₀.628,Fe³⁺₀.372)₂O₄. There is no sextet in the postspinel phases of Mn₂FeO₄ and MnFe₂O₄ proving they are paramagnetic at high pressures.

In the Mössbauer spectra, the relative intensities of individual components possibly give a suggestion of the corresponding population. The intensities of the various peaks reflect the relative concentrations of cations. Observed site occupancies are estimated from the peak intensities of the Mössbauer spectra of MnFe₂O₄ and Mn₂FeO₄ at various pressures. The following data: (1) the isomer shift (δ), (2) the quadruple splitting (Δ) and (3) the magnetic hyperfine field (B₀) are presented in Table 2. Peak intensity (Int) ratios of two or three spectra are also presented.

Two sextets of the spectra of MnFe₂O₄ cubic spinel at pressures from 1 atm to 12.5 GPa do not show a big difference in their peak intensities in Table 2 but show a slight increase in the intensity ratio with increasing pressure. The hypothetical structure proposed from the intensity ratio of two sextet spectra of the MS experiment gives the cation distribution, which is somewhat different from the result of the neutron diffraction structure analysis.

The distortion of Mn₃FeO₄ and MnFe₂O₄ spinels under compression are related to their elastic properties. The compression behavior of MnₓFe₄O₄ spinels can be described by third-order Birch–Murnaghan equation of state. The equation of state is given by

\[ P(V) = \frac{3B_0}{2} \left[ \frac{V_0}{V} \right]^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \left\{ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right\} \]  

where \( P \) is the pressure, \( V_0 \) is the reference volume, \( V \) is the deformed volume with respect to pressure, \( B_0 \) is the bulk modulus, and \( B'_0 \) is the derivative of the bulk modulus. The bulk modulus and its derivative are usually obtained from fits to experimental data and are defined as

\[ B_o = -V(\partial P/\partial V)_{P=0} \quad \text{and} \quad B'_o = (\partial B/\partial P)_{P=0}. \]  

The equations of state of MnFe₂O₄ and Mn₂FeO₄ show the difference in their transition pressures. Bulk modules of Mn₃₋ₓFeₓO₄ spinel solid solutions are presented in Table 3. MnFe₂O₄ and Mn₂FeO₄ are characterized by cation disorder and are more compressible than the end-members of the solid solution. MnFe₂O₄ is less compressible than Mn₂FeO₄.

**High-pressure polymorph postspinel phase**

Magnetite undergoes a phase transition to a high-pressure (HP) form, called h-Fe₃O₄ above 25 GPa and defined to be postspinel of CaMn₂O₄ (Pbcm) structure. Postspinel is characterized by herringbone structure, shown in Fig. 11. The present X-ray Mössbauer spectra analyses and neutron diffraction experiments describe the cation distributions of Mn and Fe. The structure refinements of postspinel of Mn₃FeO₄ at pressures up to 26.8 GPa are presented in Supplement Table 3. (The refinement of the quenched sample is also presented in the table.) The VIIIM₁ site volume is much larger than the VIIM₂ site. The VIIIM₁ site of Mn₂FeO₄ and MnFe₂O₄ postspinel is mostly occupied by Mn²⁺.
Mn$_2^+$, which increases with increasing pressure. The VIM$_2^+$ site of MnFe$_2$O$_4$ is occupied by mainly Fe and only small amount of Mn. On the other hand, the VIM$_2^+$ of Mn$_2$FeO$_4$ is half-occupied by Mn. The phase of Mn$_2$FeO$_4$ is composed of an almost ideal ordered structure of VIII[Mn$_2^+$]VI(Mn$_{3+}$0.5 Fe$_{3+}$0.5)$_2$O$_4$. The atoms in the VIM$_2^+$ site are located on the edge-sharing plane perpendicular to the c-axis, as shown in Fig. 11. Mn$_2$O$_{10}$ dimers of two octahedra in the structures are linked via common edges.

**Table 2** Mössbauer spectra analyses of MnFe$_2$O$_4$ (cubic spinel), Mn$_2$FeO$_4$ (tetragonal spinel) and postspinel (CaMn$_2$O$_4$ type) of Mn$_2$FeO$_4$

| Pressure | Structure | Site | Ion                  | $\sigma$ mm/s | $\Delta$mm/s | Int % | $B_{HF}$ Oe |
|----------|-----------|------|---------------------|---------------|--------------|-------|-------------|
| 0.0001 GPa | Tetra     | IV A | Fe$^{3+}$           | 0.072(0.032)  | 0.032(0.020) | 12.3  | 366(12)     |
|          |           | VIB  | Fe$^{2+}$ + Fe$^{3+}$ | 0.056(0.016)  | 0.025(0.056) | 87.7  | 406(7)      |
| 10.0 GPa | Tetra     | IV A | Fe$^{3+}$           | -0.094(0.029) | 0.668(0.024) | 5.9   |     |
|          |           | VIB  | Fe$^{2+}$           | -0.034(0.016) | 0.018(0.056) | 7.5   |     |

The isomer shift (IS), quadruple splitting (QS), relative intensity (Int) and internal magnetic field (BIF) of each site of MnFe$_2$O$_4$ spinel are presented in the table spinel

σ isomer (chemical) shift, $\Delta$ quadruple splitting, Int intensity ratio of area ratio of two spectra. BIF hyperfine magnetic field

The number in parentheses is the error of the last decimal. (1kOe = 103/4π[kA/m])

**Magnetic structure of Mn$_2$FeO$_4$ and Mn$_2$Fe$_2$O$_4$ spinel**

Present magnetic structure analysis of Mn$_2$FeO$_4$ and Mn$_2$Fe$_2$O$_4$ as a function of pressure is executed using the neutron diffraction intensity $I_p$. Integrated intensity $I_o$ is a combination of both magnetic scattering factor $|F_M(h)|^2$ and nuclear scattering factor $|F_N(h)|^2$ by Eq. (1). Present Rietveld refinement based on the ferrimagnetic structure discloses the tetrahedral and octahedral symmetry of the tetragonal-to-cubic transition with increasing pressure. The site symmetry 0.2$m$ of the octahedral (B) site in the tetragonal symmetry of $I4_1/amd$ changes to the symmetry of -3$m$ of the cubic symmetry of $Fd_{3m}$.

The diffraction peaks of 101 and 112 of tetragonal phase have a large contribution of magnetic scattering. The temperature evolution of the diffraction intensity of Mn$_2$FeO$_4$ at ambient pressure indicates that both peak intensities suddenly drop around 100 °C, which is displayed in Fig. 12. The magnetic transition temperature at 100 °C of ferrimagnetic-to-paramagnetic is different from the tetragonal-to-cubic structure transition temperature at 180 °C. The magnetic transition temperature is lower than that of the nuclear structure transition. The structure change is not coupled with magnetic transition.
The present magnetic refinement shown in Table 4 confirms the site occupancies at the A and B sites of Mn$_2$FeO$_4$ postspinel under elevating pressure. Magnetic moment distribution of the spinel and postspinel structure requires the effective magnetic susceptibility of cations. Effective Bohr magneton is used from extant published data defined by previous experiments: Mn$^{2+}$ (5.92 $\mu$B), Mn$^{3+}$ (4.90 $\mu$B), Fe$_2^+$ (4.90 $\mu$B) and Fe$_3^+$ (5.92 $\mu$B) (Neel 1948). Iron-rich members of the Mn$_{3-x}$Fe$_x$O$_4$ spinels have the magnetic structure of two-dimensional Yafet-Kittel triangular spin configuration. The magnetic structure of a powder sample of MnFe$_2$O$_4$ was determined by thermal neutron diffraction (Levy 2015). Spin moments of the A and B sites of the

![Postspinel structure of Mn$_2$FeO$_4$](image)

**Fig. 11** Postspinel is constructed by herringbone structure of the M1 octahedra array. The dimer of octahedra is distributed in three-dimensional space, eightfold M2 cation has shared edges with M1 cation and chained in the direction of the $b$ axis.

**Fig. 12** Difference in the transition temperature between the magnetic (ferrimagnetic-to-paramagnetic) and structure (tetragonal-to-cubic) transition of Mn$_2$FeO$_4$. Magnetic transition temperature is 100 °C and structure transition temperature is 180 °C.

The values of $B_0$ and $B'_0$ are changed with the site occupancy of Mn and Fe at the A and B sites. The equations of state of MnFe$_2$O$_4$ and Mn$_2$FeO$_4$ show the difference in their transition pressure.
Iron substitution on the magnetic property were clarified at temperatures 10 K and 295 K (Baron et al. 1998).

The influence of iron substitution on the magnetic properties is clarified in both ordered and disordered ferrimagnetic spinel-phases. Magnetic cations of Mn and Fe are located at the crystallographically special position in the tetragonal and cubic structure. Positional parameters of these cations are variable and magnetic moments are also variable parameters besides thermal variables. The reliability factor for the refinement is enhanced by the inclusion of magnetic moment effect. Nuclear structure analysis without consideration of magnetic moment effect was not converged properly.

Several possible magnetic space groups in nine subgroups of the tetragonal spinel structure of $I4_1$ are examined for the observed intensities. The magnetic space group of $I4_1$ is the most reliable subgroup of the space group symmetry of $I4_1$. Rietveld refinement of Mn$_2$FeO$_4$ at 2.2 GPa 20°C tetragonal $I4_1$ with the paramagnetic structure model is $\chi^2 = 10.51$ and $R(F^2) = 0.211$. We analyzed the diffraction intensities of the observed data in this study, because the quality of the data taken at high pressures in this study is not sufficient to discuss the detail of counted spins. The ferrimagnetic structure model based on the orthorhombic space group Pmma, (which is of an isomorphic subgroup of $I4_1$) shows much better agreement of $\chi^2 = 2.157$ and $R(F^2) = 0.117$. The lattice constants ($a_M$, $b_M$, $c_M$) of Mn$_2$FeO$_4$ of the present orthorhombic ferrimagnetic structure are derived from the nuclear tetragonal structure ($a_N$, $a_N$, $c_N$). The $b_M$ cell edge is twice larger than $b_N$ of the paramagnetic lattice, because the magnetic moment is ordered between A and B sites with the anti-parallel distribution along the $b_M$ axis. The Rietveld analysis is shown in Fig. 13. The distribution of the anti-parallel magnetic spins in A and B site are presented in the figure. Pressure dependence of magnetic structure was suggested by X-ray Mössbauer experiment. Deviations from ian profile may be induced from variations of local environments or fluctuations of parameters.

### Table 4

| Lattice constant | site occupancy | magnetic moment | $\chi^2$ | $R(F^2)$ |
|------------------|----------------|-----------------|---------|---------|
| Press(GPa) | $a$ (Å) | $c$ (Å) | Vol (Å$^3$) | Mn(tet) | Mn(oct) | A(tet) | B(oct) | total |
| 0.0001 | 5.9453 | 8.7844 | 10.98 | 0.902 | 0.548 | – | 2.002 | 4.655 | 2.653 | 2.173 | 0.222 |
| 2.2 | 5.9466 | 8.7498 | 309.41 | 0.916 | 0.542 | – | 1.186 | 3.314 | 2.128 | 2.957 | 0.167 |
| 4 | 5.9392 | 8.6494 | 305.1 | 0.934 | 0.533 | – | 0.077 | 2.043 | 1.966 | 3.866 | 0.178 |
| 6.4 | 5.9232 | 8.5094 | 301.39 | 0.964 | 0.524 | – | 1.556 | 3.166 | 1.61 | 3.099 | 0.139 |
| 10 | 5.9106 | 8.4167 | 294.69 | 0.962 | 0.519 | – | 0.003 | 3.381 | 1.378 | 6.239 | 0.211 |

Ferrimagnetic magnetic moments of individual A and B sites are shown. And the moment in the unit cell is presented in total. $\chi^2$ and $R(F^2)$ are accuracy parameters in the magnetic structure refinement.

### Fig. 13

Paramagnetic Mn$_2$FeO$_4$ tetragonal structure at 2.2 GPa is shown in the left figure. Right figure shows anti-parallel magnetic spin moments along the $c_M$ axis of the ferrimagnetic Mn$_2$FeO$_4$ orthorhombic structure at 2.2 $\chi^2R(F^2) = 0.117$. Only cations are presented in the figure. They are similar positions in the paramagnetic tetragonal structure. Ferrimagnetic lattice has $a_M$, $b_M$, $c_M$, and $b_M$ is twice large $b_N$ of the paramagnetic lattice becomes smaller at higher pressure before the transformation to the high-pressure postspinel phase.

Pressure dependence of magnetic structure was suggested by X-ray Mössbauer experiment. Deviations from ian profile may be induced from variations of local environments or fluctuations of parameters.

### Conclusion

Magnetic studies of minerals are reliable witnesses of paleomagnetism by high-resolution studies of these structures. The magnetic structures are built during the cooling of molten rock and reflect the earth’s magnetic field at the time of their formation. This record provides information on the past behavior of Earth’s magnetic field and geomagnetic reversal. The magnetic properties are reset by the interaction...
of the magnetic spin inside the Earth’s magnetic field. The geomagnetic reversal is an indicator of magnetic field change in plate tectonics. However, the pressure effect of the plate tectonics still remains to be seen in the magnetic study of minerals.

The present neutron diffraction and synchrotron X-ray Mössbauer spectroscopic study provide the comprehension of the magnetic and structure change under extreme conditions. Some of oxide spinels with transition elements have a ferrimagnetic property at ambient conditions. They transform to the postspinel structures under high-pressure condition. Cation distributions in Mn$_{3-x}$Fe$_x$O$_4$ solid solutions under extreme conditions are significant research subjects not only for geophysical understands such plate tectonics and geomagnetic reversals but also for the basic magnetic ferrite industrial materials. Magnetic and structure transition studies are possible by neutron time-of-flight scattering diffraction at PLANET J-PARC. Besides the neutron diffraction, X-ray Mössbauer experiment is a significant and complementary study to investigate the magnetic property of Mn$_{3-x}$Fe$_x$O$_4$ solid solutions from the hyperfine structure of Zeeman splitting. The present experiments disclosed the following new discoveries of magnetic properties:

(1) The lattice distortion is not coupled with magnetic transition. The magnetic transition temperature from ferrimagnetic-to-paramagnetic of spinels is lower than the structure transition temperature from tetragonal-to-cubic structure transition. The structure transition temperature decreases with increasing pressure.

(2) Pressure dependence of cooperative Jahn–Teller distortion in Mn$_2$FeO$_4$ is observed by the interaction between localized orbital electronic states of Mn$^{3+}$ and the compression of the octahedral site. The transition temperature from tetragonal-to-cubic phase decreases with increasing pressure. The transition of Mn$_2$FeO$_4$ is an extremely rare case for the JT transition with increasing pressure. Generally many spinels show cubic-to-tetragonal transition at high pressure and the tetragonal distortion is of flattening octahedral distortion of $c/a < 1$. However, the tetragonal phase of Mn$_2$FeO$_4$ shows the transformation from tetragonal-to-cubic and the octahedral site is elongated along to the $c$-axis and the lattice constant ratio is $c/a > 1$.

(3) Inverse parameter change under compression.

X-ray Mössbauer measurement and neutron diffraction study confirm that the occupancy of Fe$^{3+}$ in the tetrahedral site is decreased with increasing pressure, indicating more ordered structure. The inverse parameter is increased with increasing pressure.

(4) The cubic MnFe$_2$O$_4$ spinel and tetragonal Mn$_2$FeO$_4$ transform to the high-pressure orthorhombic postspinel phase at pressure 18.4 GPa and 14.0 GPa, respectively. The transition pressure decreases with increasing Mn content. The observed charge distribution of postspinel becomes an almost ideally ordered structure expressed by VIII[Mn$^{2+}$]VI(Mn$^{3+}$0.5Fe$^{3+}$0.5)$_2$O$_4$, transformed from cubic Mn$_2$FeO$_4$ spinel.

(5) The magnetic refinements clarify the paramagnetic and ferrimagnetic structure of MnFe$_2$O$_4$ and Mn$_2$FeO$_4$ spinel as a function of pressure. The magnetic moment is ordered between A and B sites with the anti-parallel distribution along the $b$ axis.

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