Study on magnetite oxidation using synchrotron X-ray diffraction and X-ray absorption spectroscopy: Vacancy ordering transition in maghemite (γ-Fe₂O₃)

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The oxidation process from magnetite to hematite through maghemite was investigated by X-ray diffraction (XRD) and X-ray absorption spectroscopic techniques. The XRD pattern of magnetite heated at 100 °C for 3 h showed small reflections of maghemite with partially ordered distribution of vacancy (space group P4₁32 or P4₃32). Thereafter, the XRD pattern of magnetite heated at 250 °C for 3 h exhibited extra reflections corresponding to the tetragonal maghemite with fully ordered distribution of vacancy (space group P4₁2₁2 or P4₃2₁2). Diffraction peaks of hematite occurred from the magnetite heated at 250 °C, in which maghemite and hematite coexisted with magnetite. Diffraction peaks of maghemite subsequently disappeared at 300 °C. Instead, maghemite and hematite dominated the XRD pattern, but the amount of maghemite reduced from 300 °C. The maghemite completely disappeared at 500 °C, and hematite finally dominated the XRD pattern. Rietveld fitting results clearly showed that the a lattice parameter and site occupancy factor of Fe at the octahedral site continuously decreased at the temperatures from 25 to 300 °C. The X-ray absorption near edge structure (XANES) result showed that the Fe³⁺/ΣFe increased up to 300 °C and remained constant until 500 °C, indicating that Fe²⁺ in oxidized magnetite was completely oxidized to Fe³⁺ at 300 °C. Furthermore, the intensities of radial structure function (RSF) peaks at 1.7 and 3.1 Å corresponding to the Fe–O bonds in octahedral site and the Fe–Fe interaction between the octahedral sites reduced continuously from 25 to 300 °C. The fitting results of the first shells indicated that the coordination number and site occupancy factor at the octahedral site continuously decreased at the temperature range from 25 to 300 °C, which were approximately consistent with those of Rietveld fitting analysis. The a lattice parameter of the oxidized magnetite displayed a linear trend between stoichiometric magnetite and stoichiometric maghemite with a relationship of \( a = 0.0985x + 8.3397 \) (for \( x = \frac{Fe²⁺}{Fe³⁺} \)). It was clearly confirmed that during the magnetite oxidation, Fe was continuously removed from the octahedral sites, which resulted in the formation of maghemite with partially ordered distribution of vacancy. Just after magnetite oxidation was completed, the vacancy ordering further progressed by the diffusion of Fe³⁺ within the structure, leading to the formation of maghemite with fully ordered distribution of vacancy.

Keywords: Magnetite, Cubic maghemite, Tetragonal maghemite, Oxidation, XRD, XAFS

INTRODUCTION

Magnetite (Fe₃O₄) is one of the most abundant iron oxide minerals distributed in the Earth’s crust. Since magnetite contains Fe²⁺ as well as Fe³⁺ in its structure, it is thermodynamically unstable under atmospheric partial pressure of oxygen. Magnetite is progressively oxidized to hematite (α-Fe₂O₃) through maghemite (γ-Fe₂O₃) in air. Magnetite is commonly found in soils and sediments as a weathering product of magnetite (Schwertmann and Cornell, 1991). Because the oxidation from magnetite to maghemite is an exothermic event (Lilova et al., 2012; Mamani et al., 2013; Stoia et al., 2016), the emitted heat could result in a temperature elevation and trigger the transformation to hematite. Magnetite has an inverse spinel structure with a face-centered cubic lattice with space group \( Fd\bar{3}m \). The structural formula of magnetite can be represented as \( (Fe³⁺)_{8}[Fe²⁺Fe³⁺]_{16}O_{32} \), where the brackets ( ) and [ ] represent tetrahedral and octahedral sites.
Maghemite possesses the inverse spinel structure as well. The oxidation of magnetite to maghemite was achieved by removal of Fe cations from the octahedral site. The tetrahedral sites are filled with Fe$^{3+}$, but only 5/6 of the octahedral positions are occupied by Fe$^{3+}$, resulting in formation of 1/6 cation vacancies at the octahedral positions. A single-crystal XRD study has confirmed that cation vacancies invariably occur at the octahedral site even at high temperatures (Okudera, 1997). The vacancy ordering has been theoretically investigated from an energetic point of view (Grau-Crespo et al., 2010), which suggested that if temperature and reaction time are high and long enough, respectively, to allow complete equilibration of all the configurations, the cation vacancies should become fully ordered.

The oxidation state of magnetite is often expressed by the amount of Fe$^{2+}$ in magnetite ($x = \text{Fe}^{2+}/\text{Fe}^{3+}$), which can be discussed quantitatively as magnetite stoichiometry. For magnetite with an ideal Fe$^{2+}$ content, the mineral phase is known as stoichiometric magnetite ($x = 0$). As magnetite is partially oxidized, the Fe$^{2+}/\text{Fe}^{3+}$ decreases ($x < 0.50$). When magnetite is completely oxidized ($x = 0$), it can be regarded as stoichiometric maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$). The oxidized magnetite behaves as a solid solution between stoichiometric magnetite and stoichiometric maghemite, which is referred to as oxidized magnetite or nonstoichiometric magnetite (Pearce et al., 2006; Gorski et al., 2010; Okudera et al., 2012; Lilova et al., 2012; Piquer et al., 2014). It can be considered that maghemite is formed by topotactic (topochemical) reaction that takes place without a significant structural rearrangement. For the oxidized magnetite, chemical formula can be written as $\text{Fe}^{3+}[^{2+}2\delta\text{Fe}^{3+}_3\delta\square]_2\text{O}_4$ ($0 \leq \delta \leq 1/3$).
(Trone et al. 1982; Goss 1988; da Costa et al. 1996). Recently, the magnetite nanoparticles have been described by a core–shell model that accounts for an unoxidized magnetite core surrounded by a stoichiometric maghemite shell (Frison et al., 2013; Cervellino et al., 2014; Dehsari et al., 2018; Li et al., 2019). Gorski and Scherer (2010) measured the stoichiometry of magnetite nanoparticles with approximately 20 nm in diameter and indicated that the particle size does not influence the magnetite stoichiometry.

In the last two decades, there have been a considerable number of researches in which oxidation of iron oxides has been studied by various techniques (Shebanova and Lazor, 2003; Murbe et al., 2008; Gotic et al., 2009; Piquer et al., 2014; Jafari et al., 2015; Cuenca et al., 2016; Fock et al., 2017; Malek et al., 2018; Tamura et al., 2018; Yuan et al., 2019; Righi and Magri, 2019; Ponomar et al., 2020). However, very little empirical research has been conducted to observe closely the continuous structural change during oxidation of magnetite. The thermodynamics of vacancy ordering in maghemite has been still unclear because of difficulty to control experimentally the level of ordering of cation vacancies. Several authors indicated that oxidation products resulting from thermal treatment of magnetite are strongly dependent on the conditions such as temperature, oxygen pressure, heating time, particle size, and preparation methods (Shmakov et al., 1994; Lilova et al., 2012; Babay et al., 2015). It remains therefore uncertain under what conditions these maghemites (Fig. 1) would appear. In the study, hence, we conducted the synchrotron X-ray diffraction and X-ray absorption spectroscopy to investigate structural change in short and long-range orders during the magnetic oxidation process. Here, we especially focused on the thermodynamics of vacancy ordering in maghemite.

**EXPERIMENTAL METHODS**

**Sample characterization**

Commercially available magnetite (FUJIFILM Wako Pure Chemical Corp., purity >95.0%) was used as a starting material. Oxidation state of magnetite was controlled by thermal treatment. It was placed in a Pt crucible and heated in air at temperatures of 100, 150, 200, 250, 300, 400, and 500 °C. After heated for 3 h, they were naturally cooled to room temperature. The oxidized magnetite powders prepared were stored in a vacuum desiccator until use.

**Synchrotron powder XRD measurements**

Synchrotron powder XRD measurements were performed at the BL–8B in Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Japan. The magnetite powders were inserted into the Lindemann glass capillary (φ = 0.7 mm). The incident beam was monochromatized to a wavelength of 0.6525(1) Å by the Si(111) double crystal monochromator. The X-ray beam was collimated to 50 μm in diameter. The exposure time was set to 5 min. The obtained XRD data were analyzed using the Rietveld method with the RIETAN–FP program (Izumi and Momma, 2007). The background function, profile function, scale factor, and structural parameters were refined using the XRD data in the 2θ range from 5 to 140°. In the all refinements, displacement parameters (B values) for Fe and O atoms were fixed at 0.5 and 1.0, respectively. The starting lattice parameters and atomic coordinates were taken from the literature: Bosi et al. (2009) for magnetite, Pecharromán et al. (1995) for maghemite, and Maslen et al. (1994) for hematite.

**Fe K-edge XAFS measurements**

Fe K-edge X-ray absorption fine structure (XAFS) measurements were performed at the BL–9C in PF, KEK, Japan. The XAFS station was equipped with the Si(111) double crystal monochromator. 4 mg of the sample was diluted with 150 mg of BN powder (FUJIFILM Wako Pure Chemical Corp., purity >99%) and pressed into a pellet with a diameter of 10 mm. The pellets were transferred to polyethylene bags for measurements. Ionization chambers filled with 100% N₂ and 15% Ar in N₂ were used to measure the incident and transmitted X-ray intensities, respectively. All spectra were collected in transmission mode. Size of the X-ray incident beam at the sample was approximately 1.5 (H) × 0.5 (V) mm². Energy measurement range was set from 6606.2 to 8211.3 eV. Energy calibration was carried out using spectrum of Fe foil. The obtained XAFS spectra were corrected and normalized using the Athena software (Ravel and Newville, 2005). The Fe³⁺/ΣFe was estimated based on the method by Bajt et al. (1994) from energy of the pre-edge peak in XANES. The pre-edge peaks were fitted to Gaussian curves, whereas the backgrounds were fitted to 4th-order polynomials. Magnetite and hematite were used as calibration lines. The extended X-ray absorption fine structure (EXAFS) spectra were analyzed by fitting to the structural model generated via Atoms (Ravel, 2005) and FEFF6 code software packages (Rehr et al., 1991) using Artemis (Ravel and Newville, 2005). The Fourier transformation and fitting ranges were set to 2.5 ≤ k ≤ 11.5 Å⁻¹ and 1.0 ≤ r ≤ 2.1 Å, respectively. The structure model during oxidation at the temperature range from 25 to 300 °C was developed by considering that Fe diffused...
from the octahedral site in magnetite. In the fitting, coordination number of the tetrahedral site was fixed at 4.

RESULTS AND DISCUSSION

Synchrotron powder XRD pattern

It has been proposed that as magnetite becomes more oxidized, the 111 peak intensity decreases due to octahedral vacancies (Gallagher et al. 1968; Volenik et al. 1975). Although the relative intensity of the 111 peak has been used to characterize magnetite stoichiometry, some studies have noticed no correlation between them (Annersten and Hafner, 1973; Goss, 1988; Gorski and Scherer, 2010). Figure 2 shows the XRD pattern of magnetite at 25 °C and that heated at temperatures between 100 and 500 °C. In the present study, intensities of the 111 peak observed at \(2\theta = 7.7°\) decreased constantly as increasing the heating temperature. Very weak diffraction peaks due to maghemite were detectable in magnetite heated at 100 °C. The diffraction pattern was exactly consistent with that of partially ordered maghemite with space group \(P4_132\) or \(P4_332\) (Pecharrromán et al., 1995). Thereafter, the peak intensities of maghemite progressively increased as increasing the heating temperature. The most noteworthy finding in this study was that extra diffraction peaks due to the symmetry lowering on the fully ordered maghemite with space group \(P4_1212\) or \(P4_3212\) were detected from magnetite heated at 300 °C and 400 °C. The extra reflections were obviously observed at \(2\theta = 5.4, 7.0, 9.1, \) and \(11.7°\) from the XRD pattern of magnetite heated at 300 °C. To our knowledge, a continuous change from the partially ordered maghemite to the fully ordered maghemite had not been experimentally verified. There is no certain evidence that the fully disordered maghemite with space group \(Fd\bar{3}m\) occurred at heating temperatures below 100 °C, because the XRD pattern of maghemite with space group \(Fd\bar{3}m\) cannot be distinguished from that of magnetite. The theoretical approach indicated that maghemite becomes fully ordered structure in equilibrium, but deviations from this behavior generate the partially ordered structure (Grau-Crespo et al., 2010). This study provided direct experimental evidence that the cation vacancies become fully ordered when temperature is high enough to allow complete equilibration of all the configurations. The heating time of 3 h at 300 °C would be sufficient to form a fully ordered distribution of Fe vacancies. Jørgensen et al. (2007) performed in situ high-temperature powder XRD study on the amorphous FeOOH at the temperature of 305 °C. After 4 min, the fully disordered maghemite with space group \(Fd\bar{3}m\) occurred. After 41 min, maghemite transformed to the fully ordered maghemite with space group \(P4_1212\) or \(P4_3212\). No intermediate crystalline phase such as the partially ordered maghemite with space group \(P4_132\) or \(P4_332\) was detected in the report. In our study, on the other hand, since magnetite was used as a starting material, the partially ordered maghemite may occurred during oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) in maghemite. Just after Fe\(^{2+}\) was totally oxidized to Fe\(^{3+}\) in maghemite, the fully ordered maghemite occurred. A common feature with the previous study (Jørgensen et al. 2007) is that the fully ordered maghemite emerged after the precursor was dominated by Fe\(^{3+}\). Furthermore, there is a possibility that the partially ordered maghemite occurs when Fe\(^{2+}\) remains in maghemite.

It has been long suggested that the XRD intensity of the fully ordered maghemite reduces with decreasing the particle size. It vanishes at particle sizes between 17 and 30 nm (Haneda and Morrish, 1977). However, the particles with average sizes of 12–13 nm exhibited the characteristic extra reflections resulting from the fully ordered maghemite (Jørgensen et al., 2007). Here, we estimated the crystallite size from XRD line broadening using the Scherrer equation, 

\[
d_{\text{crystallite}} = \frac{K\lambda}{B\cos\theta},
\]

with the wavelength \(\lambda\), the peak width \(B\), the Bragg angle \(\theta\), and the shape factor \(K = 0.90\). The average crystallite size of magnetite used as a starting material in the study was 28(1) nm.
Although it was approximately 30 nm, we could detect the characteristic extra reflections from the fully ordered maghemite. Therefore, this study could establish one sufficient condition for the appearance of the fully ordered maghemite.

Diffraction peaks of hematite started to occur at 250 °C, where maghemite and hematite were coexisted with magnetite. It is worthwhile to keep in mind that the 111 and 222 peaks of magnetite observed at 2θ = 7.8 and 15.5° were replaced with those of maghemite with oxidation of magnetite. Diffraction peaks of magnetite were therefore considered to have disappeared at 300 °C. As mentioned later, the disappearance of magnetite was confirmed by both Rietveld analysis and XANES spectra. Instead of magnetite, maghemite and hematite dominated the XRD pattern. In the study, hematite seemed to be directly formed from the partially ordered maghemite, but neither from the fully disordered maghemite nor the fully ordered maghemite. It was unlikely that the cation vacancy ordering in maghemite (γ-Fe2O3) necessarily triggers the phase transition to hematite (α-Fe2O3). Subsequently, maghemite and hematite were coexisted at temperature range from 300 to 400 °C, but the amount of maghemite was reduced from 300 °C. Finally, maghemite was completely disappeared at 500 °C, and hematite dominated the XRD pattern.

Figure 3 displays the result of Rietveld refinement fitting of the XRD pattern collected from magnetite heated at 200 °C, which was fitted with the partially ordered maghemite with space group P4132. It was in reasonable agreement with the simulated powder pattern. We attempted to fit the XRD patterns of magnetite heated at 300 °C with the fully ordered maghemite with space group P41212. The Rietveld refinement consequently failed to fit the XRD pattern. The resulting a lattice parameter and site occupancy factors led to quite unreliable values as a tetragonal maghemite with fully ordered distribution of vacancy due to the relatively low XRD intensities. The all XRD patterns of oxidized magnetite were therefore fitted with the partially ordered maghemite. The results are given in Table 1. The a lattice parameter of maghemite at 25 °C was approximately consistent with the literature value of 8.3967 Å (Bosi et al., 2009). Since all Fe and O atoms occupied the special equivalent positions in the partially ordered maghemite, only the a lattice parameter and the site occupancy factor of Fe in the octahedral site at the 4b Wyckoff position (Feoct1) were refined as structural parameters. With increasing heating temperature, the a lattice parameter and site occupancy factor in the Feoct1 site were continuously decreased from 8.3940(3) Å to 8.3363(5) Å and from 1.000 to 0.335(2), respectively (Table 1, Fig. 4). The a lattice parameter at 300 °C was exactly consistent with that of maghemite of 8.33 Å reported by Pecharroman et al. (1995). The Fe release from the Feoct1 site yielded an increase of the Fe3+, resulting in a decrease of the Fe2+ in the octahedral sites to maintain charge balance during oxidation (Fig. 5). Finally, at 300 °C, the vacancy and Fe3+ in the octahedral sites almost reached to the ideal values in stoichiometric maghemite of 1/3 and 5/3, respectively.

**Fe K-edge XAFS spectra**

Figure 6a shows the evolution of pre-edge peak in the Fe K-edge XANES spectra of the oxidized magnetite. The pre-edge peak appearing at 7108.6 eV was apparently shifted to the higher energy with increase of heating temperature. As a result, the Fe3+/ΣFe continuously increased in the temperatures from 25 to 300 °C (Fig. 6b). At 300

| Temperature (°C) | Rrup | Rb | a lattice parameter (Å) | Feoct1 Site occupancy factor |
|-----------------|------|----|------------------------|-----------------------------|
| 25              | 7.002| 6.622| 8.3940(3)               | 1.0000                     |
| 100             | 6.954| 6.542| 8.3821(2)               | 0.8618(3)                  |
| 150             | 6.523| 6.328| 8.3763(8)               | 0.7917(5)                  |
| 200             | 6.335| 6.317| 8.3571(10)              | 0.6391(7)                  |
| 250             | 6.619| 6.201| 8.3529(3)               | 0.4836(2)                  |
| 300             | 6.415| 6.001| 8.3363(5)               | 0.335(2)                   |
it reached 1.00, and thereafter remained constant until 500 °C. That is, in magnetite heated at 300 °C, Fe$^{2+}$ in the octahedral site was fully oxidized to Fe$^{3+}$. This result was in a good agreement with the XRD result that diffraction peaks from magnetite disappeared at 300 °C. The EXAFS spectra of Fe $K$–edge in the sample were displayed in Figure 6c. It is apparent that the shape of the EXAFS oscillations gradually changed depending on the temperature. The evolution of RSF profiles is provided in Figure 7. The RSF profiles were roughly composed of two shells. In magnetite and maghemite, the first coordination shell includes the Fe–O bonds at the tetrahedral and octahedral sites. The second coordination shell consists of the Fe–Fe interaction between Fe atoms in the octahedral and tetrahedral sites and between Fe atoms in the octahedral site. The shape of the RSF profile at 300 °C was the essentially same as that of maghemite previously reported by Okudera et al. (2012). The most striking result was that intensities of RSF peaks at 1.7 and 3.1 Å corresponding to the Fe–O bonds in the octahedral site and the Fe–Fe interaction between the octahedral sites reduced continuously from 25 to 300 °C. It strongly implied that the Fe was removed from the octahedral site during the magnetite oxidation. The fitting results of the first shell at the temperatures between 25 and 300 °C are shown in Figure 8a. The structural parameters obtained from the fitting were presented in Table 2. The coordination number at the octahedral site and the site occupancy factor of Fe were continuously decreased from 25 to 300 °C (Figs. 8b and 8c). In hematite, the first coordination shell is attributed to the Fe–O bonds at the octahedral sites, whereas the second coordination shell is due to the Fe–Fe in-
Interaction between Fe atoms in the octahedral site. Above 300 °C, the intensity of peak derived from the second neighbor Fe atoms around Fe atom increased until 500 °C. This change corresponds to the phase transition from maghemite to hematite.

The relationship between the \( a \) lattice parameter and magnetite stoichiometry

Gorski and Scherer (2010) provided the variation of the \( a \) lattice parameter as a function of the magnetite stoichiometry (\( \chi = \text{Fe}^{2+}/\text{Fe}^{3+} \)). In their paper, the linear least-squares fit to the all data yielded the equation of \( a = 0.1094x + 8.3424; \) coefficient of determination \( R^2 = 0.920; \) number of samples \( n = 43, \) but the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratios determined using various techniques such as Mössbauer spectroscopy, acidic dissolution, and change in mass were plotted together in their figure (Fig. 7 in Gorski and Scherer, 2010). Figure 9 shows variation of the \( a \) lattice parameter onto the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratios determined by XANES spectra in the study. There is a linear trend between stoichiometric magnetite and stoichiometric maghemite. The least-squares fit provided a linear relationship of \( a = 0.0985x + 8.3397; \) \( R^2 = 0.9465; \) \( n = 6. \) To evaluate the accuracy of oxidation state of magnetite, the \( a \) lattice parameter against the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratios determined by Mössbauer spectroscopy (Gotic et al. 2009; Gorski and Scherer, 2010) was plotted in the same figure, in which only the data of the partially ordered maghemite were utilized. The resulting linear trend can be represented by the equation of \( a = 0.1001x + 8.3419; \) \( R^2 = 0.827; \) \( n = 12, \) which was in good agreement with our result. The linear least-squares fit to the data given by Gotic et al. (2009) and Gorski and Scherer (2010) was slightly deviated upward from our result, but the deviation may lie within measurement errors. The equation determined in the study would be a useful predictor for estimating the oxidation state of magnetite.
samples when it is difficult to determine accurately the magnetite stoichiometry. However, it is important to keep in mind that the lattice parameter of magnetite is readily affected by cation substitution. For example, maghemite containing 20 mol% Al formed from Al–magnetite by heating at 250 °C for 5 h shows the lattice parameter of 8.31 Å (Wolska and Schwertmann, 1989). In the solid solution between magnetite and ulvöspinel, the lattice parameter varies from 8.3967 to 8.5322 Å with increasing Ti4+ (Bosi et al. 2009). Therefore, care should be taken to avoid misleading results, especially when the method is applied to natural samples.

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REFERENCES

Annersten, H. and Hafner, S.S. (1973) Vacancy distribution in synthetic spinels of the series magnetite–γ–iron(III) oxide. Zeitschrift für Kristallographie, 137, 321–340.

Babay, S., Mhiri, T. and Toumi, M. (2015) Synthesis, structural and spectroscopic characterizations of maghemite γ–Fe2O3 prepared by one-step coprecipitation route. Journal of Molecular Structure, 1085, 286–293.

Bajić, S., Sutton, S.R. and Delaney, J.S. (1994) X-ray microprobe analysis of iron oxidation states in silicates and oxides using X-ray absorption near edge structure (XANES). Geochimica et Cosmochimica Acta, 58, 5209–5214.

Bosi, F., Hälenius, U. and Skogby, H. (2009) Crystal chemistry of the magnetite–ulvöspinel series. American Mineralogist, 94, 181–189.

Cervellino, A., Frison, R., Cernuto, G., Guagliardi, A. and Masciocchi, N. (2014) Lattice parameters and site occupancy factors of magnetite–maghemite core–shell nanoparticles. A critical study. Journal of Applied Crystallography, 47, 1755–1761.

Cuenca, J.A., Bugler, K., Taylor, S., Morgan, D., et al. (2016) Study of the magnetite to maghemite transition using microwave permittivity and permeability measurements. Journal of Physics: Condensed Matter, 28, 106002.

da Costa, G.M., De Grave, E. and Vandenberge, R.E. (1996) Mössbauer studies of magnetite and Al-substituted maghemites. Hyperfine Interactions, 117, 207–243.

Dehsari, H.S., Ksenofontov, V., Moller, A., Jakob, G. and Asadi, K. (2018) Determining magnetite/maghemite composition and core–shell nanostructure from magnetization curve for iron oxide nanoparticles. The Journal of Physical Chemistry C, 122, 28292–28301.

Fock, J., Bogart, L.K., Gonzalez-Alonso, D., Espeso, J.J., et al. (2017) On the ‘centre of gravity’ method for measuring the composition of magnetite/maghemite mixtures, or the stoichiometry of magnetite–maghemite solid solutions, via 57Fe Mössbauer spectroscopy. Journal of Physics D: Applied Physics, 50, 265005.

Frison, R., Cernuto, G., Cervellino, A., Zaharko, O., et al. (2013) Magnetite–maghemite nanoparticles in the 5–15 nm range: correlating the core–shell composition and the surface structure to the magnetic properties. A total scattering study. Chemistry of Materials, 25, 4820–4827.

Gallagher, K.J., Feitknecht, W. and Mannweiler, U. (1968) Mechanism of oxidation of magnetite to γ–Fe2O3. Nature, 217, 1118–1121.

Gorski, C.A. and Scherer, M.M. (2010) Determination of nanoparticulate magnetite stoichiometry by Mossbauer spectroscopy, acidic dissolution, and powder X-ray diffraction: A critical review. American Mineralogy, 95, 1017–1026.

Table 2. The fitting result of the first shell with the oxidized magnetite

| Temperature (°C) | Fe3+,O– | R (Å) | CN | ΔE0 (eV) | R factor | σ2 (Å²) 
|-----------------|---------|------|----|----------|----------|----------
| 25              | 1.871(11) | 4    | 2.028(8) | 6   | 4.7(1.1) | 0.001 | 0.0020(16) |
| 100             | 1.872(18) | 4    | 2.027(10) | 5.8(2) | 4.5(4) | 0.002 | 0.0025(4) |
| 150             | 1.865(14) | 4    | 2.020(3) | 5.7(3) | 4.3(3) | 0.003 | 0.0022(19) |
| 200             | 1.860(6)  | 4    | 2.001(5) | 5.5(3) | 4.1(8) | 0.001 | 0.0029(10) |
| 250             | 1.858(9)  | 4    | 2.006(8) | 5.3(2) | 4.4(8) | 0.005 | 0.0070(18) |
| 300             | 1.862(7)  | 4    | 2.008(8) | 5.03(10) | 4.4(9) | 0.037 | 0.0088(17) |

Figure 9. The dependence of the a lattice parameter on magnetite stoichiometry. Solid and dotted lines denote the least squares linear regressions through the data points obtained from this study and from the literatures, respectively.
