

Structural properties of magnetite under high pressure studied by Mössbauer spectroscopy

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We have measured the Mössbauer spectra of magnetite (Fe_3O_4) under a pressure of up to 18 GPa at room temperature using nonenriched high-quality samples. An analysis of the observed Mössbauer spectra confirms that Fe_3O_4 does not undergo a magnetic or crystalline structural transition up to 18 GPa at room temperature. In the pressure dependences of the refined hyperfine interaction parameters, however, small but distinct anomalies are found at 7.0 GPa in the center shifts of two crystallographically nonequivalent Fe sites, which are caused by the discontinuous decrease of an oxygen internal coordinate in the cubic inverse spinel structure. We believe that the pressure-induced discontinuous change of the Fe-O bond length is related to the absence of a metal-insulator transition above 7.5 GPa.

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I. INTRODUCTION

Magnetite (Fe_3O_4) exhibits many interesting physical properties such as a mixed valence and metal-insulator transition. At ambient conditions, Fe_3O_4 has an inverse spinel structure where eight Fe^{3+} ions occupy the A sites with tetragonal symmetry, locally, and the B sites that locally exhibit octahedral symmetry are occupied by eight Fe^{3+} and Fe^{2+} ions within a simple ionic chemical formula. Neither Mössbauer spectroscopy nor NMR detect any difference between the Fe^{3+} and Fe^{2+} ions on the B sites. Furthermore, the results of resonant x-ray scattering¹ show that the Fe ions on the B site are electronically equivalent at time scales lower than 10^{-16} s, which is much faster than the characteristic time scale of ^{57}Fe Mössbauer and NMR measurements.

In 1939, Verwey discovered the metal-insulator transition at about 120 K, where the resistivity increases sharply by two orders of magnitude.² In the early stages of Fe_3O_4 research, charge ordering on the B sites was used to explain the metal-insulator transition because of the mixed valence state of the Fe ion on the B site in a simple ionic chemical formula. However, recent NMR relaxation results indicate that the states of Fe ions on the B sites are mixed strongly, even below the metal-insulator transition temperature.³ The mechanism of this metal-insulator transition remains an open question despite considerable efforts. Hydrostatic pressure

provides an important experimental technique for studying the mechanism of the metal-insulator transition. This is because pressure allows one to control the hybridization between the $3d$ state and the conduction bands and the bandwidth. It was reported, on the basis of electrical resistivity measurements of Fe_3O_4 under pressure, that the metal-insulator transition temperature decreased with increasing pressure and then remained at about 83 K up to 16 GPa.⁴ Recently, Todo *et al.* reexamined this transition under homogeneous quasihydrostatic pressure using single-crystalline Fe_3O_4 and found that this transition disappears at 7.5 GPa.⁵

Meanwhile, a structural analysis under pressure was carried out by x-ray diffraction measurements at room temperature.⁶ No structural phase transition was found up to 32 GPa. This result was confirmed by recent x-ray diffraction using synchrotron radiation.⁷ However, Mössbauer spectroscopy⁸ revealed that a pressure-induced crossover from the inverse to the normal spinel structure occurred in Fe_3O_4 at about 8 GPa and room temperature.

In the present study, we investigate the electronic states of the iron ions on two different sites and the structural properties of Fe_3O_4 under pressure at room temperature by ^{57}Fe Mössbauer spectroscopy. We show that the center shift derived from the refined hyperfine data is a useful parameter for determining an oxygen internal coordinate in Fe_3O_4 . The distinct anomalies in the pressure dependences of the center

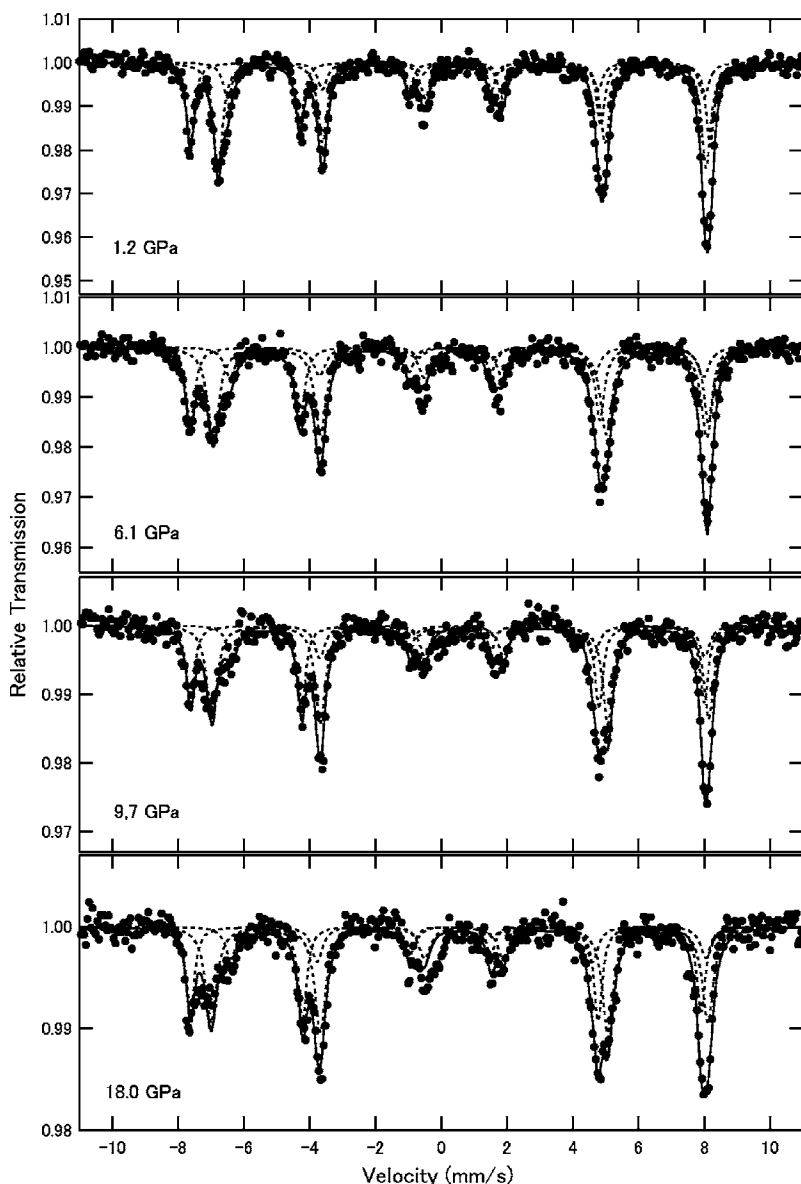


FIG. 1. Mössbauer spectra of Fe_3O_4 under pressure at room temperature. The closed circles represent the measured data and the solid lines represent fitting curves obtained by the analysis. Three extracted subspectra are shown by broken lines.

shifts reveal that a pressure-induced discontinuous change of the Fe-O bond length occurs at 7.0 GPa.

II. EXPERIMENTAL

Nonenriched high-quality single crystals of Fe_3O_4 were synthesized by a floating zone melting method. The crystals were annealed at around 1200 °C in a controlled atmosphere of a mixture of CO and CO_2 in order to homogenize the composition of the specimen and to release internal strain. The composition of the sample used in this experiment was determined to be $\text{Fe}_3\text{O}_{4.002}$ by thermogravimetry. At ambient pressure, the sample shows a metal-insulator transition at 123 K, which is called the Verwey transition.

The high-pressure Mössbauer spectra were measured at room temperature up to 18 GPa using a clamp-type diamond anvil cell (DAC). The single-crystal sample was finely ground and mixed with fine BN powder in order to get a uniform resonant-absorber thickness. The mixed sample

loaded with ruby crystals into a sample cavity of 0.4 mm diameter, in a 0.3 mm thick Inconel 625 alloy gasket.⁹ Pressure was calibrated by measuring the wavelength shift of the R_1 luminescence line of the ruby crystals. The clamp-type DAC was mounted on a translation stage with the sample at a distance of approximately 3 mm from a 5 mCi ^{57}Co (Rh) point source with an active area of $0.5 \times 0.5 \text{ mm}^2$. The 14.4 keV γ ray was detected with a 1 atm Kr- CO_2 -filled proportional counter. The velocity scale was calibrated by α iron at room temperature. As seen in Fig. 1, the spectra of satisfactory quality were obtained in about two days. Even though we used two different pressure-transmitting media, namely, mixtures of Fluorinert FC70-FC77 1:1 and methanol-ethanol 4:1, to check pressure conditions, no pressure-transmitting media dependence was observed in the Mössbauer spectra to within experimental accuracy.

III. EXPERIMENTAL RESULTS

Typical Mössbauer spectra of Fe_3O_4 under pressure are shown in Fig. 1, where the closed circles represent the mea-

sured data. The resolution, i.e., the width of absorption lines, in the present experiment is much higher than those obtained using enriched samples.^{8,10} As previously assigned, the subspectra with larger and smaller magnetic hyperfine fields, H_{hf} , correspond, respectively, to the A and B sites at ambient pressure. In a simple ionic chemical model, electron hopping from a Fe^{2+} ion to a Fe^{3+} ion at the B site is faster than the characteristic time scale of ^{57}Fe Mössbauer measurement at ambient conditions. Recently, the band calculation of Fe_3O_4 predicted a half-metallic state in the cubic spinel structure.¹¹ In the half-metallic state, the Fermi level stays in the band-gap between the unoccupied $3d$ state of site A and the completely occupied $3d$ state of site B in the majority spin band and in the de bands of site B in the minority spin band. Thus, the hyperfine parameters at site B are practically identical.

It should be noted that the width of the absorption line at -6.8 mm/s of site B is much larger than that at -7.6 mm/s of site A at 1.2 GPa, as seen in Fig. 1. A shoulder in the absorption line appears at around -6.5 mm/s and becomes more distinct with increasing pressure. Although earlier observed Mössbauer spectra of Fe_3O_4 (20 at. % ^{57}Fe) under pressure were explained using the crossover from the inverse to the normal spinel structure at about 8 GPa,⁸ there is no structural phase transition up to 32 GPa.⁶ Since the absorption lines on the B site have an anisotropic shape, the crystallographically equivalent B sites are subdivided into magnetically nonequivalent sites, depending on the direction of the principle axis of the electric-field-gradient (EFG) tensor.

One of the principle axes of EFG at the B site is parallel to one of $\langle 111 \rangle$ because the local symmetry in the spinel structure is $\bar{3}m$. At ambient conditions, the easy axis of magnetization in Fe_3O_4 is along $[111]$. If we assume that the magnetic hyperfine interaction is much larger than the electric quadrupole interaction, and use first-order perturbation theory with an axial symmetry approximation, the B site gives two subspectra with the intensity ratio of 3:1. Hence, the observed Mössbauer spectra were analyzed with three subspectra, assuming the intensity ratio of 2:3:1 under these conditions. Thickness broadening and geometrical effects were taken into account in this analysis.⁹ As seen in Fig. 1, the shoulder in the absorption line at around -6.5 mm/s in each spectrum was well fitted with the three subspectra up to 18.0 GPa.

Figure 2 shows the pressure dependences of the refined hyperfine interaction parameters. Figs. 2(a) and 2(b) show the decrease and increase observed in the refined center shifts (δ_{cs}) of the A and B sites, respectively, both changes occurring at $P_c = 7.0(5)$ GPa. Within the accuracy of the data, we obtain linear fits for the A site of the form

$$\delta_{cs}^A = 0.286(3) - 0.004(1)P \text{ mm/s below 6 GPa}$$

and

$$\delta_{cs}^A = 0.258(6) - 0.0019(5)P \text{ mm/s above 8 GPa.}$$

The decrease in δ_{cs}^A at P_c is estimated to be 0.013 mm/s. We also obtain linear fits for the B sites of the form

$$\delta_{cs}^{B_1} = 0.677(3) - 0.0088(8)P \text{ mm/s,}$$

and

$$\delta_{cs}^{B_2} = 0.684(4) - 0.009(1)P \text{ mm/s below 6 GPa}$$

and

$$\delta_{cs}^{B_1} = 0.68(1) - 0.0025(10)P \text{ mm/s,}$$

and

$$\delta_{cs}^{B_2} = 0.675(8) - 0.0032(6)P \text{ mm/s above 8 GPa,}$$

where the B_1 and B_2 sites represent $\frac{3}{4}$ and $\frac{1}{4}$ of the B sites, respectively. The increases in δ_{cs} of the B_1 and B_2 sites are evaluated to be 0.047 and 0.031 mm/s, respectively.

As seen Figs. 2(c) and 2(d), the pressure dependences of the refined $\Delta E_Q = \frac{1}{2}eV_{zz}Q[(3\cos^2\vartheta - 1)/2]$ for the A and B sites change at around P_c , where Q is the nuclear electric quadrupole moment, $V_{zz} = \partial^2 V / \partial z^2$ represents the principal component of the diagonalized EFG tensor, and ϑ is the angle between the directions of the z axis of EFG and H_{hf} . The ΔE_Q^A value remains constant at zero below P_c within experimental accuracy and decreases linearly with increasing pressure. The $\Delta E_Q^{B_1} / \Delta E_Q^{B_2}$ ratios are estimated to be about -3 up to 18 GPa within the accuracy of the data. Accordingly, the z axis of EFG at the B site is along $\langle 111 \rangle$. The value of H_{hf}^A decreases monotonically with increasing pressure and the pressure dependences of H_{hf}^B change at around P_c , as seen Figs. 2(e) and 2(f), respectively. Thus, Fe_3O_4 undergoes no crystalline or magnetic structural change up to 18 GPa at room temperature.

IV. DISCUSSION

If there are changes of valence and/or spin states of the irons in Fe_3O_4 at P_c , the change of δ_{cs} is roughly estimated to be over 0.1 mm/s, as observed in FeS.⁹ Furthermore, no discontinuous anomaly was observed in the pressure dependences of H_{hf} . Consequently, these small but definite anomalies in the pressure dependences of δ_{cs} do not indicate changes of valence and spin states of the irons. Therefore, we have no evidence for the crossover from the inverse to the normal spinel structure up to 18 GPa at room temperature. This is qualitatively consistent with the recent x-ray diffraction measurements under pressure using synchrotron radiation.⁷

In general, the observed variation of δ_{cs} with pressure at constant temperature is split into two parts, as expressed by

$$\left[\frac{\partial \delta_{cs}}{\partial P} \right]_T = \left[\frac{\partial \delta}{\partial P} \right]_T + \left[\frac{\partial \delta_{SOD}}{\partial P} \right]_T.$$

The first term on the right-hand side represents the pressure dependence of the isomer shift, δ , which is directly related to the variation of electron density at the nucleus. The second term describes the changes of second-order Doppler (SOD) shift, which is related to the vibration modes of the atom. The value of $[\partial \delta_{SOD} / \partial P]_T$ is positive and very small for materials with a small volume reduction. The main effect in $[\partial \delta_{cs} / \partial P]_T$ for Fe_3O_4 is presumably caused by a change of

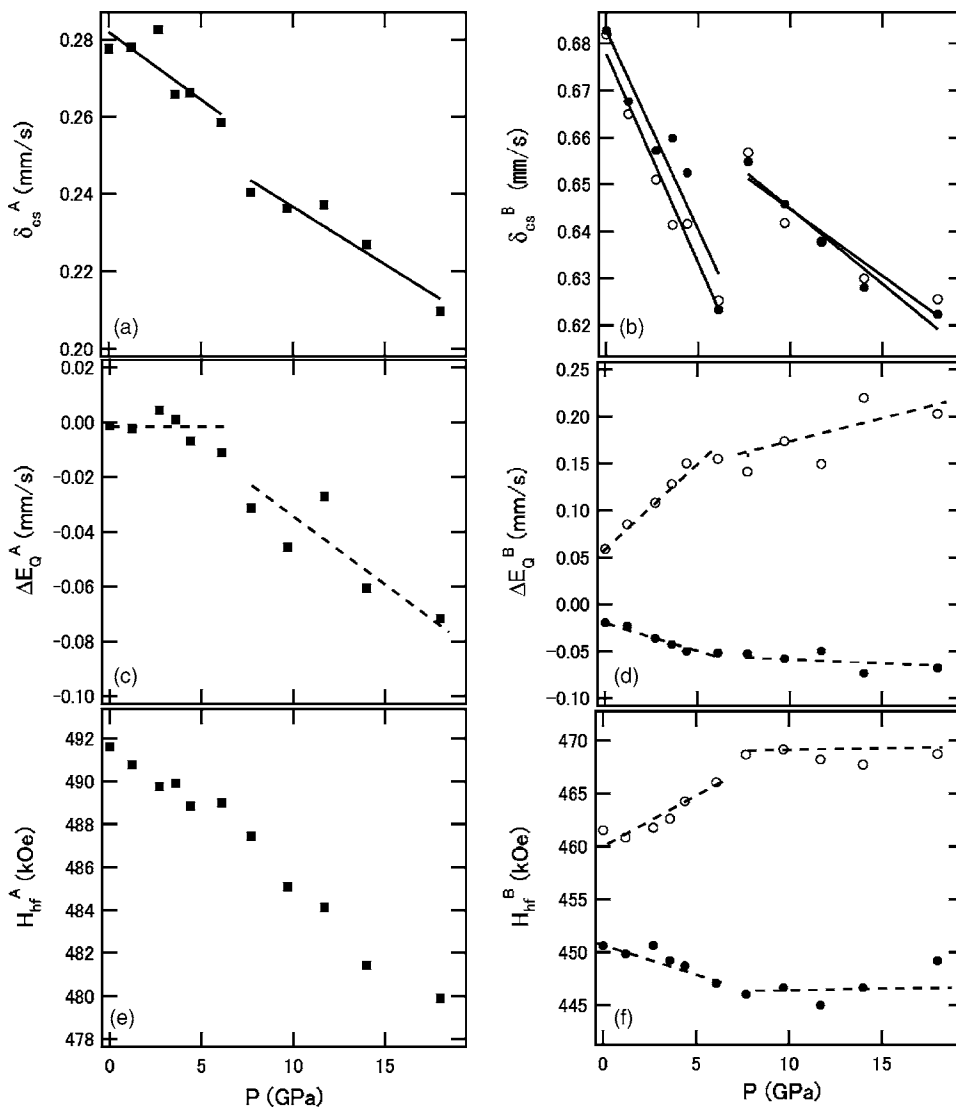


FIG. 2. Pressure dependences of the refined hyperfine interaction parameters: (a) and (b) the center shift, δ_{cs} ; (c) and (d) the quadrupole splitting, ΔE_Q ; and (e) and (f) the magnetic hyperfine field, H_{hf} . The open and closed circles indicate the B₁ and B₂ sites, respectively. The solid lines represent the results of fitting, and the broken lines are guides to the eye.

electron density at the ^{57}Fe nucleus since the volume reduction is less than 7% at about 20 GPa.⁶ Consequently, the electron density at the ^{57}Fe nucleus on the A site increases, while that on the B site decreases at P_c because the isomer-shift calibration constant is negative for the ^{57}Fe nucleus. If there is no change in the $3d$ configuration of the irons in a compound, the hybridization of electronic states and the $4s$ electron density of the iron influence the charge density at the iron nucleus.

We discuss the hybridization between the Fe- $3d$ and the nearest neighbor O- $2p$ electrons. Generally, the degree of covalence in the Fe-O bond is changed by both bond length and angle under pressure. Since the Fe ion on the A site in the cubic spinel structure is coordinated by four O ions forming a regular FeO_4 tetrahedron, the bond angle remains constant at 70.53° under pressure. Thus, the degree of covalence in the bond on the A site depends only on the bond length. On the other hand, the FeO_6 octahedra at the B site have a trigonal distortion from O_h symmetry except for an oxygen internal coordinate, $u=0.375$. Although it is not easy to determine u in Fe_3O_4 under pressure experimentally, u below 20 GPa at room temperature was estimated to be in the range

from 0.376 to 0.379 on the basis of recent x-ray diffraction measurements.⁷ The estimated deviation in the bond angle from 90° is 1.5° at ambient conditions and decreases to 0.5° at 18 GPa and room temperature. Thus, the degree of covalence in the bond on the B site also depends mainly on the bond length.

Usually, a volume reduction under pressure means a reduction of bond lengths, as a result of which the degree of covalence in the bond increases. This is attributed to a decrease of δ_{cs} . If we explain the anomalies in the pressure dependences of δ_{cs} by the change of Fe-O bond length, l , the bond length on the A site, l^A , decreases, while that on the B site, l^B , increases at P_c . In the cubic spinel structure, l^A and l^B are represented as $a(u-\frac{1}{4})\sqrt{3}$ and $a(\frac{5}{8}-u)$, respectively, where a is the lattice parameter. There is no structural phase transition below 32 GPa, and the bulk modulus was estimated to be 183 GPa in Fe_3O_4 .^{6,7} The reduction of a is less than 1.5% at about 10 GPa. Namely, if u rapidly decreases at P_c with pressure, l^B increases despite the volume reduction.

We assume that other long-range influences on the charge density at the iron nucleus depend on a . An approximately linear relationship exists between δ_{cs} and Δl and Δa , where

$\Delta l = l_0 - l(P)$ and $\Delta a = a_0 - a(P)$ because of the small volume reduction in Fe_3O_4 up to 32 GPa. X-ray diffraction measurements using synchrotron radiation⁷ have revealed that the refined u value increases gradually with increasing pressure below 9 GPa, but decreases above 9.5 GPa. There is an inconsistency in P_c between the present Mössbauer effect and previous x-ray diffraction measurements, where no discontinuous anomaly was observed in the pressure dependence of refined u . However, the accuracy of the refined u value is not sufficient to discuss the pressure dependence of δ_{cs} . Thus, we assume a linear pressure dependence of u below and above P_c , and obtain linear fits of the form

$$\delta_{cs}^A = 0.286(1) - 0.59(2)\Delta l^A \\ - 0.149(5)\Delta a \text{ mm/s for the A site}$$

and

$$\delta_{cs}^B = 0.682(2) - 3.45(3)\Delta l^B \\ + 0.324(2)\Delta a \text{ mm/s for the B site.}$$

Since the coefficients of Δl are much larger than those of Δa , we can exactly determine l using the pressure dependences of δ_{cs} . It is difficult to determine u in Fe_3O_4 under pressure experimentally by x-ray diffraction measurements using synchrotron radiation because oxygen has about three times fewer electrons than iron. In this analysis, we use

$$u = 0.3781 + 5.0 \times 10^{-5}P \text{ below } P_c$$

and

$$u = 0.3776 - 5.8 \times 10^{-5}P \text{ above } P_c.$$

These linear pressure dependences are quantitatively consistent with the pressure dependence of refined u below 7 GPa and above 9 GPa, respectively.⁷ The decrease in u at P_c is estimated to be 0.0013 using these pressure dependences, which is at most twice as large as the error of refined u from x-ray diffraction measurements.

We have made preliminary band calculations for Fe_3O_4 in a cubic spinel structure with several a and u values to confirm our scenario to explain the present experimental results. The calculated charge densities at the iron nuclei in the A and B sites depend linearly on Δl and Δa . The predicted δ values with increasing pressure are qualitatively consistent with obtained δ_{cs} values. Thus, we conclude that the observed anomalies in the pressure dependences of δ_{cs} at P_c are most likely caused by the discontinuous decrease of u in the cubic inverse spinel structure.

It was recently found that the pressure dependence of resistivity shows a kinklike anomaly at 7.5 GPa and room temperature.¹² This anomaly corresponds to the pressure-induced discontinuous decrease of u in the cubic inverse spinel structure. The anomaly in the pressure dependence of resistivity was observed at 7.5 GPa down to 150 K. Furthermore, the Verwey transition disappears at 7.5 GPa under the quasihydrostatic condition.⁵ Thus, we believe that the disappearance of the Verwey transition is due in part to the pressure-induced discontinuous decrease of u with the cubic inverse spinel structure.

V. SUMMARY

Mössbauer effect measurements of Fe_3O_4 were carried out under pressure up to 18 GPa at room temperature using nonenriched high-quality samples. All observed Mössbauer spectra were well fitted assuming the cubic inverse spinel structure. Thus, Fe_3O_4 does not undergo a magnetic or crystalline structural change up to 18 GPa at room temperature. However, the pressure dependences of the refined hyperfine interaction parameters change at 7.0 GPa. In these pressure dependences, a decrease and increase in δ_{cs} are observed in the A and B sites, respectively, at 7.0 GPa. These anomalies are explained by the pressure-induced discontinuous decrease of u in the cubic inverse spinel structure. Our results suggest that this pressure-induced discontinuous decrease of u is related to the disappearance of the Verwey transition above 7.5 GPa.

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