

High-Spin–Low-Spin Transition in $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ Magnesiowüstite at High Pressures under Hydrostatic Conditions

I. S. Lyubutin^{a,b}, A. G. Gavriiliuk^{a,c}, K. V. Frolov^a, J. F. Lin^d, and I. A. Troyan^a

^a Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, 119333 Russia
e-mail: lyubutin@ns.crys.ras.ru

^b Russian Research Centre Kurchatov Institute, pl. Akademika Kurchatova 1, Moscow, 123182 Russia

^c Institute of High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow region, 142190 Russia

^d Department of Geological Sciences, University of Texas at Austin, Austin, Texas 78712-0254, USA

Received October 1, 2009

The spin states of Fe^{2+} ions in $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ magnesiowüstite crystals at high hydrostatic pressures up to 90 GPa created in a diamond-anvil cell with helium as a pressure-transmitting medium have been investigated by transmission and synchrotron Mössbauer spectroscopy at room temperature. An electron transition from the high-spin (HS) state to the low-spin (LS) state (HS–LS crossover) has been observed in the pressure range of 55–70 GPa. The true HS–LS transition occurs in a narrow pressure range and the extension of the electron transition to ~ 15 GPa is attributed to the effect of the nearest environment and to thermal fluctuations between the high-spin and low-spin states and at finite temperatures. It has been found that the lowest pressure at which the electron HS–LS transition can occur in the $\text{Mg}_{1-x}\text{Fe}_x$ system is 50–55 GPa.

PACS numbers: 74.62.Fj, 75.50.-y, 78.70.En, 81.40.Rs

DOI: 10.1134/S0021364009210061

1. INTRODUCTION

Magnesiowüstite (Mg,Fe)O has an fcc rock salt structure and is one of the main minerals in the Earth's lower mantle [1–3]. For this reason, the investigation of its properties at high pressures and temperatures is of high fundamental significance and is very important for geophysics.

Pressure-induced transitions in (Mg,Fe)O at which the physical properties of the crystal such as the electric and heat conductivities, density, compressibility, speed of sound, and viscosity radically change are of large interest [4, 5]. In particular, the transition of the Fe^{2+} ions from the high-spin (HS) state with $S = 2$ to the low-spin (LS) state with $S = 0$ was observed in [5–9]. This effect was studied using three methods providing information on the electronic state of a crystal in high-pressure diamond-anvil cells. In addition to traditional transmission Mössbauer spectroscopy based on the absorption of γ radiation passed through a sample, nuclear resonant forward scattering of synchrotron radiation (NFS or synchrotron Mössbauer spectroscopy of ^{57}Fe nuclei) and $\text{Fe } K_{\beta}$ high-resolution X-ray emission spectroscopy (XES) also involving synchrotron radiation were used.

Since experiments at high and ultrahigh pressures on micron samples in diamond-anvil cells are complicated, it is difficult to interpret the experimental results. In particular, the character of the electron transition in iron ions is discussed. For example, Kan-

tor et al. [10] stated that the HS–LS transition of Fe^{2+} in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal occurs in a wide pressure range of $\sim (50\text{--}100)$ GPa, whereas the transition revealed in [7] occurs at (62 ± 6) GPa, i.e., in a much narrower pressure range. It was shown in [7] that the character of the electron transition observed by various methods can strongly depend on the effective thickness of the crystal and the degree of the nonhydrostaticity of the experimental conditions. For this reason, the real character of the electron transition remains unclear.

In this work, we report the investigations of the transmission and synchrotron Mössbauer spectra from the ^{57}Fe nuclei in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ magnesiowüstite crystal at hydrostatic pressures up to 90 GPa created in a diamond-anvil cell with helium as a pressure-transmitting medium.

2. EXPERIMENTAL PROCEDURE

Polycrystalline $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ and $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ magnesiowüstite samples were synthesized using ceramic technology and contained iron atoms enriched in the ^{57}Fe isotope up to 96% [5].

For high-pressure measurements up to 90 GPa, the diamond-anvil cell was used. The diameter of the working area of the diamond anvils was about 300 μm . The sample powder was preliminarily pressed between the diamond anvils in the high-pressure cell; as a

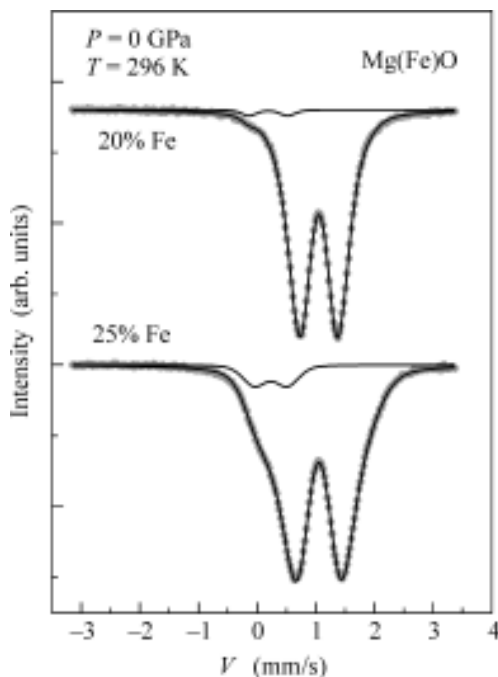


Fig. 1. (Color online) Mössbauer absorption spectra from the ^{57}Fe nuclei in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ and $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ crystals (points) recorded at room temperature and normal pressure in comparison with the calculated spectra for the (blue doublet) Fe^{2+} and (cherry blossom doublet) Fe^{3+} ions.

result, a plate 3 μm in thickness and $70 \times 70 \mu\text{m}$ in size was obtained. Such a sample was placed into the hole in a rhenium gasket with a diameter of about 80 μm . To measure the pressure in the ruby scale, several ruby pieces about 5 μm in size were placed in the working hole of the cell at different points of the working volume in order to estimate the pressure gradient in the cell. To create the hydrostatic condition of the experiment, the working volume of the cell was filled with helium as a medium transferring pressure. The control measurements of the pressure at the center and periphery of the working volume of the cell show that the pressure gradient on the sample was no more than 0.2 GPa at a maximum pressure of 90 GPa in the experiment.

The Mössbauer absorption spectra from the ^{57}Fe nuclei in the sample were detected at room temperature on a standard MS1100Em spectrometer in the constant-acceleration regime. The $^{57}\text{Co}(\text{Rd})$ gamma source was at room temperature. The isomeric shifts were measured with respect to the reference $\alpha\text{-Fe}$ sample (18- μm foil annealed in hydrogen) at room temperature. The computer procession of the spectra was performed with the Univem MS program.

The synchrotron Mössbauer spectra were recorded at room temperature on the 16-IDD and 3-IDB beam

lines at the synchrotron source at the Argonne National Laboratory (United States). The measurement procedure was described in more detail in [5, 7].

3. RESULTS OF THE EXPERIMENTS AND DISCUSSION

3.1. Mössbauer Spectra of Magnesiowürstite at Normal Pressure

At room temperature and normal pressure, the Fe^{2+} ions in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal are in the paramagnetic state and the Mössbauer absorption spectrum includes an intense quadrupole doublet (see Fig. 1), which is attributed to the splitting of the excited level of the ^{57}Fe nuclei (spin $I = \pm 3/2$) by the nonuniform crystal field. In addition to the central doublet, a low-intensity component in the left wing of the spectrum is observed (see Fig. 1) with parameters (isomeric chemical shift IS and quadrupole splitting QS) typical of trivalent Fe^{3+} ions.

The appearance of Fe^{3+} ions is typical of the nonstoichiometric wüstite FeO [11] and Mg-FeO solid solutions [12, 13] both in natural minerals and in synthetic samples. For comparison, Fig. 1 shows the spectrum of the $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ magnesiowürstite, which also exhibits the component from the Fe^{3+} ions. The contents of the Fe^{3+} ions in $\text{Mg}_{0.82}\text{Fe}_{0.2}\text{O}$ and $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ are estimated to be about 2 and 7% of the total amount of iron in the samples, respectively. The trivalent iron ions can be localized both at interstices and at manganese ion sites in the main MgO lattice, forming dimers with a cation vacancy (\square) necessary for the conservation of the electroneutrality of the molecule [12]:



The main central doublet from Fe^{2+} ions is strongly broadened and obviously consists of several components whose lines overlap.

It is worth noting that the strictly stoichiometric compounds FeO and MgO have a purely cubic crystal structure and, therefore, the Mössbauer spectra from Fe^{2+} ions both in FeO [11] and MgO weakly doped with iron [13] contain a singlet line unsplit by quadrupole interaction. This is because the ground state of the Fe^{2+} ion ($^5T_{2g}$ term) in the ideal cubic lattice is degenerate due to the absence of the gradients of the crystal field. In MgO-FeO solid solutions, local distortions of oxygen octahedra occupied by iron and manganese ions arise owing to the difference between the ion radii and the electronic structures of these ions. The local symmetry of the crystal field is violated and the Mössbauer spectrum has the form of a quadrupole doublet owing to the appearance of the gradients of the electric field on the ^{57}Fe nucleus.

3.2. Local-Environment Effects

In the presence of a partial substitution of iron for manganese, nonequivalent sites for the Fe^{2+} ions appear in $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ magnesiowüstite owing to the presence of different numbers of the Mg and Fe ions in the nearest cation environment of iron. As a result, the Mössbauer lines are broadened, because the parameters of the hyperfine interaction for the Fe ions at the nonequivalent sites can be different. Moreover, the lines can be broadened owing to the nonstoichiometry effects, which are also responsible for the appearance of cation vacancies [12].

The nearest environment of the central Fe cation in the (Mg, Fe)O fcc structure consists of six oxygen anions (the first anion coordination sphere) located at a distance of $a/2$ (a is the unit cell parameter). Then, the 12 nearest cations (Mg, Fe) are located at the center of the faces of the cube at a distance of $a\sqrt{2}/2$ (the first cation sphere). Further, six Mg (and/or Fe) cations following oxygen, are located on the faces of the cube at a distance of a from the central cation, and form the second cation coordination sphere.

The number of the nearest neighbors in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ crystal where the Fe ions are located randomly at the manganese sites satisfies the binomial law [14, 15]

$$P_n(m) = \frac{n!}{m!(n-m)!} (1-x)^{n-m} (x)^m, \quad (1)$$

where $P_n(m)$ is the probability that an ion in the n th coordination has m impurity ions (or ions of another kind) among the nearest neighbors and x is the fraction of the impurity ions. Expression (1) with $x = 0.25$ for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ is represented in the form

$$P_n^{\text{Fe}}(m) = \frac{n!}{m!(n-m)!} (0.75)^{n-m} (0.25)^m. \quad (2)$$

Here, $P_n^{\text{Fe}}(m)$ is the probability that an iron ion in the n th coordination has m Fe ions among the nearest neighbors.

First, we consider the nearest environment of the central iron ion consisting of six Mg and/or Fe cations at a distance of a (cations following oxygen). The calculation of the probabilities by Eq. (2) for $n = 6$ shows that the most probable configurations with the probabilities $P_6^{\text{Fe}}(m)$ in the environment of the iron ion are

$$\begin{aligned} (6\text{Mg} + 0\text{Fe}) - P_6^{\text{Fe}}(0) &\approx 18\%, \\ (5\text{Mg} + 1\text{Fe}) - P_6^{\text{Fe}}(1) &\approx 36\%, \\ (4\text{Mg} + 2\text{Fe}) - P_6^{\text{Fe}}(2) &\approx 30\%, \\ (3\text{Mg} + 3\text{Fe}) - P_6^{\text{Fe}}(3) &\approx 13\%. \end{aligned} \quad (3)$$

The contribution from each of the other configurations is less than 3%.

The 12 nearest Mg and/or Fe cations at the centers of the faces of the cube at a distance of $a\sqrt{2}/2$ from the central iron ion form the following configurations with the probabilities $P_{12}^{\text{Fe}}(m)$:

$$\begin{aligned} (12\text{Mg} + 0\text{Fe}) - P_{12}^{\text{Fe}}(0) &\approx 3\%, \\ (11\text{Mg} + 1\text{Fe}) - P_{12}^{\text{Fe}}(1) &\approx 13\%, \\ (10\text{Mg} + 2\text{Fe}) - P_{12}^{\text{Fe}}(2) &\approx 23\%, \\ (9\text{Mg} + 3\text{Fe}) - P_{12}^{\text{Fe}}(3) &\approx 26\%, \\ (8\text{Mg} + 4\text{Fe}) - P_{12}^{\text{Fe}}(4) &\approx 19\%, \\ (7\text{Mg} + 5\text{Fe}) - P_{12}^{\text{Fe}}(5) &\approx 10\%, \\ (6\text{Mg} + 6\text{Fe}) - P_{12}^{\text{Fe}}(6) &\approx 4\%. \end{aligned} \quad (4)$$

The contribution from each of the other configurations is no more than 3%.

The six cations following oxygen are located at the edges of the cube and their distance from the central cation is slightly larger than that of the 12 cations at the centers of the faces of the cube. However, the $180^\circ d-p$ interaction with them via σ bonds through oxygen is more efficient than the 90° interaction with the nearest cations at the centers of the faces. Therefore, the effect of the second cation coordination sphere of the iron ion on the exchange interaction and the distortion of the structure can be stronger than the effect of the first coordination sphere. The radius of the Fe^{2+} ion (0.78 \AA for the high-spin state) is much larger than the radius of the Mg^{2+} ion (0.72 \AA) [16]; for this reason, the introduction of iron to the MgO matrix deforms both the cation framework as a whole and the local oxygen octahedra containing iron.

The distortion degree of the local environment of the Fe^{2+} ion naturally depends both on the number of cations of different kinds (Mg and Fe) in the nearest environment and on the character of their arrangement. The possibility of various variants of the local environment should give rise to the broadening of the Mössbauer lines owing to the difference between the parameters of the hyperfine interaction for iron ions at nonequivalent sites.

3.3. Gradients of the Electric Field and Their Pressure Dependence

The electric-field gradient q at the location point of the ^{57}Fe nucleus includes two main contributions: the lattice contribution q_{lat} (from the crystal field of the surrounding ligand ions) and the electron contribution q_{el} (from the nonspherical distribution of the charge of the electronic shell of the iron ion) [17, 18]. For the case of the Fe^{2+} ions, the $3d^6$ term in the cubic crystal field O_h can be split into the upper orbital 5E doublet

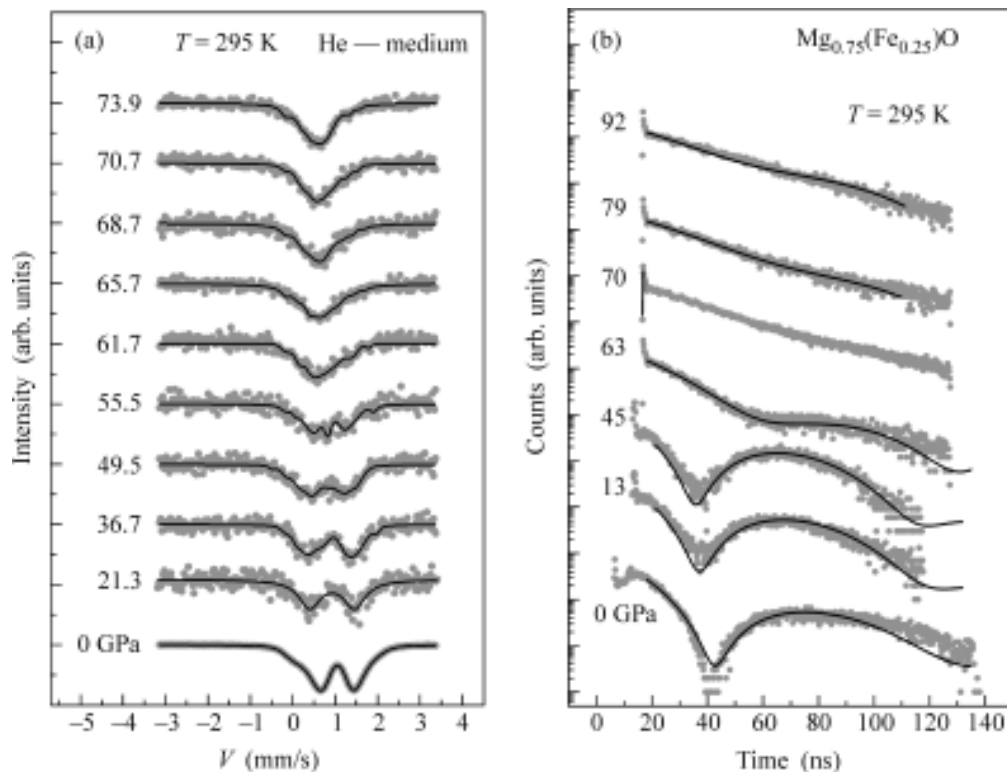


Fig. 2. (a) Mössbauer absorption spectra and (b) NFS spectra from the ^{57}Fe nuclei in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal (points) recorded in the diamond-anvil cell at various pressures in comparison with the calculated spectra shown by the lines.

and the lower orbital 5T_2 triplet, which are separated by a $10Dq$ energy gap. Two electrons in the high-spin state of the Fe^{2+} ion ($e_g^2 t_{2g}^4$) occupy two orbitals on the upper e_g sublevel and four electrons are uniformly distributed over the three orbitals of the lower t_{2g} sublevel. However, the 5E and 5T_2 levels in the ideal cubic environment are degenerate and both contributions q_{lat} and q_{el} should vanish [17]. The quadrupole splitting is absent and a singlet line is observed in the Mössbauer spectrum of the stoichiometric FeO and MgO compounds [11, 13].

Distortions of the lattice lift the degeneracy. The nonuniform occupancy of three orbitals on the t_{2g} sublevel by four electrons gives rise to a significant electric-field gradient owing to the q_{el} contribution. Both contributions q_{lat} and q_{el} in the (Fe, Mg)O magnesio-wüstite are nonzero, but the electron contribution to the electric field gradient is much larger than the lattice contribution as shown in [7]. As a result, the Mössbauer line is split into the quadrupole doublet, which is observed in the experiment for the high-spin state of $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$.

At $P > 50$ GPa, a singlet line appears in the Mössbauer spectrum in addition to the doublet structure (see Fig. 2a). Its intensity increases with pressure

owing to a decrease in the intensity of the doublets. This behavior indicates that some Fe^{2+} ions undergo the electronic transition at which the quadrupole splitting QS vanishes. This can be attributed only to a change in the electron spin structure and the transition of the iron ions from the high-spin state to the low-spin one.

The transitions between the high-spin and low-spin states are possible when the energy of the splitting of the e_g and t_{2g} sublevels in the crystal field is comparable with the Hund energy of the atomic exchange interaction. In the transition from the high-spin ($e_g^2 t_{2g}^4$) state to the low-spin ($e_g^0 t_{2g}^6$) state, two electrons from the upper e_g level pass to the lower t_{2g} sublevels. As a result, three sublevels t_{2g} are completely occupied by six spin-compensated electrons (a diamagnetic state with the spin $S = 0$) and the electron contribution q_{el} to the electric field gradient becomes zero [7, 17].

We observed the same effect in the synchrotron NFS spectra (see Fig. 2b). The quadrupole quantum beats observed in the spectra at pressures below 50 GPa begin to be “damped” with a further increase in the pressure, which is associated with a decrease in the quadrupole interaction parameter. The beats disappear at $P \approx 70$ GPa, indicating that the parameter q

vanishes. A smooth line in the NFS spectrum at $P > 70$ GPa corresponds to the singlet line in the Mössbauer absorption spectrum typical of the low-spin state of the Fe^{2+} ions (see Figs. 2a, 2b).

3.4. HS–LS Transition

The relative contents of the high-spin and low-spin components can be determined in both methods from the areas of the spectral lines for each pressure value in the electron transition region. Figure 3 shows the pressure dependence of the content of the high-spin component, which is obtained from the transmission and synchrotron Mössbauer spectra recorded at room temperature. It is seen that the HS–LS transition begins at a pressure of about 55 GPa and ends near 70 GPa. Above 70 GPa, all of the iron ions in $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ are in the low-spin state.

Taking into account the hydrostatic conditions of the experiment, we can conclude that the expansion of the electron transition in a pressure up to ≈ 15 GPa in this case cannot be explained by the nonuniform distribution of the pressure over the sample. As was shown in Section 3.2, this is primarily attributed to the local-environment effects. The Fe^{2+} ions at different nonequivalent sites apparently pass from the high-spin state to the low-spin one at different pressures.

In [5], it was found that the pressure at which the LS–HS transition occurs in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ crystals increases with the iron concentration x . As was shown above, the increase in x is accompanied by an increase in the fraction of the sites with the mixed content of Mg and Fe cations in the nearest environment of iron. Therefore, Fe^{2+} ions in the uniform local environment pass to the low-spin states earlier (i.e., at a lower pressure) than ions in the nonuniform environment. In particular, according to our experiments, the spin transition in a weakly doped MgO compound should occur at a pressure of about 50–55 GPa. Thus, this is the lowest pressure at which the HS–LS electron transition can occur in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ system.

In [19–21], it was found that the pressure width of the spin transition also depends on the temperature. This is due to thermal fluctuations between the high-spin and low-spin states of the iron ion, and the high-spin and low-spin states can coexist in the transient range at finite temperatures.

The ab initio DFT–GGA + U calculations (U is the Coulomb energy of electron correlations) of the pressures at which the HS–LS transition should occur in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ system at various iron concentrations (at zero temperature) were performed in [22]. It was shown that the critical transition pressure P_C should increase with x and depends strongly on the parameter U . In particular, for our case ($x = 0.25$), $P_C = 106$ and 69 GPa at $U = 5$ and 3 eV, respectively. The second value more correctly describes the experiment. Hence, the lower correlation energy U better

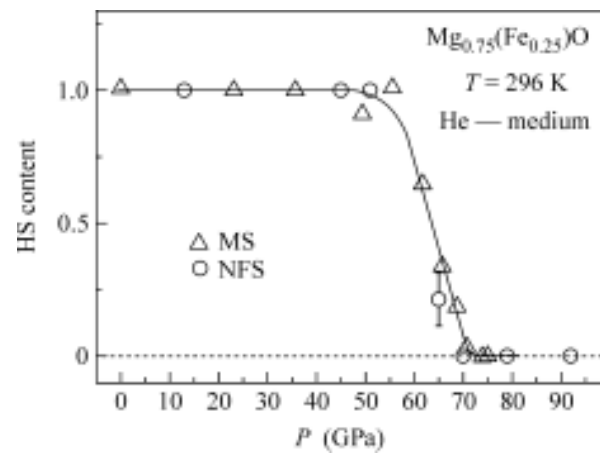


Fig. 3. Pressure dependence of the relative content of the high-spin component in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal in the electron spin transition obtained from the area of the resonance lines in the transmission (MS) and synchrotron (NFS) Mössbauer experiments.

describes the electron structure of $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ at pressures above the HS–LS transition.

To summarize, we have found that the spin crossover occurs in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal at room temperature; the iron ions pass from the high-spin paramagnetic state ($S = 2$) to the low-spin diamagnetic state ($S = 0$). The experiment performed under hydrostatic conditions indicates that this transition occurs in a quite narrow pressure interval (about 15 GPa in width) rather than in a wide range as was erroneously assumed in [10]. It has been found that the lowest pressure at which the electron HS–LS transition can occur in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ system is 50–55 GPa.

It is worth noting that the magnetic order is absent in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ magnesiowüstite crystal at room temperature and normal pressure; for this reason, the HS–LS transition is not accompanied by a magnetic collapse as was observed in a number of crystals such as FeBO_3 , BiFeO_3 , $(\text{La}, \text{Pr})\text{FeO}_3$, Fe_2O_3 , and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ [23]. In the framework of classical notions, the order parameter (magnetization) is absent in the $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ crystal at room temperature and such a transition cannot be treated as a magnetic phase transition. At zero temperature, the spin transition can be considered as a quantum critical point [24].

We are grateful to T.V. Dmitrieva for stimulating discussions. This work was supported by the Federal Agency for Science and Innovation of the Russian Federation (state contract no. 01.164.12.NV11,12); by the Russian Foundation for Basic Research (project no. 08-02-00897-a); and by the Division of Physical Sciences, Russian Academy of Sciences (program “Strongly Correlated Electronic Systems”).

REFERENCES

1. D. M. Sherman, *J. Geophys. Res.* **96**, 14299 (1991).
2. D. Yu. Pushcharovskii, *Priroda* **11**, 119 (1980).
3. D. Yu. Pushcharovskii, *Usp. Fiz. Nauk* **172**, 480 (2002) [*Phys. Usp.* **45**, 439 (2002)].
4. J.-F. Lin, V. V. Struzhkin, S. D. Jacobsen, et al., *Nature* **436**, 377 (2005).
5. J.-F. Lin, A. G. Gavriiliuk, V. V. Struzhkin, et al., *Phys. Rev. B* **71**, 113107 (2006).
6. I. Yu. Kantor, L. S. Dubrovinsky, and C. A. McCammon, *Phys. Rev. B* **73**, 100101 (2006).
7. A. G. Gavriilyuk, J. F. Lin, I. S. Lyubutin, and V. V. Struzhkin, *Pis'ma Zh. Eksp. Teor. Fiz.* **84**, 190 (2006) [*JETP Lett.* **84**, 161 (2006)].
8. J. F. Lin, V. V. Struzhkin, A. G. Gavriiliuk, and I. S. Lyubutin, *Phys. Rev. B* **75**, 177102-1 (2007).
9. J.-F. Lin, A. G. Gavriiliuk, W. Sturhahn, et al., *Am. Mineralogist* **94**, 594 (2009).
10. I. Yu. Kantor, L. S. Dubrovinsky, and C. A. McCammon, in *Proceedings of the Joint 20th AIRAPT and 43th EHPRG, June 27 to July 1, Karlsruhe, Germany, 2005*.
11. R. I. Chalabov, I. S. Lyubutin, Z. I. Zhmurova, et al., *Kristallografiya* **27**, 516 (1982) [*Sov. Phys. Crystallogr.* **27**, 312 (1982)].
12. D. P. Dobson, N. S. Cohen, Q. A. Pankhurst, and J. P. Brotholt, *Am. Mineralogist* **83**, 794 (1998).
13. H. R. Leider and D. N. Pipkorn, *Phys. Rev.* **165**, 494 (1968).
14. M. A. Gilleo, *J. Phys. Chem. Solids* **13**, 33 (1960).
15. I. S. Lyubutin and T. V. Dmitrieva, in *Results of Science and Technology*, Ser. Crystallochemistry, vol. 12 (Moscow, 1977), p. 5 (p. 13).
16. R. D. Shannon, *Acta Crystallogr. A: Found. Crystallogr.* **32**, 751 (1976).
17. P. Gutlich, in *Spin Transition in Iron Compounds in Chemical Mossbauer Spectroscopy*, Ed. by R. H. Herber (Chapman and Hall, London, 1978), p. 27.
18. H. Spiering, E. Meissner, H. Koppen, et al., *Chem. Phys.* **68**, 65 (1982).
19. I. S. Lyubutin, A. G. Gavriilyuk, V. V. Struzhkin, et al., *Pis'ma Zh. Eksp. Teor. Fiz.* **84**, 610 (2006) [*JETP Lett.* **84**, 518 (2006)].
20. I. S. Lyubutin, A. G. Gavriilyuk, V. V. Struzhkin, *Pis'ma Zh. Eksp. Teor. Fiz.* **88**, 601 (2008) [*JETP Lett.* **88**, 524 (2008)].
21. A. G. Gavriiliuk, V. V. Struzhkin, I. S. Lyubutin, et al., *Phys. Rev. B* **77**, 155112-1 (2008).
22. K. Persson, A. Bengtson, G. Ceder, and D. Morgan, *Geophys. Res. Lett.* **33**, L16306 (2006).
23. I. S. Lyubutin and A. G. Gavriilyuk, *Usp. Fiz. Nauk* **179**, 1047 (2009) [*Phys. Usp.* **52**, 1047 (2009)].
24. A. I. Nesterov and S. G. Ovchinnikov, *Pis'ma Zh. Eksp. Teor. Fiz.* **90**, 580 (2009); arXiv:0907.1310v1 [cond-mat.str-el] (7 Jul 2009).

Translated by R. Tyapaev

SPELL: OK