Phys. Status Solidi B **250**, No. 4, 750–754 (2013) / **DOI** 10.1002/pssb.201200487

physica status solidi b
www.pss-b.com
basic solid state physics

Iron in magnesium oxide at high pressures: a first principles theoretical investigation

Rolando Larico[*,1], **João F. Justo**[1], and **Lucy V. C. Assali**[2]

[1] Escola Politécnica, Universidade de São Paulo, CP 61548, CEP 05424-970, São Paulo, SP, Brazil
[2] Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo, SP, Brazil

Received 16 July 2012, revised 5 November 2012, accepted 13 November 2012
Published online 2 April 2013

Keywords ferropericlase, Hubbard potential, spin states

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[*] Corresponding author: e-mail rlarico@if.usp.br, Phone: +55 11 3091 5310, Fax: +55 11 3091 5585

An iron-related high-to-low spin transition in ferropericlase, (MgFe)O, has been identified at high pressures. Since this is one of the major minerals of Earth's lower mantle, and the respective transition occurs at mantle pressure and temperature conditions, this transition could have important geophysical implications. Here, we performed a theoretical investigation on the properties of a substitutional iron impurity in magnesium oxide, (MgO: Fe_{Mg}), and the respective changes with increasing isotropic pressure. This microscopic configuration represents the limiting case of absent iron–iron interactions in ferropericlase, which allowed us to explore the magnetic properties of the isolated iron center. The calculations were performed using the WIEN2k package, within the density functional theory plus a Hubbard potential correction. The structural, electronic, and magnetic properties of those centers at several charge states and pressures (up to 100 GPa) were compared. We also discussed the possibility of an iron-related intermediate spin (IS) state in ferropericlase. Our results on the quadrupole splitting indicate that such IS state should have properties similar to the respective spin state in ferrosilicate perovskite.

1 Introduction A high-pressure iron-related spin transition in ferropericlase ($(Mg_{1-x}Fe_x)O$) and ferrosilicate perovskite ($Mg_{1-x}Fe_xSiO_3$) has been identified [1, 2]. Since those are the two major minerals in Earth's lower mantle, with the respective spin transitions observed in mantle pressure and temperature conditions, this transition should have important geophysical implications [3, 4]. The electronic structure of the iron-related energy levels in ferropericlase could be described as follows. An iron atom replaces a magnesium one in a magnesium oxide structure, donating two valence electrons to its nearest neighboring oxygen atoms. The six remaining 3d iron-related electrons generate a $t_2 + e$ pair of orbitals, with the t_2 orbital staying below the e one. Therefore, for a neutral charge state, iron has a 2+ net charge. At low pressures, the spin polarization splitting prevails over the crystalline field, favoring the high spin (HS) $S = 2$ state. The crystalline field splitting becomes more important than spin polarization one with increasing pressure, favoring the low spin (LS) $S = 0$ state beyond a certain transition pressure. Early experiments suggested that this transition should be very sharp [5], occurring in a narrow pressure range. More recent theoretical [6, 7] and experimental [8–11] investigations indicated that it should be smooth at high temperatures, across a wide pressure range. This transition has been theoretically described by a thermodynamic model, in which ferropericlase was described as an ideal solid solution with simultaneous concentrations of iron atoms in HS and LS states [6, 7].

Investigations on the iron properties in mantle minerals represent a fundamental step toward an understanding on the Earth's deep underground. There are many open questions that still need to be addressed, in order to get a better description of those minerals, related to their elasticity, radiative conductivity, and iron–iron interactions. Additionally, a high-to-low spin transition has been observed for iron in both ferropericlase and ferrosilicate perovskite [2, 12]. An intriguing result is that while for ferropericlase only two spin states have been identified so far, in ferrosilicate perovskite an intermediate ($S = 1$) spin state has also been observed [12]. This leads directly to the question if this intermediate spin (IS) state could also be energetically favorable in ferropericlase at some pressure. Several other questions also deserve attention, such as the charge state of iron atoms in minerals of the lower mantle.

Here, we present a theoretical investigation that addresses some of those questions. We explored the case of an isolated substitutional iron atom in magnesium oxide. In that case, iron was considered as an impurity, representing ferropericlase with very low iron concentrations, in which the effects of iron–iron spin interactions could be neglected. The first principles calculations were performed using the all-electron full-potential linearized augmented plane wave (FP-LAPW) method, within the density functional theory/generalized gradient approximation (GGA) plus the Hubbard potential correction. The introduction of this correction was fundamental to get an appropriate description of this strongly correlated electronic system. Our calculations provided information on the structural, electronic, and magnetic properties of iron impurities in several charge states and pressures. We discuss the properties of this IS state, and how it could be identified in ferropericlase by electron paramagnetic resonance (EPR) or Mössbauer spectroscopy.

2 Methodology The calculations were performed using the WIEN2k package, based on the all-electron FP-LAPW method [13]. The electronic exchange interactions were described within the GGA [14] plus the U Hubbard potential correction (GGA + U) [15]. It is well established in the literature that the density functional theory provides a poor description on the electronic interactions of strongly correlated systems, such as the 3d iron-related energy levels in those systems. Calculations based on both the local density approximation (LDA) or GGA lead to a metallic state for ferropericlase and iron oxide, although experimental results indicate that those systems are insulators. The introduction of a Hubbard U potential correction increases the correlation interactions of 3d-related electronic levels, providing results consistent with experimental data. Here, the on-site Hubbard potential values, for the 3d iron states, were obtained self-consistently [16].

We considered a reference supercell with 54 atoms, describing the host MgO in a rocksalt structure, with a substitutional Fe atom in a Mg site. The convergence in total energy was achieved using a 7.0/R parameter, which defines the total number of plane waves to describe the electronic wave functions in the interstitial regions, where R is the sphere radius of all the atomic regions ($R = 0.90$ Å). For a certain atomic configuration, self-consistent iterations to solve the Kohn–Sham equations were performed until reaching convergence on both the total energy (10^{-4} eV atom^{-1}) and the total charge in the atomic spheres (10^{-5} electronic charges per atom). The positions of all atoms were relaxed, with no symmetry constrains, until the forces were smaller than 0.02 eV Å^{-1} in any atom. Additionally, the irreducible Brillouin zone was sampled by a $2 \times 2 \times 2$ k-point grid. For the calculations of the hyperfine parameters and electric field gradients (EFGs), we used results converged with a 64 k-point grid. All those approximations and convergence criteria have been shown to provide an accurate description on the electronic and structural properties of defect centers in several materials [17, 18].

The formation energy of an iron impurity in MgO, $E_{\mathrm{F}}^{q}(\mathrm{MgO}:\mathrm{Fe_{Mg}})$, is given by [19, 20]

$$E_{\mathrm{f}}^{q}(\mathrm{MgO}:\mathrm{Fe_{Mg}}) = E_{\mathrm{tot}}^{q}(\mathrm{MgO}:\mathrm{Fe_{Mg}}) - E_{\mathrm{tot}}(\mathrm{MgO}) + \mu_{\mathrm{Mg}} - \mu_{\mathrm{Fe}} + q(\varepsilon_{\mathrm{v}} + \varepsilon_{\mathrm{F}}), \quad (1)$$

where $E_{\mathrm{tot}}^{q}(\mathrm{MgO}:\mathrm{Fe_{Mg}})$ is the total energy of a supercell (in the q charge state) containing the iron impurity, $E_{\mathrm{tot}}(\mathrm{MgO})$ is the total energy of a MgO crystal considering the same reference supercell, ε_{v} is valence-band maximum, and ε_{F} is the Fermi level. Additionally, μ_{Fe} and μ_{Mg} are respectively the Fe and Mg chemical potentials, computed for their bulk stable crystalline phases, using the same approximations described in the previous paragraphs.

3 Results Under ambient conditions, MgO crystallizes in the rocksalt structure, with measured lattice parameter of $a_{\mathrm{expt}} = 4.216$ Å and bulk modulus in the 154–166 GPa range [21]. In this study, we found a lattice parameter of $a_{\mathrm{th}} = 4.21$ Å, with a Mg–O interatomic distance d(Mg–O) = 2.126 Å, and an oxygen octahedron volume around a Mg atom of 12.81 Å^3. The bulk modulus was 152 GPa, using a third-order Birch–Murnaghan equation of state. Those structural parameters are fully consistent with the values obtained by other theoretical investigations using similar approximations [22] and in excellent agreement with experimental data [21]. The equation of state was used to obtain the dependence of the MgO lattice parameter with external pressure.

We found a direct bandgap of $E_{\mathrm{g}} = 4.49$ eV for MgO at ambient conditions, which is an underestimation of the experimental value (≈7.67 eV) [21]. This reasonably poor description of the bandgap value by the density functional theory is well documented in the literature, although such theory provides a proper description on the ground state of the system. Our calculations showed that the MgO bandgap increases with pressure, going to 6.77 eV for $P = 50$ GPa and 8.32 eV for $P = 100$ GPa.

We initially investigated the structural properties of substitutional Fe impurity center in MgO, (MgO: $\mathrm{Fe_{Mg}}$), at zero pressure, and then observed the changes on those properties with increasing pressure. We considered pressures up to 100 GPa, which is the range in which ferropericlase is expected to be found in the lower mantle. At zero pressure, the introduction of a substitutional Fe atom in a Mg site causes important relaxations on the neighboring oxygen atoms. For the $\mathrm{Fe_{Mg}}$ center in the neutral charge state, there are two known spin states (HS and LS). For the HS state, the system presents a small outward relaxation with respect to the original MgO crystalline structure, due to a larger atomic Fe size compared to Mg one. Additionally, the center presents a Jahn–Teller distortion, which resulted from partially occupied iron-related energy levels. There are four neighboring oxygen atoms at a distance d(Fe–O) = 2.173 Å and two oxygen atoms at a distance d(Fe–O) = 2.136 Å, all

Table 1 *Ab initio* results for (MgO: Fe_{Mg})^q at zero pressure: spin state configuration, total spin (S), volume of the oxygen octahedron around the Fe atom (V_{oct}), and formation (E_f) and transition (E_t) energies for different q charge states.

center	state	S	V_{oct}	E_f	E_t
(MgO: Fe_{Mg})$^{2+}$	HS	2	11.94	$5.53 + 2\varepsilon_F$	0.78 (2+/+)
	LS	1	10.45	$6.31 + 2\varepsilon_F$	2.12 (2+/+)
(MgO: Fe_{Mg})$^{+}$	HS	5/2	12.02	$6.31 + \varepsilon_F$	3.83 (+/0)
	LS	1/2	11.20	$8.43 + \varepsilon_F$	3.15 (+/0)
(MgO: Fe_{Mg})^{0}	HS	2	13.45	10.14	
	IS	1	13.30	11.41	
	LS	0	13.08	11.58	

Transition energies were computed with respect to the MgO valence band top (ε_v).
Volumes and energies are in Å^3 and eV, respectively.

larger than the d(Mg–O) of the original MgO crystal. The oxygen octahedron around the Fe impurity is 13.45 Å^3.

Going from HS to LS state, there is a substantial inward relaxation, with the oxygen octahedron going to 13.08 Å^3, a 3% volume reduction with respect to that in HS. The LS center has an octahedral symmetry, such that the iron atom has all six oxygen neighboring atoms at d(Fe–O) = 2.138 Å. This volume reduction is fully consistent with the respective one of 7% computed in ferropericlase ($Mg_{1-x}Fe_xO$ with $x = 0.18$) [23].

Table 1 presents formation and transition energies of the impurity in HS and LS states for several charge states at zero pressure. The results indicated that there are only three stable charge states (neutral, positive, and doubly positive), those that present levels in the MgO bandgap, while there is no stable negative charge state. For neutral charge state, (MgO: Fe_{Mg})^0, the formation energy of the LS state is about 1.44 eV higher than that of the HS state. Consistent with theoretical [23, 6] and experimental [5] results, the HS state is more stable than the LS one at low pressures.

Our calculations also indicated that in the neutral charge state, there is a metastable IS state with $S = 1$, with a formation energy of 1.27 eV higher than that of the HS state. It is interesting to observe that an IS has been previously investigated in ferrosilicate perovskite [12, 24], but there is still no evidence of such spin state in ferropericlase. This IS state has an structural configuration that resembles the one of the HS state, with the Fe impurity with four neighboring oxygen atoms at d(Fe–O) = 2.135 Å and two neighboring ones at d(Fe–O) = 2.188 Å. The IS state presents an oxygen octahedron volume of 13.30 Å^3, which is a little smaller than that of the HS state.

According to Table 1, the (MgO: Fe_{Mg})$^+$ center has two possible spin states, HS ($S = 5/2$) and LS ($S = 1/2$), with the HS state about 2.12 eV lower in energy than the LS one. The (MgO: Fe_{Mg})$^{2+}$ has also two possible spin states, HS ($S = 2$) and LS (S = 1), with the HS state lower in energy than the LS one. The results indicated that, for low pressures, the HS state is more stable than the LS one irrespective of the charge state of the center.

Table 1 presents the structural properties of the impurity in positive and doubly positive charge states at zero pressure. Going from a neutral charge state to a positive one, there is a substantial volume reduction in the oxygen octahedron, which is a result of reduction in the electronic repulsion. On going from the positive charge state to the doubly positive one, there is an additional volume reduction. Consistent with the neutral charge state, the positive and doubly positive charge states present a substantial inward relaxation for the system following a high-to-low spin transition.

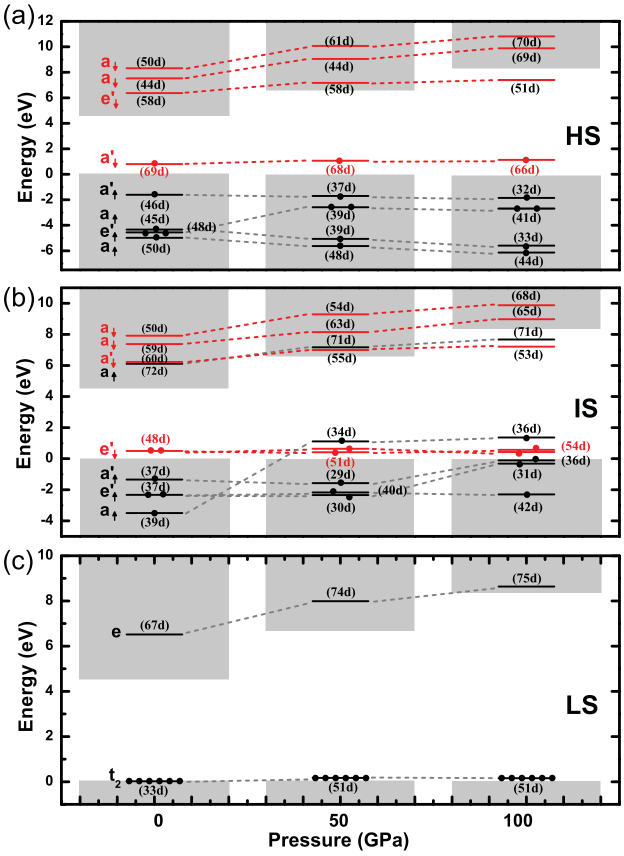

Figure 1 The 3d-related energy levels of (MgO: Fe_{Mg})^0, at several pressures, in (a) $S = 2$ (HS), (b) $S = 1$ (IS), and (c) $S = 0$ (LS) states. Level occupations are given by the numbers of filled circles. Numbers in parentheses represent the d-character percentage inside the Fe atomic sphere. Up (down) arrows represent the spin up (down) levels.

We observed that, for all charge states, the external pressure does not modify the symmetry of the centers, only compresses the respective oxygen octrahedra. Therefore, pressure does not modify the structure of the centers, although it affects more strongly the electronic structure. Figure 1 presents the electronic structure of $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ in the HS, IS, and LS states at several pressures. In the LS state, the system presents a close shell configuration, with a fully occupied t_2 level near the valence band top of MgO and an unoccupied e one in the conduction band. For the HS state, due to the Jahn–Teller distortion, the t_2 level splits into $a+e$ ones. The HS state consists of five electrons with spin up and one with spin down. Such picture for the HS and LS states does not change with increasing pressure, the energy levels are only shifted as the materials bandgap increases with pressure.

The electronic structure is more complex for the IS state. At zero pressure, the highest occupied level is the $e_\downarrow$ with two electrons, near the valence band top, while the first unoccupied level is inside the conduction band. On the other hand, with increasing pressure of the highest occupied level changes from an e character to an a one.

Identifying experimentally the IS state in ferropericlase could be challenging, since the concentrations of magnetic centers modify with increasing pressure [6, 7]. Therefore, it is important to identify isolated magnetic centers, and a possible way is to use EPR or Mösbauer spectroscopy, in which the hyperfine parameters could be measured and compared. Figure 2 presents the theoretical hyperfine parameters for the HS and IS states in the neutral charge state as a function of pressure. The large differences in the hyperfine parameters, between HS and IS states, may allow a proper identification of this IS state in ferropericlase. The figure also shows that those parameters are essentially insensitive to external pressure.

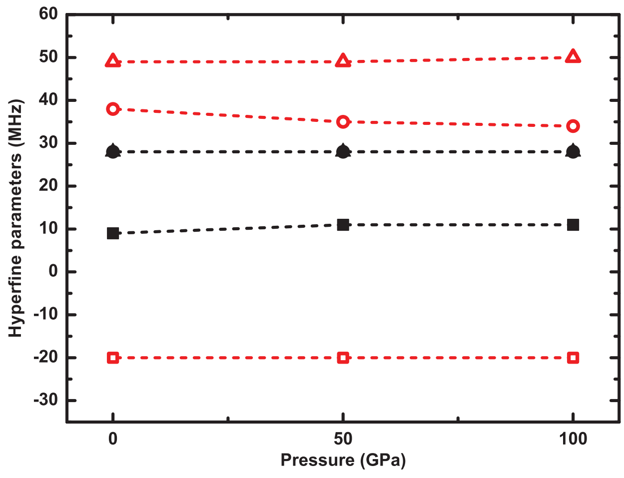

Figure 2 Hyperfine parameters: A_1 (square), A_2 (triangle), and A_3 (circle) for the $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ center, in HS (close symbols) and IS (open symbols) states, as a function of pressure. Hyperfine parameters are given in MHz.

Nuclear quadrupole resonance measurements is another technique that could allow to distinguish the HS and IS states, in which the measurements are associated to the EFG of each center. We computed the EFG of all spin states in the $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ as a function of pressure. The computed EFG, V_{zz}, at the center of the iron nucleus is converted to the QS value, using the relation $\mathrm{QS} \simeq eQV_{zz}/2h$, where $(h/e) = 4.1356692 \times 10^{-15}\,\mathrm{V\,MHz^{-1}}$ and Q denotes the nuclear electric quadrupole moment of iron. The EFGs were converted to the QS values using the $^{57}\mathrm{Fe}$ nuclear quadrupole moment $Q = 0.16 \pm 0.02$ barn (1 barn $= 10^{-28}\mathrm{m}^2$) [25].

Figure 3a shows the QS of the $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ center in HS, IS, and LS states. There is a large difference of the QS for the HS and IS states, which may help to distinguish the HS and IS states. Additionally, the behavior of the QS is very sensitive to the external pressure. Figure 3b compares our results of $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ with those of theoretical [27] and experimental [26] investigations of the $(\mathrm{MgSiO_3{:}\ Fe_{Mg}})^0$, i.e. iron in ferrosilicate perovskite. In $\mathrm{MgSiO_3}$, there are two

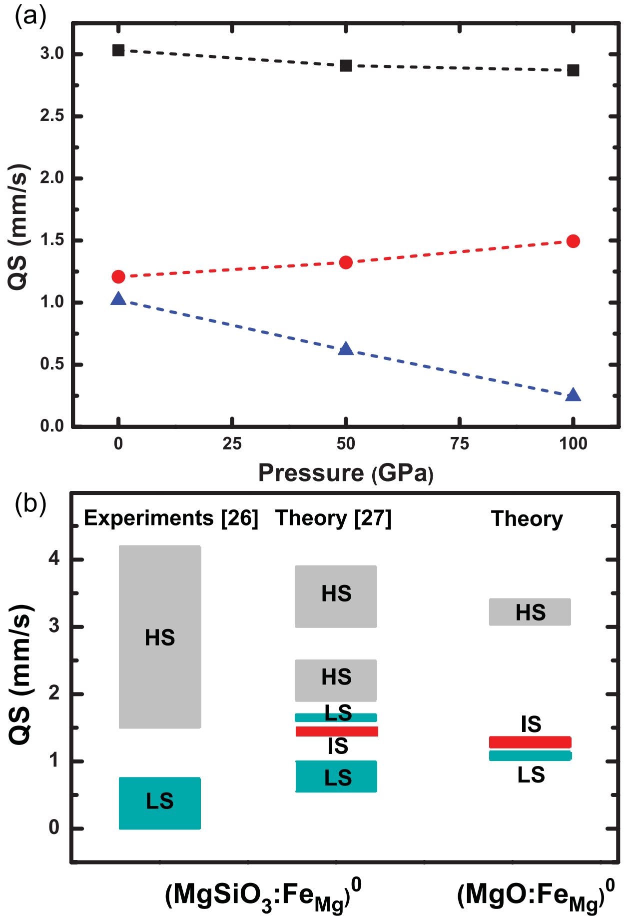

Figure 3 (a) Quadrupole splitting (QS) of $(\mathrm{MgO{:}\ Fe_{Mg}})^0$ center in HS (squares), IS (circles) and LS (triangles) states as a function of pressure. (b) Our results, for zero pressure, compared to experimental [26] and theoretical [27] values at the Fe atom in ferrosilicate perovskite, $(\mathrm{MgSiO_3{:}\ Fe_{Mg}})^0$. QS is given in $\mathrm{mm\,s^{-1}}$.

different Mg substitutional sites, and, for the neutral charge state, substitutional iron can assume a 2+ or 3+ total net charge in each of those sites. Here, we compare our results for the neutral iron center in MgO (in which Fe stays a 2+ total net charge) with the neutral iron center (in which Fe is in the site that leads to a 2+ total net charge). The results are fully consistent, indicating the similarities of iron in ferropericlase and ferrosilicate perovskite. In both cases, the QS splitting of the HS state is considerably larger than the one of the IS state.

4 Summary In summary, we performed a first principles investigation on the properties of iron impurities in magnesium oxide. We find that iron can stay stable in three charge states (neutral, positive, and doubly positive). Our results indicate that in the neutral charge state, there are three possible spin states, HS, LS, and IS. This IS state has been previously identified in ferrosilicate perovskite, but there is still no experimental evidence of its existence in ferropericlase. In order to help identify this IS state, we present results on the hyperfine parameters and quadrupole splitting of all possible spin states. Our results indicate that this IS state in MgO is fully consistent with the one observed in ferrosilicate perovskite.

Acknowledgements We acknowledge partial support from Brazilian agencies FAPESP and CNPq.

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