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MgFeO ($x \leq 0.25$)

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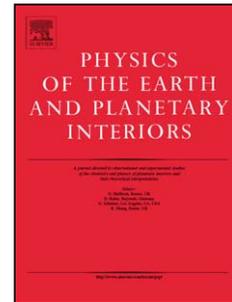
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Ab initio calculations of the elastic properties
of ferropericlase $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ ($x \leq 0.25$)

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Abstract

Ferropericlase $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ is believed to be the second most abundant mineral in the Earth's mantle. Therefore, the electronic and elastic properties of ferropericlase are important for the understanding of the Earth's interior. *Ab initio* total energy calculations have been performed for Fe concentrations $x \leq 0.25$. The equation of state (EOS) clearly shows a volume expansion as a function of Fe concentration, consistent with experimental data. Magnetic moment calculations as a function of

pressure show a high-spin to low-spin transition of Fe^{2+} , and the theoretical transition pressure increases with iron composition. At ambient pressure, we have found that the shear constant C_{44} reproduces well the experimental data as a function of Fe concentration. The MgO and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$ minerals show an increasing C_{44} with pressure, whereas the $\Delta C_{44}/\Delta P$ is slightly negative after 26 GPa for $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$. The C_{44} softening could be related to the transition from the cubic to a rhombohedrally distorted phase, recently found by experiment.

1 Introduction

Abundant minerals in the Earth's lower mantle, between 660 km and 2900 km in depth (Anderson, 1989), are believed to be Mg-Fe silicate perovskite $(\text{Mg,Fe})\text{SiO}_3$, rock-salt structured ferropericlase $(\text{Mg,Fe})\text{O}$ and calcium silicate perovskite CaSiO_3 (Irifune, 1994; Wood, 2000). The geodynamical importance of $(\text{Mg,Fe})\text{O}$ is primarily related to the elastic properties of this compound. Its stress and strain relation has been studied recently (e.g. Madi et al., 2005), and the predicted large elastic anisotropy of $(\text{Mg,Fe})\text{O}$ (Karki et al., 1997; Wentzcovitch et al., 1998) could contribute to the seismic anisotropy development. Based on the models of the Earth's interior, high pressure experiments have shown that the FeO content in the ferropericlase phase is about 10-20 mol % (Mao et al., 1997; Wood, 2000). For a better understanding of the mineralogy in the mantle, the high-pressure properties of ferropericlase are highly important from a geophysical aspect (Kung et al., 2002; Holzappel et al., 2003).

The physical properties of $(\text{Mg,Fe})\text{O}$ have been studied extensively by both

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static and dynamic methods (Jackson et al., 1978; Fei et al., 1992; Kung et al., 2002; Zhang and Kostak, 2002). However, experimental determination of mineral properties at extreme conditions is a challenging task. Therefore, theoretical studies are useful as present-day quantum-mechanical simulations have reached a high accuracy. To investigate the composition of the mantle, comparisons have to be made between the elasticity of candidate minerals and seismological data. Elastic property studies of ferropericlase have mainly been done at ambient conditions or at pressures below 10 GPa (Jackson et al., 1978; Bonczar and Graham, 1982; Jacobsen et al., 2002b; Kung et al., 2002; Jacobsen et al., 2004, 2005). Recent calculations based on the finite element method have shown an elastic discrepancy between $(\text{Mg,Fe})\text{SiO}_3$ and $(\text{Mg,Fe})\text{O}$ as perovskite shows a significantly higher stress level, whereas $(\text{Mg,Fe})\text{O}$ accommodates most of the strain (Madi et al., 2005).

As iron is the most frequently occurring transition-metal element in the mantle, its properties at extreme conditions is highly interesting. High-pressure studies of iron-bearing minerals such as magnesiowüstite and silicate perovskite have indicated high-spin (HS) to low-spin (LS) transitions (Badro et al., 2003, 2004). The transition has a major impact on the mineral properties such as the density, iron-partitioning and thermal conductivity (Sherman, 1988, 1991; Sherman and Jansen, 1995; Cohen et al., 1997; Li et al., 2004; Goncharov et al., 2006; Keppler et al., 2007).

In this work, we have performed *ab initio* calculations to study the magnetic moment, the equation of state (EOS) and the elastic constants of $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ at high pressure. At ambient conditions, the wide band gap insulator MgO (periclase) and the Mott insulator FeO (wüstite) both have the cubic rock-salt structure and similar lattice parameters. However, the properties of the minerals differ at high pressure. In this study, $(\text{Mg,Fe})\text{O}$ was examined ap-

proximately up to 100 GPa. At these pressures there are no phase transitions for periclase, retaining the NaCl structure to at least 227 GPa (Duffy et al., 1995). Wüstite, however, undergoes a transition to a rhombohedrally distorted $B1$ structure at ~ 16 GPa. (Zhou et al., 1980; Yagi et al., 1985; Kondo et al., 2004) At this pressure, Kondo et al. (2004) have also reported a distortion for 0.8, 0.9 and 0.95 for $Mg_{1-x}Fe_xO$ whereas Kantor et al. (2005) have shown the existence of a trigonal distortion of $Mg_{0.8}Fe_{0.2}O$. However, other studies have emphasized that the addition of Mg in wüstite can stabilize the rock-salt structure to higher pressures: the transition pressure was found above 20 GPa for $Mg_{0.1}Fe_{0.9}O$ and above 60-100 GPa for $Mg_{0.25}Fe_{0.75}O$ (Mao et al., 2002; Lin et al., 2003). For $Mg_{0.39}Fe_{0.61}O$, no transition was reported up to 102 GPa (Lin et al., 2003). As only Mg rich compounds were examined in this study, the calculations were performed with the NaCl structure.

2 Theory

2.1 Methods

The equation of state and elastic constant calculations were performed using the Exact Muffin-Tin Orbitals (EMTO) method (Andersen et al., 1994; Kollár et al., 2000; Vitos, 2001; Vitos et al., 2001; Vitos, 2004) based on the density functional theory (DFT) (Hohenberg and Kohn, 1964). The EMTO-CPA method is a mean-field approach to treat substitutional random systems. It neglects the short-range order and local lattice relaxation effects, but, at the same time, it gives highly accurate total energies for completely disor-

dered solid-solutions (Vitos et al., 2001; Magyari-Köpe et al., 2002, 2004; Taga et al., 2005). By keeping the accuracy for both ordered and disordered systems at the same footing, this method represents an ideal tool for tracing the effect of dopands on the thermodynamical and mechanical properties of solid-solutions (Olsson et al., 2003; Vitos et al., 2003; Korzhavyi et al., 2004; Vitos et al., 2006a), including minerals (Dubrovinsky et al., 2003; Dubrovinskaia et al., 2005; Vitos et al., 2006b; Dubrovinsky et al., 2007). For the exchange-correlation functional, the Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al., 1996) was applied. Self-consistent calculations for the magnetic structure of (Mg,Fe)O were carried out using the code VASP (Vienna *Ab Initio* Simulation Program) (Kresse and Hafner, 1993, 1994; Kresse and Furthmüller, 1996a,b). In this study, both lattice parameters and internal coordinates of the atoms were fully relaxed. The VASP calculations were carried out using the PBE functional and the Projector-Augmented Wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999) as implemented in the VASP package.

2.2 Equation of state

To calculate the EOS, the third-order Birch-Murnaghan (B-M) equation was used (Birch, 1947, 1978). According to this, the pressure is given by

$$P(x) = \frac{3}{2}K_0[x^{\frac{7}{3}} - x^{\frac{5}{3}}](1 + \chi[x^{\frac{2}{3}} - 1]) \quad , \quad (1)$$

and the total energy is

$$E(x) = E_0 + \frac{3}{2}K_0V_0\left[\frac{3}{2}(\chi - 1)x^{\frac{2}{3}} + \frac{3}{4}(1 - 2\chi)x^{\frac{4}{3}} + \frac{1}{2}\chi x^{\frac{6}{3}} - \frac{2\chi - 3}{4}\right] \quad , \quad (2)$$

where $x = V/V_0$ and $\chi = \frac{3}{4}(K'_0 - 4)$. The equilibrium volume V_0 , the equilibrium bulk modulus K_0 and its pressure derivative K'_0 were determined by fitting Eq. (2) to the total energies calculated for different volumes.

2.3 Elastic constant calculations

The three independent elastic constants for a cubic lattice are C_{11} , C_{12} and C_{44} . To deduce the elastic moduli, strains were applied to the lattices, yielding energy deviations from the equilibrium. If a Taylor expansion is performed for the energy $E(V, e)$, where V is the volume and e a small strain of the lattice, the truncated energy becomes

$$E(V, e) = E(V_0, 0) + V_0 \left(\sum_i \tau_i e_i \eta_i + \frac{1}{2} \sum_{ij} C_{ij} e_i \eta_i e_j \eta_j \right) , \quad (3)$$

where V_0 is the equilibrium volume and τ_i are elements in the stress tensor. Following the Voigt notation, $\eta_i=1$ if $i=1,2$ or 3 and $\eta_i=2$ if $i=4,5$ or 6 . The distortions were applied according to the rule

$$\mathbf{a}' = [\mathbf{I} + \epsilon(e)]\mathbf{a} , \quad (4)$$

where \mathbf{I} is the 3×3 identity matrix, \mathbf{a} (\mathbf{a}') are the undistorted (distorted) lattice vectors, and $\epsilon(e)$ is the strain component matrix. For volume conserving deformations, $\det \epsilon(e) = 0$, and the first order terms in Eq. (3) disappear. To find the shear modulus $C' = (C_{11} - C_{12})/2$, the orthorhombic deformation

$$\epsilon_o(e) = \begin{pmatrix} e & 0 & 0 \\ 0 & -e & 0 \\ 0 & 0 & \frac{e^2}{1-e^2} \end{pmatrix} \quad (5)$$

was applied. Analogously, for C_{44} a monoclinic deformation was used,

$$\epsilon_m(e) = \begin{pmatrix} 0 & e/2 & 0 \\ e/2 & 0 & 0 \\ 0 & 0 & \frac{e^2}{1-e^2} \end{pmatrix} \quad (6)$$

For the distortion e , Eq. (3) can be written as

$$\frac{E(V, e) - E(V_0, 0)}{V_0} = 2 C e^2 + O(e^4) . \quad (7)$$

The total energy differences $\Delta E_o(e)$ and $\Delta E_m(e)$ were calculated for six distortions $e=0.00, 0.01, 0.02, \dots, 0.05$. To minimize the numerical noise, the energy expressions were fitted to a second order polynomial of the distortion e by means of least squares approximations.

2.4 Numerical data

For the EMTO calculations, the Green's function was calculated for 44 energy points on the complex contour. The k -point mesh for the Brillouin zone was selected such that the total energy for the elastic constant calculations

converged to within $\sim 1 \mu\text{Ry}$. For the VASP calculations, the mesh was set to $5 \times 5 \times 5$ and the kinetic energy cutoff on the wave functions was 500 eV. Convergence of the total energy with the number of k-points and the plane-wave cutoff energy was checked. The effect of Fe was modeled using supercells, where iron atoms were inserted in MgO corresponding to 25, 18.75, 12.5 and 6.25 % of Fe doping.

3 Results

3.1 MgO

Elastic constant studies of $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ at high pressure are scarce. On the other hand, several properties of MgO have been studied extensively both theoretically and experimentally. Therefore, high-pressure calculations of the MgO properties can serve as test cases for the validity of the methods used. The EOS as shown in Fig. 1 is found above the theoretical data by Oganov and Dorogokupets (2003) and Karki et al. (1997) and the experimental data by Duffy et al. (1995). The small volume overestimation could be due to the PBE in the EMTO code, as this effect of the functional has been reported in several studies (Demuth et al., 1999; Christensen and Carter, 2001; Muscat et al., 2002; Nabi et al., 2005).

The calculated bulk modulus B and the elastic constants C_{44} and $(C_{11} - C_{12})$ for MgO are shown in Table 1. Our calculated C_{44} is in excellent agreement with both theoretical (Karki et al., 1997; Oganov and Dorogokupets, 2003) and experimental data (Sinogeikin and Bass, 1999; Zha et al., 2000). For C_{11} and C_{12} , the results agree well with theory but show a somewhat erratic be-

havior compared to experiment. However, this discrepancy is within the errors which could arise for elastic constant calculations. Therefore, we conclude that the EMTO method correctly describes the properties of MgO. Based on numerous studies (Vitos et al., 2001; Magyari-Köpe et al., 2002; Vitos et al., 2003; Magyari-Köpe et al., 2004; Dubrovinskaia et al., 2005; Taga et al., 2005; Vitos et al., 2006a; Dubrovinsky et al., 2007), we can therefore assume that when small concentrations of Fe are introduced into the compound, the EMTO method still gives feasible results.

3.2 $(Mg,Fe)O$

3.2.1 *Magnetic structure*

Recent measurements on ferropericlase $Mg_{0.83}Fe_{0.17}O$ show that there is a high-spin to low-spin transition occurring at 60 to 70 GPa (Badro et al., 2003; Lin et al., 2005). The electronic spin transition of iron in minerals found at the Earth's mantle conditions has been reported to have a significant impact on several geophysical properties such as the density and thermal conductivity (Sherman, 1988, 1991; Sherman and Jansen, 1995; Cohen et al., 1997; Li et al., 2004; Goncharov et al., 2006; Keppler et al., 2007). Speziale et al. (2005) have shown by means of high-pressure Mössbauer spectroscopy that the transition is found at 40 ± 10 GPa for $Mg_{0.8}Fe_{0.2}O$ and 60 ± 10 GPa for $Mg_{0.5}Fe_{0.5}O$.

In Fig. 2, we show the magnetic moment as a function of pressure and iron composition. In these calculations, the magnetic moments were determined self-consistently, i.e. the floating spin approximation was employed. For 6.25 and 12.5% Fe, the magnetic moment is almost vanished at 60 GPa. The results

agree perfectly compared to recent spin state measurements of ferroperricite $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{O}$ and $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$, predicting the high-spin to low-spin transition to occur between 46 and 55 GPa and between 60 and 70 GPa, respectively (Badro et al., 2003; Lin et al., 2005). For the Fe-richer structures, 18.8% Fe shows a transition just below 90 GPa, whereas for 25%, the behavior is smoother, without any clear transition. This implies a possible co-existence of high-spin and low-spin states as reported both theoretically (Sturhahn et al., 2005; Hofmeister, 2006; Tsuchiya et al., 2006) and experimentally (Speziale et al., 2005; Kantor et al., 2006b; Lin et al., 2006). Furthermore, as the knowledge of the iron properties is crucial for understanding seismological observations, this gradual transition agrees well with the interpretation of seismological data (van der Hilst and Kárason, 1999), rejecting rapid discontinuities. For FeO, Badro et al. (1999) show no HS-LS transition for wüstite up to at least 143 GPa whereas Lin et al. (2006) report that it could occur at a pressure above 160 GPa. Another recent study has indicated the stability of the HS state for magnesiowüstite throughout the Earth's mantle (Hofmeister, 2006). More specifically, the transition pressure increases with iron concentration and temperature for (Mg,Fe)O as $\Delta P_{tr}/\Delta T \sim 0.18, 0.20$ and 0.31 GPa/K for 17, 25 and 40 % Fe, respectively. In this work, the studied pressure range for the elastic constants in this work was below 100 GPa with an iron composition $\leq 25\%$. In order to avoid the numerical difficulties near the magnetic transition, the self-consistent elastic constant calculations for the solid solutions were performed in the HS state using the fixed spin approximation.

3.2.2 EOS and elastic constants

In Fig. 3, the increase of Fe leads to a volume increase in the EOS, evaluated at the same pressure. This is expected, as the molar volume of wüstite and periclase at ambient conditions is 12.25 and 11.25 cm³/mol (Fabrichnaya, 1995), respectively. Furthermore, the volume expansion as a function of iron agrees with the comparison of the experimental data for MgO (Mao and Bell, 1979; Duffy et al., 1995; Utsumi et al., 1998; Fei, 1999; Dewaele et al., 2000; Speziale et al., 2001) with that of Mg_{0.6}Fe_{0.4} (Fei et al., 1992).

The calculated C_{44} as a function of Fe content is shown in Fig. 4. The trend from the experimentally observed C_{44} with increasing iron percentage (Jackson et al., 1978; Jacobsen et al., 2002b) is very well reproduced by the EMTO results. Analogously, a shear modulus reduction with increasing Fe content is also found in (Mg,Fe)SiO₃ perovskite (Kiefer et al., 2002).

In Fig. 5, the $\Delta C_{44}/\Delta P$ for Mg_{0.9}Fe_{0.1}O is increasing with a negative second derivative. On the other hand, for Mg_{0.8}Fe_{0.2}O, $\Delta C_{44}/\Delta P$ is slightly decreasing after approximately 26 GPa. Combined X-ray diffraction and spectroscopy experiments have reported the transformation of the cubic Mg_{0.8}Fe_{0.2}O to a rhombohedral structure at 35±1 GPa (Kantor et al., 2006a). We speculate that the softening of the C_{44} found in this work could be a sign for the phase transition observed by experiment. Jacobsen et al. (2004) have shown a softening for the C_{44} of magnesiowüstite containing > 50% Fe. The reason could be due to a magnetoelastic coupling, as reported for FeO (Struzhkin et al., 2001), indicating instability in the rock-salt structure. We point out that the maximum pressure for the stability criteria from Jacobsen et al. is 9.1 GPa, whereas the pressure region in this study is up to 100 GPa.

In Fig. 6, we show that ($C_{11}-C_{12}$) increases with pressure for all compounds.

However, similar to C_{44} , the gradient $\Delta(C_{11}-C_{12})/\Delta P$ decreases with the amount of Fe. Experimental findings in a low pressure region report a quite stable $\Delta C_{11}/\Delta P$ with iron composition as $\Delta C_{11}/\Delta P=9.35(13)$ for MgO (Jacobsen et al., 2002b) and $\Delta C_{11}/\Delta P=9.3(2)$ and $9.6(4)$ for $\text{Mg}_{0.76}\text{Fe}_{0.24}\text{O}$ and $\text{Mg}_{0.44}\text{Fe}_{0.56}\text{O}$, respectively (Jacobsen et al., 2005). However, Jackson *et al.* (2006) have shown the lower gradient 8.35 for ferropericlase with 6 % Fe. As $\Delta C_{11}/\Delta P \gg \Delta C_{12}/\Delta P$, the trend of the $(C_{11}-C_{12})$ pressure gradient can be assumed to follow the one of C_{11} . From a polynomial fit to the experimental data, the elastic constants as a function of iron composition x can be written $(C_{11}-C_{12})=192 - 184x + 139x^2 - 51x^3$ GPa (Jacobsen et al., 2002b). For the concentrations studied in this work, $x = 0, 0.10$ and 0.20 , the function yields $P=192, 175$ and 160 GPa respectively, i.e. a lowering of pressure with Fe content.

4 Discussion and summary

Knowledge about the composition and pressure behavior of the (Mg,Fe)O minerals at extreme conditions is crucial for developing accurate models of the Earth's interior. The high-spin to low-spin transition for iron-bearing mantle compounds significantly influences their elastic, thermodynamic and vibrational properties (Lin et al., 2005).

On the basis of this study, we have shown that for ferropericlase $\text{Mg}_{1-x}\text{Fe}_x\text{O}$, the magnetic transition is increasing with the iron composition $0.0625 \leq x \leq 0.25$. This is consistent with experimental results (Badro et al., 2003; Lin et al., 2005) where an increasing Fe content stabilizes the high-spin state to higher pressures. Furthermore, recent theoretical studies show that the intermedi-

ate mixed-spin state increases with temperature and that the transition takes place without any discontinuous changes in the optical or elastic properties (Sturhahn et al., 2005; Tsuchiya et al., 2006).

Based on single-crystal data, Jacobsen et al. (2002a) have reported that the two independent shear modes C_{44} and $C'=(C_{11}-C_{12})/2$ decrease with Fe addition. Meanwhile, the bulk modulus $B=1/3(C_{11}+2C_{12})$ from Kung et al. (2002) was found to be relatively insensitive when comparing $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ to MgO . This is in accordance with the increasing C_{12} and the decreasing C_{11} elastic constants with iron composition (Jackson et al., 1990; Jacobsen et al., 2002a). In this paper, the softening of the C_{44} is found for $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ at approximately 26 GPa, where the pressure gradient $\Delta C_{44}/\Delta P$ turns negative. The softening of C_{44} could be the result of a phase transition, as recent experimental results show a cubic to rhombohedral phase transition for this compound at approximately 35 GPa (Kantor et al., 2006a). In this work, we have found that the Fe composition in the Earth's mantle has a considerable effect on the shear mode properties.

5 Acknowledgments

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Fig. 1 The EOS for MgO. The EMTO calculations are compared to theoretical data by Oganov and Dorogokupets (2003) and Karki et al. (1997) and experiment by Duffy et al. (1995)

Fig. 2 Magnetic moment of (Mg,Fe)O as a function of composition and pressure. For the iron poor compounds (6.25 and 12.5% Fe), the magnetic moment vanishes at approximately 60 GPa. The somewhat wider spin transition range for $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ (Lin et al., 2005) is inserted as vertical lines in the figure, separating the high-spin (HS) from the low-spin (LS) region. For the richer Fe phases, 18.8% Fe shows a transition just below 90 GPa, whereas for 25% Fe, the transition occurs within a wide (~ 100 GPa) pressure window.

Fig. 3 EOS as a function of the Fe content in $\text{Mg}_{1-x}\text{Fe}_x\text{O}$. The effect of increasing the amount of iron into the ferroperricline yields a volume increase. This is consistent with the higher molar volume for FeO compared to MgO.

Fig. 4 Shear constant C_{44} as a function of (Mg,Fe)O composition. A softening of the C_{44} with iron content is shown both for theory (this work) as well as for experiment (Jackson et al., 1978; Jacobsen et al., 2002b; Jackson et al., 2006).

Fig. 5 Shear constant C_{44} as a function of pressure and (Mg,Fe)O composition. Consistent with the results in Fig. 4, the effect of iron is a softening of the elastic constant. MgO and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$ show increasing data as a function of pressure. A kink is found for the C_{44} for $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ at 26 GPa, which could be due to a phase transition.

Fig. 6 The elastic constants (C_{11} - C_{12}) as a function of pressure and $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ compound. For MgO, the results from this work in the low pressure range is somewhat underestimated compared to experiment (Sinogeikin and Bass, 1999), as shown in Table 1. The results from $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$ and $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ are consistent with earlier findings, implying a softening with iron content.

Table 1

Bulk modulus and elastic constant calculations for MgO. The EMTO method (this work) is compared to VASP calculations with the GGA from Oganov and Dorogokupets (2003) and LDA calculations from Karki et al. (1997). Included is also experimental DAC data from Sinogeikin and Bass (1999) and Zha et al. (2000). All data presented are in GPa.

P	B	B ^c	C_{44}					C_{11}					C_{12}				
			EMTO	GGA ^a	LDA ^b	Exp. ^c	Exp. ^d	EMTO	GGA ^a	LDA ^b	Exp. ^c	Exp. ^d	EMTO	GGA ^a	LDA ^b	Exp. ^c	Exp. ^d
8	177	194	152	148	144	164	161	316	335	359	371	365	107	103	105	104	105
20	226	242	160	157	154	176	171	417	440	464	466	480	130	120	123	124	110
36	289	306	169	168	164	189		571	580	602	565		144	143	148	164	
57	361	390	176	180	173	203		738	744	770	645		172	170	178	239	
83	454	494	183	191	183			923	945	968			220	203	220		

^a(Oganov and Dorogokupets, 2003)

^b(Karki et al., 1997)

^c(Zha et al., 2000)

^d(Sinogeikin and Bass, 1999)

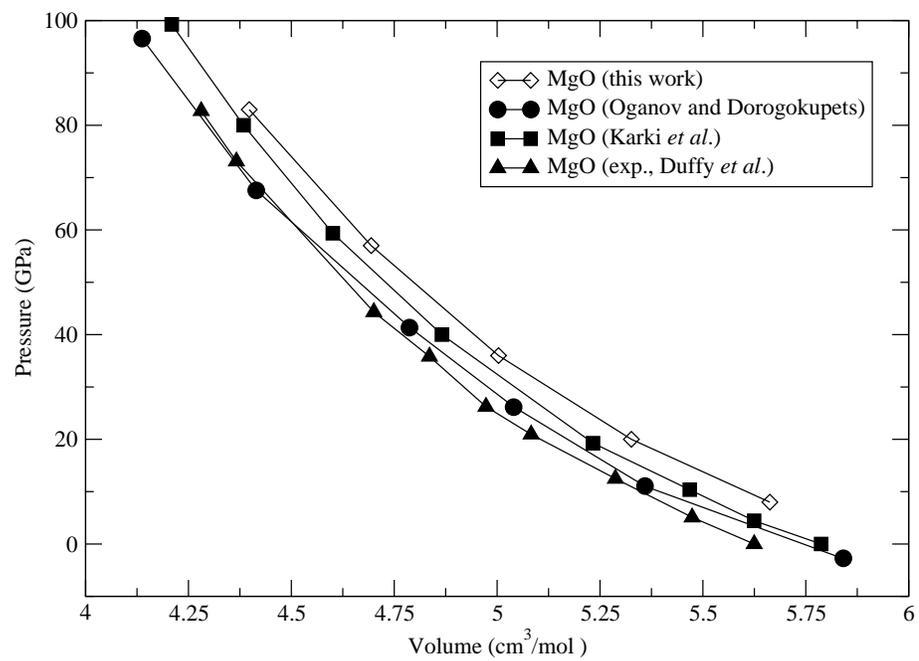


Fig. 1.

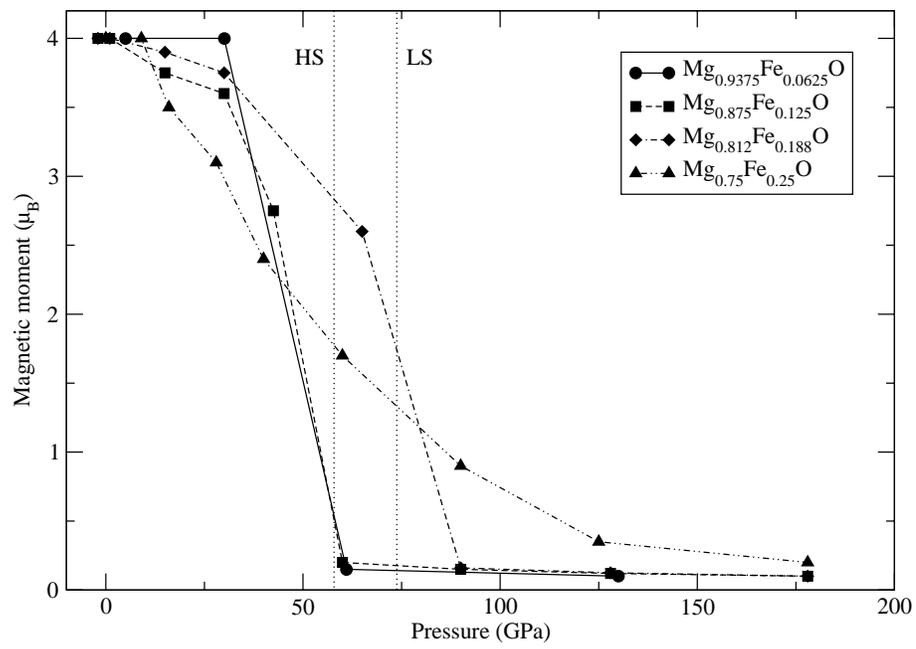


Fig. 2.

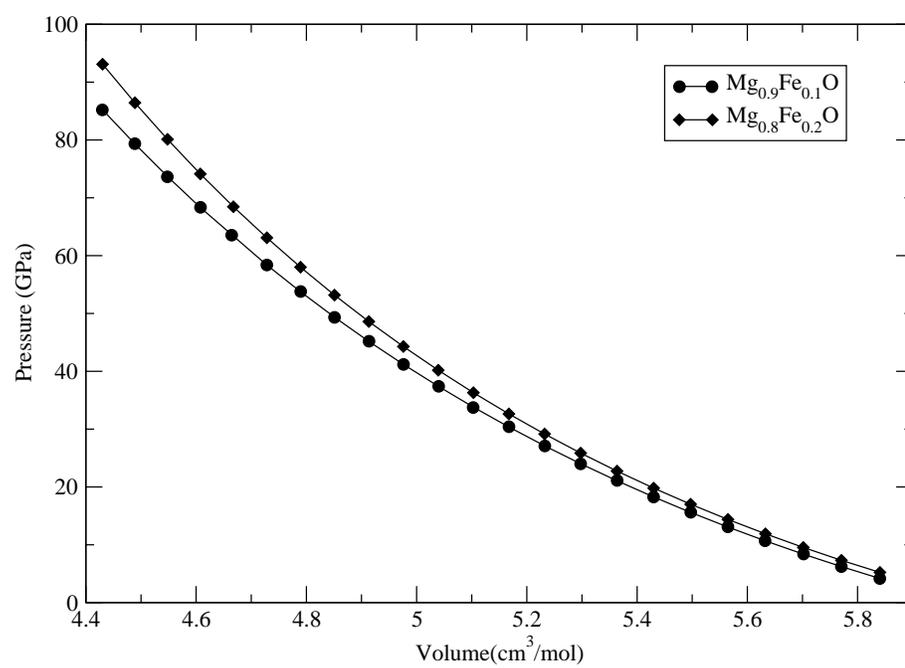


Fig. 3.

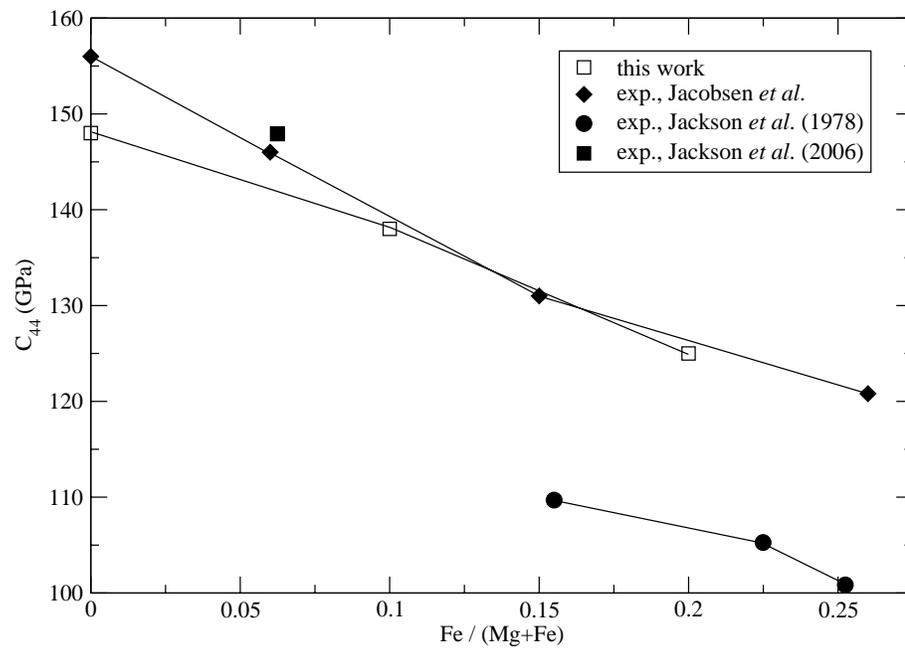


Fig. 4.

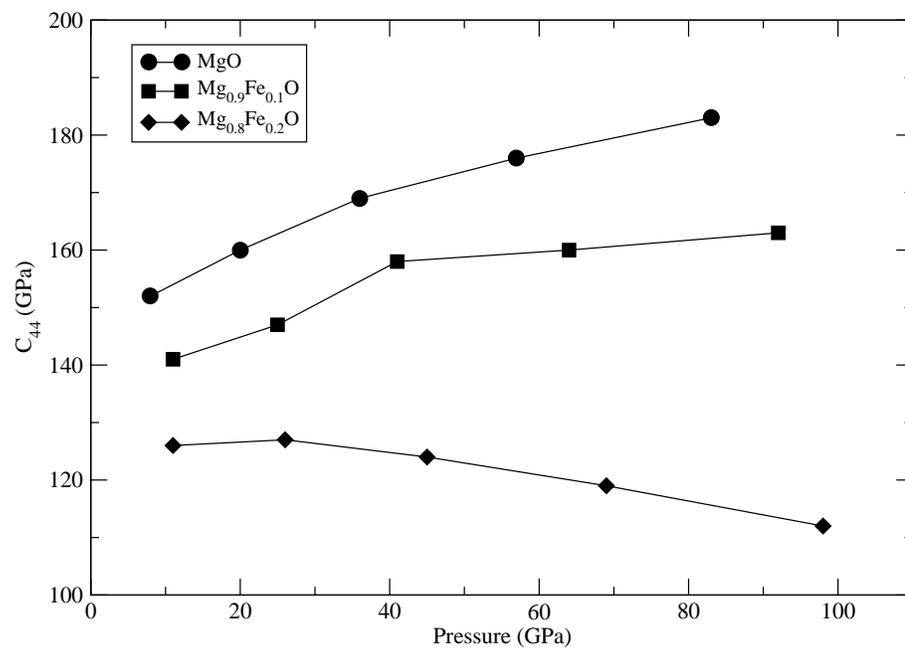


Fig. 5.

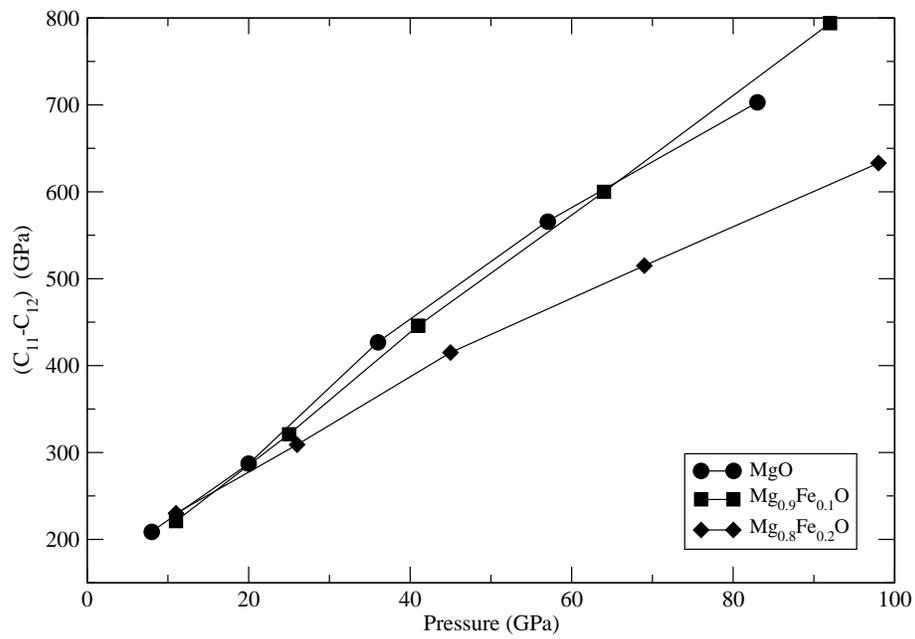


Fig. 6.

References

- Andersen, O. K., Jepsen, O., Krier, G., 1994. In: V. Kumar, O. K. Andersen, A. Mookerjee, Editors, Lectures on Methods of Electronic Structure Calculations, World Scientific, Singapore, pp. 63-124.
- Anderson, D. L., 1989. Theory of the Earth. Blackwell Scientific, Boston, 366 pp.
- Badro, J., Fiquet, G., Guyot, F., Rueff, J.-P., Struzhkin, V. V., G. Vankó, Monaco, G., 2003. Iron Partitioning in Earth's Mantle: Toward a Deep Lower Mantle Discontinuity. *Science* 300, 789–791.
- Badro, J., Rueff, J.-P., Vankó, G., Monaco, G., Fiquet, G., Guyot, F., 2004. Electronic Transitions in Perovskite: Possible Nonconvecting Layers in the Lower Mantle. *Science* 305, 383–386.
- Birch, F., 1947. Finite elastic strain of cubic crystals. *Phys. Rev.* 71, 809–824.
- Birch, F., 1978. Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressure and 300 K. *J. Geophys. Res.* 83, 1257–1269.
- Blöchl, P. E., 1994. Projector augmented-wave method. *Phys. Rev. B* 50, 17953–17979.
- Bonczar, L. J., Graham, E. K., 1982. The pressure and temperature dependence of the elastic properties of polycrystal magnesiowüstite. *J. Geophys. Res.* 87, 1061–1078.
- Christensen, A., Carter, E. A., 2001. Adhesion of ultrathin ZrO₂(111) films on Ni(111) from first principles. *J. Chem. Phys.* 114, 5816–5831.
- Cohen, R. E., Mazin, I. I., Isaak, D. G., 1997. Magnetic collapse in transition metal oxides at high pressure: implications for the Earth. *Science* 275, 654–657.

- Demuth, T., Jeanvoine, Y., Hafner, J., Ángyán, J. G., 1999. Polymorphism in silica studied in the local density and generalized-gradient approximations. *J. Phys.: Cond. Mat.* 11, 3833–3874.
- Dewaele, A., Fiquet, G., Andrault, D., Hausermann, D., 2000. P-V-T equation of state of periclase from synchrotron radiation measurements. *J. Geophys. Res. B* 105, 2869–2877.
- Dubrovinskaia, N., Dubrovinsky, L., Kantor, I., Crichton, W. A., Dmitriev, V., Prakapenka, V., Shen, G., Vitos, L., Ahuja, R., Johansson, B., Abrikosov, I. A., 2005. Beating the miscibility barrier between iron group elements and magnesium by high-pressure alloying. *Phys. Rev. Lett.* 95, 245502.
- Dubrovinsky, L., Dubrovinskaia, N., Langenhorst, F., Dobson, D., Rubie, D., Gessmann, C., Abrikosov, I., Baykov, V. I., Vitos, L., Johansson, B., Bihan, T. L., Crichton, W. A., 2003. Iron-silica interaction at extreme conditions and the electrically conducting layer at the base of Earth's mantle. *Nature* 422, 58–61.
- Dubrovinsky, L., Dubrovinskaia, N., Narygina, O., Kuznetsov, A., Prakapenka, V., Vitos, L., Johansson, B., Mikhaylushkin, A. S., Simak, S. I., Abrikosov, I. A., 2007. *Science*, in press.
- Duffy, T. S., Hemley, R. J., Mao, H. K., 1995. Equation of State and Shear Strength at Multimegabar Pressures: Magnesium Oxide to 227 GPa. *Phys. Rev. Lett.* 74, 1371–1374.
- Fabrichnaya, O. B., 1995. Thermodynamic data for phases in the FeO-MgO-SiO₂ system and phase relations in the mantle transition zone. *Phys. Chem. Min.* 22, 323–332.
- Fei, Y., 1999. Effects of temperature and composition on the bulk modulus of (Mg,Fe)O. *Am. Mineral.* 84, 272–276.

- Fei, Y., Mao, H. K., Shu, J., Hu, J., 1992. P-V-T equation of state of magnesiowüstite ($\text{Mg}_{0.6}\text{Fe}_{0.4}\text{O}$). *Phys. Chem. Miner.* 18, 416–422.
- Goncharov, A. F., Struzhkin, V. V., Jacobsen, S. D., 2006. Reduced Radiative Conductivity of Low-Spin (Mg,Fe)O in the Lower Mantle. *Science* 312, 1205–1208.
- Hofmeister, A. F., 2006. Is low-spin Fe^{2+} present in Earth's mantle? *Earth Planet. Sci. Lett.* 243, 44–52.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev.* 136, B864–B871.
- Holzappel, C., Rubie, D. C., Mackwell, S., Frost, D. J., 2003. Effect of pressure on Fe-Mg interdiffusion in ($\text{Fe}_x\text{Mg}_{1-x}\text{O}$), ferropericlasite. *Phys. Earth Planet. Inter.* 139, 21–34.
- Irifune, T., 1994. Absence of an aluminous phase in the upper part of the Earth's lower mantle. *Nature* 370, 131–133.
- Jackson, I., Khanna, S. K., Revcolevschi, A., Berthon, J., 1990. Elasticity, shear mode softening and high-pressure polymorphism of magnesiowüstite Fe_{1-x}O . *J. Geophys. Res.* 95, 21671–21685.
- Jackson, I., Liebermann, R. C., Ringwood, A. E., 1978. The elastic properties of ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$) solid solutions. *Phys. Chem. Miner.* 3, 11–31.
- Jackson, J. M., Sinogeikin, S., Jacobsen, S., Reichmann, H., Mackwell, S., Bass, J., 2006. Single-crystal elasticity and sound velocities of ($\text{Mg}_{0.94}\text{Fe}_{0.06}\text{O}$) ferropericlasite to 20 GPa. *J. Geophys. Res.* 111, B09203.
- Jacobsen, S., Reichmann, H.-J., Spetzler, H. A., Mackwell, S. J., Smyth, J. R., Angel, R. J., McCammon, C. A., 2002a. Structure and elasticity of single-crystal (Mg,Fe)O and a new method of generating shear wave for gigahertz ultrasonic interferometry. *J. Geophys. Res.* 107, 1–14.
- Jacobsen, S. D., Reichmann, H. J., Kantor, A., Spetzler, H., 2005. A gigahertz

- ultrasonic interferometer for the diamond-anvil cell and high-pressure elasticity of some iron-oxide minerals. In: J. Chen et al. (Eds.), *Advances in High-Pressure Technology for Geophysical Applications*, Elsevier, Amsterdam, pp. 25-48.
- Jacobsen, S. D., Spetzler, H., Reichmann, H. J., Smyth, J. R., 2004. Shear waves in the diamond-anvil cell reveal pressure-induced instability in (Mg,Fe)O. *Proc. Natl. Acad. Sci. USA* 101, 5867–5871.
- Jacobsen, S. D., Spetzler, H. A., Reichmann, H. J., Smyth, J. R., Mackell, S. J., Angel, R. J., Bassett, W. A., 2002b. Gigahertz Ultrasonic Interferometry at High P-T: New Tools for a Thermodynamics Equation of State (EoS). *J. Phys.: Cond. Mat.* 14, 11525–11530.
- Kantor, I., Dubrovinsky, L. S., Kantor, A. P., Urusov, V. S., McCammon, C. A., 2005. Trigonal distortion of ferroperricite ($\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$) at high pressures. *Doklady Akad. Nauk* 424, 343–345.
- Kantor, I., Dubrovinsky, L., McCammon, C., Kantor, A., Pascarelli, S., Aquilanti, G., Crichton, W., Mattesini, M., Ahuja, R., Almeida, J., Urusov, V., 2006a. Pressure-induced phase transition in $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$ ferroperricite. *Phys. Chem. Miner.* 33, 35–40.
- Kantor, I. Y., Dubrovinsky, L. S., McCammon, C. A., 2006b. Spin crossover in (Mg,Fe)O: A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data. *Phys. Rev. B* 73, 100101.
- Karki, B. B., Stixrude, J. L., Clark, S. J., Warrenand, M. C., Ackland, G. J., Crain, J., 1997. Structure and elasticity of MgO at high pressure. *Am. Mineral.* 82, 51–60.
- Keppler, H., Kantor, I., Dubrovinsky, L. S., 2007. Optical absorption spectra of ferroperricite to 84 GPa. *Am. Mineral.* 92, 433–436.
- Kiefer, B., Stixrude, L., Wentzcovitch, R. M., 2002. Elasticity of

- (Mg_{1-x},Fe_x)SiO₃-perovskite at high pressures. *Geophys. Res. Lett.* 29, 1539.
- Kollár, J., Vitos, L., Skriver, H. L., 2000. Electronic Structure and Physical Properties of Solids: The Uses of the LMTO Method. In: H. Dreysse, Editor, *Lecture Notes in Physics*, Springer-Verlag, Berlin, p. 85.
- Kondo, T., Ohtani, E., Hiro, N., Yagi, T., Kikegawa, T., 2004. Phase transitions of (Mg,Fe)O at megabar pressures. *Phys. Earth Planet. Inter.* 143-144, 201–213.
- Korzhavyi, P. A., Vitos, L., Andersson, D. A., Johansson, B., 2004. Oxidation of plutonium dioxide. *Nat. Mater.* 3, 225–228.
- Kresse, G., Furthmüller, J., 1996a. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mat. Sci.* 6, 15–50.
- Kresse, G., Furthmüller, J., 1996b. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169–11186.
- Kresse, G., Hafner, J., 1993. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 47, 558.
- Kresse, G., Hafner, J., 1994. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B* 49, 14251–14269.
- Kresse, G., Joubert, D., 1999. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 59, 1758–1775.
- Kung, J., Li, B., Weidner, D. J., Zhang, J., Liebermann, R. C., 2002. Elasticity of (Mg_{0.83},Fe_{0.17})O ferropericlase at high pressure: ultrasonic measurements in conjunction with X-radiation techniques. *Earth Planet. Sci. Lett.* 203, 557–566.
- Li, J., Struzhkin, V. V., Mao, H.-K., Shu, J., Hemley, R. J., Fei, Y., Mysen,

- B., Dera, P., Prakapenka, V., Shen, G., 2004. Electronic spin state of iron in lower mantle perovskite. *Proc. Natl. Acad. Sci. USA* 101, 14027–14030.
- Lin, J. F., Gavriluk, A. G., Struzhkin, V. V., Jacobsen, S. D., Sturhahn, W., Hu, M. Y., Chow, P., Yoo, C. S., 2006. Pressure-induced electronic spin transition of iron in magnesiowüstite-(Mg,Fe)O. *Phys. Rev. B* 73, 113107.
- Lin, J. F., Heinz, D. L., Mao, H. K., Hemley, R. J., Devine, J. M., Li, J., Shen, G., 2003. Stability of magnesiowüstite in Earth's lower mantle. *Proc. Natl. Acad. Sci. USA* 100, 4405–4408.
- Lin, J. F., Struzhkin, V. V., Jacobsen, S. D., Hu, M. Y., Chow, P., Kung, J., Liu, H., Liu, H., Mao, H. K., Hemley, R. J., 2005. Spin transition of iron in magnesiowüstite in the Earth's lower mantle. *Nature* 436, 377–380.
- Madi, K., Forest, S., Cordier, P., Boussuge, M., 2005. Numerical study of creep in two-phase aggregates with a large rheology contrast: Implications for the lower mantle. *Earth Planet. Sci. Lett.* 237, 223–238.
- Magyari-Köpe, B., Grimvall, G., Vitos, L., 2002. Elastic anomalies in Ag-Zn alloys. *Phys. Rev. B* 66, 064210.
- Magyari-Köpe, B., Vitos, L., Grimvall, G., 2004. Anomalous behavior of lattice parameters and elastic constants in hcp Ag-Zn alloys. *Phys. Rev. B* 70, 052102.
- Mao, H. K., Bell, P., 1979. Equation of state of MgO and Fe under static pressure conditions. *J. Geophys. Res.* 84, 4533–4536.
- Mao, H. K., Shen, G., Hemley, R. J., 1997. Multivariable dependence of Fe-Mg partitioning in the lower mantle. *Science* 278, 2098–2100.
- Mao, W., Shu, J., Hu, J., Hemley, R., Mao, H. K., 2002. Displacive transition in magnesiowüstite. *J. Phys.: Cond. Mat.* 14, 11349–11354.
- Muscat, J., Swamy, V., Harrison, N. M., 2002. First-principles calculations of the phase stability of TiO₂. *Phys. Rev. B* 65, 224112.

- Nabi, Z., Vitos, L., Johansson, B., Ahuja, R., 2005. Ab initio calculation of elastic properties of solid He under pressure. *Phys. Rev. B* 72, 172102.
- Oganov, A. R., Dorogokupets, P. I., 2003. All-electron and pseudopotential study of MgO: Equation of state, anharmonicity, and stability. *Phys. Rev. B* 67, 224110.
- Olsson, P., Abrikosov, I. A., Vitos, L., Wallenius, J., 2003. Ab initio formation energies of Fe-Cr alloys. *J. Nucl. Mater.* 321, 84–90.
- Perdew, J. P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865.
- Sherman, D. M., 1988. In: S. Ghose, J. M. D. Coey and E. Salje, Editors, *Structural and Magnetic Phase Transitions in Minerals*, Springer, New York, pp. 113-118.
- Sherman, D. M., 1991. The high-pressure electronic structure of magnesiowüstite (Mg,Fe)O: applications to the physics and chemistry of the lower mantle. *J. Geophys. Res.* 96, 14299–14312.
- Sherman, D. M., Jansen, H. J. F., 1995. First-principles predictions of the high-pressure phase transition and electronic structure of FeO: implications for the chemistry of the lower mantle and core. *Geophys. Res. Lett.* 22, 1001–1004.
- Sinogeikin, S. V., Bass, J. D., 1999. Single-crystal elasticity of MgO at high pressure. *Phys. Rev. B* 59, 14141–14144.
- Speziale, S., Milner, A., Lee, V. E., Clark, S. M., Pasternak, M. P., Jeanloz, R., 2005. Iron spin transition in Earth's mantle. *Proc. Natl. Acad. Sci. USA* 102, 17918–17922.
- Speziale, S., Zha, C. S., Duffy, T. S., Hemley, R. J., Mao, H. K., 2001. Quasi-hydrostatic compression of magnesium oxide to 52 GPa: Implications for the pressure-volume-temperature equation of state. *J. Geophys. Res.* B 106,

- 515–528.
- Struzhkin, V. V., Mao, H. K., Hu, J., Schwoerer-Bohning, M., Hemley, R. J., Sturhahn, W., Hu, M. Y., Alp, E. E., Eng, P., Shen, G., 2001. Nuclear Inelastic X-Ray Scattering of FeO to 48 GPa. *Phys. Rev. Lett.* 87, 255501.
- Sturhahn, W., Jackson, J. M., Lin, J. F., 2005. The spin state of iron in minerals of Earth's lower mantle. *Geophys. Res. Lett.* 32, L12307.
- Taga, A., Vitos, L., Johansson, B., Grimvall, G., 2005. Ab initio calculation of the elastic properties of $\text{Al}_{1-x}\text{Li}_x$ ($x \leq 0.20$) random alloys. *Phys. Rev. B* 71, 014201.
- Tsuchiya, T., Wentzcovitch, R. M., da Silva, C. R. S., de Gironcoli, S., 2006. Spin Transition in Magnesiowüstite in Earth's Lower Mantle. *Phys. Rev. Lett.* 96, 198501.
- Utsumi, W., Weidner, D. J., Liebermann, R. C., 1998. In: *Properties of Earth and Planetary Materials at High Pressure and Temperature*. Am. Geophys. Union, Washington, D.C., pp. 327-333.
- van der Hilst, R., Kárason, S., 1999. Compositional Heterogeneity in the Bottom 1000 Kilometers of Earth's Mantle: Toward a Hybrid Convection Model. *Science* 283, 1885–1888.
- Vitos, L., 2001. Total-energy method based on the exact muffin-tin orbitals theory. *Phys. Rev. B* 64, 014107.
- Vitos, L., 2004. Recent Research Developments in Physics. In: *Transworld Research Network*, Trivandrum, India, Vol. 5, pp. 103-140.
- Vitos, L., Abrikosov, I. A., Johansson, B., 2001. Anisotropic lattice distortions in random alloys from first-principles theory. *Phys. Rev. Lett.* 87, 156401.
- Vitos, L., Korzhavyi, P. A., Johansson, B., 2003. Stainless steel optimization from quantum mechanical calculations. *Nat. Mater.* 2, 84–90.
- Vitos, L., Korzhavyi, P. A., Johansson, B., 2006a. Evidence of large magne-

- tostructural effects in austenitic stainless steels. *Phys. Rev. Lett.* 96, 117210.
- Vitos, L., Magyari-Köpe, B., Ahuja, R., Kollár, J., Grimvall, G., Johansson, B., 2006b. Phase transformations between garnet and perovskite phases in the Earth's mantle: A theoretical study. *Phys. Earth Planet. Inter.* 156, 108–116.
- Wentzcovitch, R. M., Karki, B. B., Karato, S., Silvera, C. R. S. D., 1998. High pressure elastic anisotropy of MgSiO_3 and geophysical implications. *Earth Planet. Sci. Lett.* 164, 371–378.
- Wood, B. J., 2000. Phase transformations and partitioning relations in peridotite under lower mantle conditions. *Earth Planet. Sci. Lett.* 174, 341–354.
- Yagi, T., Suzuki, T., Akimoto, S., 1985. Static compression of wüstite ($\text{Fe}_{0.98}\text{O}$) to 120 GPa. *J. Geophys. Res.* 90, 8784–8788.
- Zha, C.-S., Mao, H.-K., Hemley, R. J., 2000. Elasticity of MgO and a primary pressure scale to 55 GPa. *Proc. Natl. Acad. Sci. USA* 97, 13494–13499.
- Zhang, J., Kostak, P., 2002. Thermal equation of state of magnesiowüstite ($\text{Mg}_{0.6}\text{Fe}_{0.4}\text{O}$). *Phys. Earth Planet. Inter.* 129, 301–311.
- Zhou, G., Mao, H. K., Bell, P. M., Virgo, D., 1980. High pressure experiments on the iron oxide wüstite (Fe_{1-x}O). *Year book Carnegie Inst. Washington* 79, 374–376.