Ab-initio determination of high-pressure and high-temperature thermoelastic and thermodynamic properties of low-spin (Mg$_{1-x}$Fe$_x$)O ferropericlase with x in the range [0.06, 0.59]

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**ABSTRACT**

In this work, we calculate the thermo-elastic properties of (Mg$_{1-x}$Fe$_x$)O ferropericlase, with x in the [0.06, 0.59] range, and the thermodynamic properties of ferropericlase having the specific stoichiometric composition (Mg$_{0.5}$Fe$_{0.5}$)O, at pressures and temperatures, which are those typical of the Earth’s lower mantle. We follow an ab-initio quantum-mechanical approach, with the use of the WC1LYP hybrid Hartree-Fock/density functional theory (HF/DFT) functional, within the framework of the quasi-harmonic approximation. Iron is assumed to be in the low-spin configuration, as it proved to be the most stable spin arrangement at the thermo-baric conditions of the deepest lower mantle. The choice of the low-spin configuration, and the use of an ab-initio approach, make this work unique as it is the first time that such a technique is applied for the calculation of the vibrational and thermodynamic properties of the low-spin ferropericlase.

We observe a linear increase of the bulk modulus and a linear decrease of the cell volume as iron content increases. More precisely, for x = 0.46, at ambient condition $K_T = 205.57$ GPa, $K'_T = 4.242$, and $V_T = 72.216$ Å$^3$; for x = 0.03, at the same conditions, $K_T = 167.42$ GPa, $K'_T = 4.085$, and $V_T = 75.145$ Å$^3$.

Some thermodynamic parameters and the thermal expansion ($C_p, C_V, S, \alpha$) for (Mg$_{0.5}$Fe$_{0.5}$)O are calculated both at ambient condition [$C_p = 36.11$ J/(mol K), $C_V = 36.38$ J/(mol K), $S = 26.62$ J/(mol K), $\alpha = 1.97\times10^{-5}$ K$^{-1}$], and at simultaneous high-pressure and high-temperature conditions as a function of the geobar and geotherm curves. The data here proposed can be seen as possible bounds to the values of thermoelastic and thermodynamic parameters employed in the construction of geophysical models and the same data could be used to revise the velocity of the seismic waves in the lower mantle.

**Keywords:** Ferropericlase, lower mantle, thermoelastic properties, thermodynamic properties

**INTRODUCTION**

The magnesium-rich (Mg$_x$Fe$_{1-x}$)O solid solution, known as the mineral ferropericlase, constitutes a significant part of the Earth, as it is the second most abundant mineral in the lower mantle (660–2890 km depth) following (Mg,Fe)SiO$_3$ perovskite (Irifune 1994; Wood 2000). Its structure (the rock-salt one; space group $Fm\bar{3}m$), is stable across the whole lower mantle depth range (Fei et al. 1992; Lin et al. 2003), so that the knowledge of its elastic properties at high-pressure (HP) and high-temperature (HT) as a function of the iron content is of crucial importance for the geophysics of the mantle. To the authors’ knowledge, despite the great importance of this phase, only a few experimental measurements at lower mantle pressure conditions do exist and they mainly address three topics: (1) the prediction of the high-spin (HS) low-spin (LS) transition (Jacobsen et al. 2002; Lin et al. 2003, 2005, 2006, 2007; Speziale et al. 2005; Tsuchiya et al. 2006; Fei et al. 2007; Komabayashi et al. 2010); (2) the measurement of the elastic properties up to HP conditions (Fei et al. 1992, 2007; Fei 1999; Kung et al. 2002; Zhang and Kostak 2002; van Westrenen et al. 2005; Jackson et al. 2006; Speziale et al. 2007; Crowhurst et al. 2008; Reichmann et al. 2008; Komabayashi et al. 2010; Matsui et al. 2012); and (3) the determination of the possible phase transitions in the lower mantle (Mao et al. 1997; Wood 2000). Of these experimental works, only a few deal in detail with ferropericlase in its low-spin configuration (Chen et al. 2012; Fei et al. 2007; Lin et al. 2005; Mao et al. 2011; Speziale et al. 2007). Regarding the computational works, although they have demonstrated to be able to correctly predict the elastic properties of oxides and silicates at simultaneous HP/HT conditions (Oganov et al. 2002; Ottonello et al. 2010; Scanavino et al. 2012) and, at the same time, to predict the correct spin states of iron through the use of appropriate methodologies, by using spin polarized Hamiltonians (Pisani 1996), there are only few papers focused on the ferropericlase with iron in LS configuration (Persson et al. 2006; Scanavino et al. 2012; Wentzovitch et al. 2009; Wu et al. 2009).

The choice of the spin state of iron in ferropericlase is extremely important as the two different states are stable at different P/T conditions and consequently at different depth in the Earth’s interior. It is known that the spin configuration of the iron in ferropericlase is strictly dependent on the temperature and on the iron concentration: in particular, it is known that