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Thermal equation of state of lower-mantle ferropericlase across the spin crossover

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[1] The thermal equation of state of ferropericlase [$(Mg_{0.75}Fe_{0.25})O$] has been investigated by synchrotron X-ray diffraction up to 140 GPa and 2000 K in a laser-heated diamond anvil cell. Based on results at high pressure-temperature conditions, the derived phase diagram shows that the spin crossover widens at elevated temperatures. Along the lower-mantle geotherm, the spin crossover occurs between 1700 km and 2700 km depth. Compared to the high-spin state, thermoelastic modeling of the data shows a ∼1.2% increase in density, a factor of two increase in thermal expansion coefficient over a range of 1000 km, and a maximum decrease of 37% and 13% in bulk modulus and bulk sound velocity, respectively, at ∼2180 km depth across the spin crossover. These anomalous behaviors in the thermoelastic properties of ferropericlase across the spin crossover must be taken into account in order to understand the seismic signatures and geodynamics of the lower mantle. **Citation:** Mao, Z., J.-F. Lin, J. Liu, and V. B. Prakapenka (2011), Thermal equation of state of lower-mantle ferropericlase across the spin crossover, *Geophys. Res. Lett.*, *38*, L23308, doi:10.1029/2011GL049915.

1. Introduction

[2] Ferropericlase [(MgFe)O], with approximately 20% Fe, is the second most abundant mineral in the Earth's lower mantle, thereby making it an essential player in our perception of the planet's interior. The pressure-induced high-spin (HS) to low-spin (LS) transition of iron in ferropericlase has attracted extensive research interest, because the spin crossover can affect a series of physical, chemical, and transport properties (see *Lin and Tsuchiya* [2008] for a review). In particular, the spin crossover influences the thermal equation of state (EoS) and sound velocities of ferropericlase at the relevant pressure-temperature (*P-T*) conditions of the lower mantle [*Lin et al.*, 2006, 2007; *Tsuchiya et al.*, 2006; *Fei et al.*, 2007a; *Speziale et al.*, 2007; *Crowhurst et al.*, 2008; *Marquardt et al.*, 2009a, 2009b; *Wentzcovitch et al.*, 2009; *Komabayashi et al.*, 2010], yet experimental results on the thermal EoS across the spin crossover at relevant *P-T* conditions remain limited.* Pressure-volume (*P-V*) curves measured by X-ray diffraction between 1600 K and 1900 K up to 120 GPa showed that the width and the onset pressure of the spin crossover was increased by elevating temperatures [*Komabayashi et al.*, 2010], consistent with previous works [*Tsuchiya et al.*, 2006; *Lin et al.*, 2007; *Wentzcovitch et al.*, 2009]. However, experiments with limited *P-T* range and relatively large uncertainties do not permit further evaluation of the thermoelastic parameters [*Komabayashi et al.*, 2010]. Precise *P-V* relations of ferropericlase over the extended *P-T* range of the lower mantle are needed to reliably decipher the spin-crossover phenomenon and to better constrain thermoelastic properties within the transition and in the LS state.

[3] In this study, we have conducted *in situ* synchrotron X-ray diffraction measurements on the *P-V* relation of ferropericlase with 25% Fe, [$(Mg_{0.75}, Fe_{0.25})O$], in a laser-heated diamond anvil cell (LHDAC). The measured unit cell volumes over an extended *P-T* range are used to model the spin-crossover diagram via derived volume deviations and fractions of the HS and LS states. We further model the thermal EoS parameters of ferropericlase and their variations caused by the spin crossover along a lower-mantle geotherm [*Brown and Shankland*, 1981].

2. Experiments

[4] Polycrystalline ferropericlase (see auxiliary material for details) was mixed with 5 wt.% Au as the pressure calibrant [*Fei et al.*, 2007b] by mechanical grinding for ∼10 hrs.[1] The mixture was then pressed into 10–15 μm thick disks for loading into DACs with Re gaskets. For experiments below 60 GPa, the disk was sandwiched between two dried KCl foils, which served as the pressure medium and thermal insulator, whereas dried NaCl was used for experiments above 60 GPa. The loaded sample chambers in DACs were evacuated for 30 minutes to remove potential residual water moisture in the KCl or NaCl before closing the cells in vacuum.

[5] High *P-T* X-ray diffraction experiments in LHDACs were conducted at GSECARS of the Advanced Photon Source, Argonne National Laboratory. We used a double-sided Nd:YLF laser heating system with a ∼25 μm diameter focused laser beam [*Prakapenka et al.*, 2008]. Temperatures of the heated samples were determined by fitting the thermal radiation spectrum between 670 nm and 830 nm to the Planck radiation function assuming the Graybody approximation. The uncertainty in temperature is estimated to be 50 K and is based on multiple measurements of temperature from both sides of the sample across the laser-heated spots [*Prakapenka et al.*, 2008]; care was taken to minimize the thermal fluctuation by selecting the region with most stable heating. Before each heating cycle, we first laser-annealed

*Errors throughout this article have been corrected here. The text as originally published appears in the HTML.

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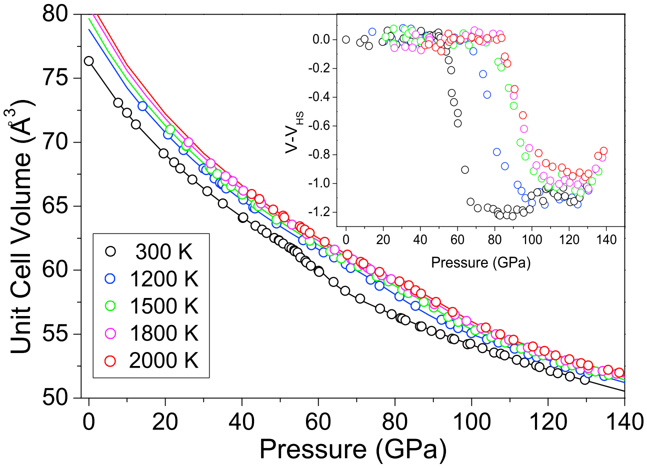

Figure 1. Pressure-volume relations of ferropericlase at high *P-T*. Open circles: experimental measurements at 300 K (black), 1200 K (blue), 1500 K (green), 1800 K (magenta), and 2000 K (red); lines: fitting results. The inset shows the volume difference between ferropericlase and its HS state.

the sample at ~1200 K for a few minutes to reduce the potential stress before collecting diffraction patterns at 300 K. Pressures were calculated from the thermal EoS of Au *in situ* [*Fei et al.*, 2007b]. Examination of the X-ray diffraction patterns from the high *P-T* quenched samples did not reveal any sign of chemical heterogeneity or chemical reaction of the sample, Au and NaCl.

3. Results

[6] X-ray diffraction patterns of the sample were collected at five given temperatures (300 K, 1200 K, 1500 K, 1800 K, and 2000 K) up to 140 GPa. The lattice parameters of the ferropericlase and Au were calculated using 3–6 diffraction lines at high *P-T* (Figure 1, inset in Figure S1, and Table S1). To ascertain the width of the transition and the occurrence of the HS and LS states systematically, we first compared our *P-V* curves with the thermal EoS of the end-member MgO as the starting reference at corresponding *P-T* conditions (see auxiliary material for details) [*Tange et al.*, 2009]. The measured *P-V* relation at a given temperature clearly shows an enhanced reduction in volume at the pressure range expected for the spin crossover (Figure 1) [*Tsuchiya et al.*, 2006; *Lin et al.*, 2007].

[7] A third order isothermal Birch-Murnaghan EoS with a fixed $K_0' = 4$ has been used to fit the *P-V* data at 300 K to derive the unit cell volume, V_0, and isothermal bulk modulus, K_{T0}, yielding: V_0 = 76.34 (±0.01) Å^3 (fixed) and K_{T0} = 162 (±1) GPa for the HS state, and V_0 = 74.4 (±0.6) Å^3 and K_{T0} = 166 (±7) GPa for the LS state (Figure 1 and Table S1). The derived K_{T0} values for the HS and LS states are in good agreement with previous reports [*Jacobsen et al.*, 2002; *Lin et al.*, 2005; *Speziale et al.*, 2005, 2007; *Fei et al.*, 2007a]. These values were then used as input parameters for thermal EoS analyses at high *P-T* because they are not subject to temperature uncertainty from laser-heating. All *P-V* data for the HS and LS state were fitted with the thermal Birch-Murnaghan EoS to derive the temperature derivative of the bulk modulus, $(\partial K/\partial T)_P$, and thermal expansion coefficient, α_0, yielding: $(\partial K/\partial T)_P$ = −0.017 (±0.002) GPa/K, and α_0 = 3.76 (±0.05) (10^{-5} K^{-1}) for the HS state; $(\partial K/\partial T)_P$ = −0.014 (±0.002) GPa/K, and α_0 = 3.37 (±0.05) (10^{-5} K^{-1}) for the LS state. We note that our derived $(\partial K/\partial T)_P$ values for the HS and LS states are both slightly smaller than that in previous studies [*Fei et al.*, 1992; *Zhang and Kostak*, 2002; *van Westrenen et al.*, 2005; *Komabayashi et al.*, 2010]. The difference may be a result of the limited pressure ranges (<30 GPa) [*Fei et al.*, 1992; *Zhang and Kostak*, 2002; *van Westrenen et al.*, 2005] or limited temperature ranges in previous studies [*Komabayashi et al.*, 2010].

[8] With the width of the transition and the thermal EoS parameters defined, we obtained the fraction of the LS state (n_{LS}) at a given *P-T* condition (Figure 2). The pressure and temperature dependence of n_{LS} can be described by:

$$n_{LS} = \frac{1}{1 + \exp(\Delta G(P,T)^*/T)} \qquad (1)$$

where $\Delta G(P,T)^*$ is the difference of the Gibbs free energy between the LS and HS state [*Tsuchiya et al.*, 2006; *Wentzcovitch et al.*, 2009]. The $\Delta G(P,T)^*$ values were obtained by a least-squares fit of n_{LS} with pressure at a given temperature (see auxiliary material for details).

4. Discussion and Geophysical Implications

[9] Based on the derived n_{LS} and equation (1), we have reconstructed the isosymmetric spin-crossover diagram of ferropericlase (Figure 3). The spin crossover occurs between 50 GPa and 75 GPa at 300 K, but widens toward higher pressures at elevated temperatures. However, the width of the spin crossover remains much narrower than expected from previous theoretical works [*Tsuchiya et al.*, 2006; *Wentzcovitch et al.*, 2009]. The onset pressure of the crossover is slightly greater than that in previous works with slightly lower Fe contents, indicating a compositional effect on the transition pressure [*Lin et al.*, 2005; *Fei et al.*, 2007a; *Speziale et al.*, 2007; *Komabayashi et al.*, 2010]. Along a

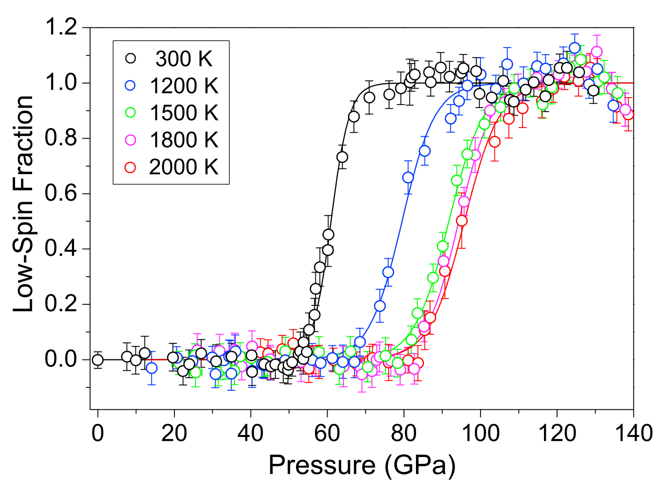

Figure 2. Derived low-spin fraction of ferropericlase as a function of pressure compared with the fitting results. Open circles: experimental measurements at 300 K (black), 1200 K (blue), 1500 K (green), 1800 K (magenta), and 2000 K (red); lines: fitting results.

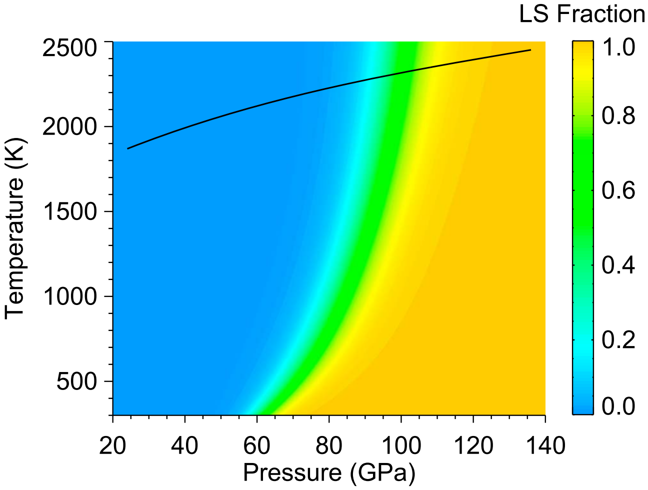

Figure 3. Spin crossover of Fe in ferropericlase at lower mantle P-T conditions. The color represents the fractions of the low-spin state in ferropericlase derived from equation (1). Black line shows the lower-mantle geotherm [*Brown and Shankland*, 1981].

mantle geotherm [*Brown and Shankland*, 1981], the transition from HS to LS would begin at ~70 GPa (1700-km depth) and 2200 K and completes at ~125 GPa (2700-km depth) and 2400 K (Figure S2). Thus, the spin crossover can occur in the middle to the lower part of the lower-mantle, and the LS state can exist in the lowermost mantle. Considering the lowermost mantle as a thermal boundary layer with a steep temperature gradient, the spin crossover, with a small fraction of the HS state, may occur in the region.

[10] Together with the thermal EoS and the spin-crossover diagram (Figures 1–3 and S3), we have modeled the density, thermal expansion coefficient, isothermal bulk modulus, and bulk sound velocity (V_Φ) of ferropericlase along the mantle geotherm (see auxiliary material for details) [*Wentzcovitch et al.*, 2009]. Using the HS state as the reference, the spin crossover produces a ~1.2% increase in density in the LS state (Figure 4). That is, the mixed HS-LS spin states and the LS state in the lower mantle are denser than expected from the HS state alone below ~1700-km depth. Since the density increase spreads over a range of 1000 km, the transition would likely not result in any detectable density discontinuity in seismic observations. On the other hand, the thermal expansion coefficient is dramatically affected across the spin crossover, consistent with theoretical calculations (Figure 4) [*Wu et al.*, 2009; *Wentzcovitch et al.*, 2009; *Shahnas et al.*, 2011]. Within the spin crossover, the thermal expansion coefficient increased drastically; at the peak of the anomaly, it is approximately two times greater than that in the HS state along the mantle geotherm. Since the thermal expansion coefficient is important for modeling lower-mantle geodynamics, this anomaly, together with the enhanced density across the spin crossover, would have significant impacts on our understanding of the lower-mantle dynamics, including slab subduction and upwelling of hot mantle plumes.

[11] Previous studies have reported abnormal behaviors of the elastic moduli across the spin crossover in ferropericlase

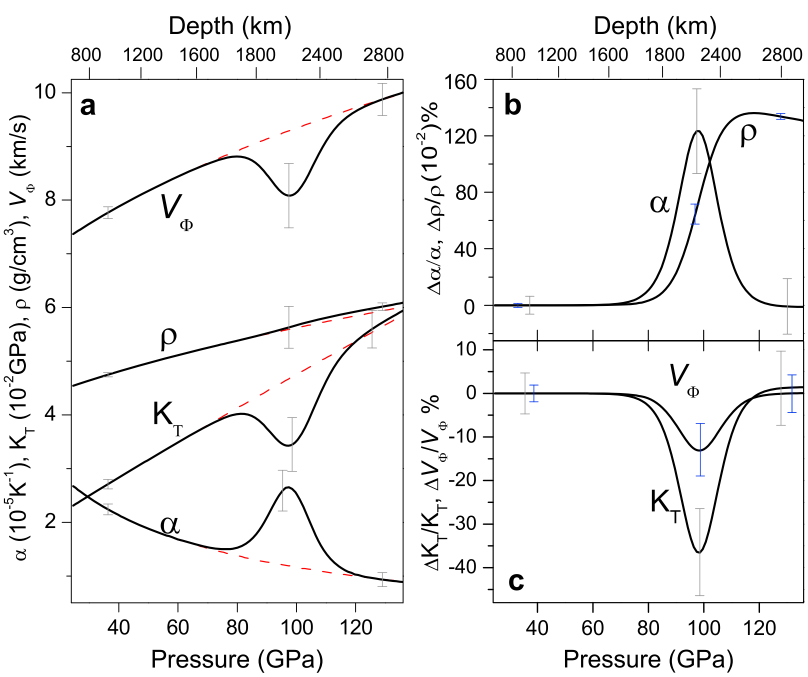

Figure 4. (a) Thermoelastic parameters of ferropericlase and (b, c) their deviations along the lower-mantle geotherm. Black lines in Figure 4a: density (ρ), thermal expansion coefficient (α), isothermal bulk modulus (K_T), and bulk sound velocity (V_Φ) of ferropericlase along the mantle geotherm; red lines: Fe at high-spin state in ferropericlase along the mantle geotherm. Figures 4b and 4c show variation of the thermoelastic parameters, ρ, α, K_T, and V_Φ, of ferropericlase using the high-spin ferropericlase as the reference. Grey vertical ticks represent the error bar for α (Figure 4b) and K_T (Figure 4c), whereas blue vertical ticks are errors bars for ρ (Figure 4b) and V_Φ (Figure 4c). Errors are calculated using standard error propagation from our modeled parameters.

at 300 K [*Speziale et al.*, 2007; *Lin et al.*, 2009; *Crowhurst et al.*, 2008; *Marquardt et al.*, 2009a, 2009b], though the high-temperature effect on the elasticity across the spin crossover remains unknown experimentally. We have modeled K_T and V_Φ behavior at high *P-T* across the spin crossover. A significant reduction in K_T and V_Φ occurs between 1700- and 2700-km depth compared to the HS state along the mantle geotherm, reaching a maximum at ~98 GPa and 2400 K (2220-km depth), with a 37% decrease in K_T and 13% in V_Φ. Considering 20 vol.% ferropericlase in a pyrolitic lower mantle, the overall reduction caused by the spin crossover is expected to be approximately 2.6% in V_Φ and 7.3% in K_T between 1700- and 2700-km depth (over a 1000-km thickness). Ferropericlase in the lower mantle is likely to contain less than 25 mol.% Fe, which would further lower the reductions. It remains to be seen if such reductions can be detected by seismic observations.

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