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Spin crossover in $(Mg,Fe^{3+})(Si,Fe^{3+})O_3$ bridgmanite: Effects of disorder, iron concentration, and temperature

Gaurav Shukla [a,b,*], Renata M. Wentzcovitch [a,b,c]

[a] School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455, USA
[b] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA
[c] Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455, USA

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ABSTRACT

The spin crossover of iron in Fe^{3+}-bearing bridgmanite, the most abundant mineral of the Earth's lower mantle, is by now a well-established phenomenon, though several aspects of this crossover remain unclear. Here we investigate effects of disorder, iron concentration, and temperature on this crossover using *ab initio* LDA + U_{sc} calculations. The effect of concentration and disorder are addressed using complete statistical samplings of coupled substituted configurations in super-cells containing up to 80 atoms. Vibrational/thermal effects on the crossover are addressed within the quasiharmonic approximation. The effect of disorder seems quite small, while increasing iron concentration results in considerable increase in the crossover pressure. Our calculated compression curves for iron-free, Fe^{2+}-, and Fe^{3+}-bearing bridgmanite compare well with the latest experimental measurements. The comparison also suggests that in a closed system, Fe^{2+} present in the sample may transform into Fe^{3+} by introduction of Mg and O vacancies with increasing pressure. As in the spin crossover in ferropericlase, this crossover in bridgmanite is accompanied by a clear volume reduction and an anomalous softening of the bulk modulus throughout the crossover pressure range. These effects reduce significantly with increasing temperature. Though the concentration of $[Fe^{3+}]_{Si}$ in bridgmanite may be small, related elastic anomalies may impact the interpretation of radial and lateral velocity structures of the Earth's lower mantle.

1. Introduction

Bridgmanite (br), $(Mg,Fe,Al)(Si,Fe,Al)O_3$ perovskite (Pv), is the main constituent of the Earth's lower mantle along with $(Mg,Fe)O$, $CaSiO_3$ Pv, and $(Mg,Fe,Al)(Si,Fe,Al)O_3$ post-perovskite (PPv). Thermodynamics and elastic properties of these minerals provide a direct link to seismic tomographic models. Understanding the effect of iron (Fe) and/or aluminum (Al) substitutions on the physical, chemical, and thermodynamic properties of the host mineral is essential to constrain the composition and thermal structure of the Earth's lower mantle. Ferropericlase (Fp), $(Mg,Fe)O$ is known to undergo a pressure induced spin crossover from the high ($S = 2$) to the low-spin ($S = 0$) state, which affects its elastic and thermal properties (Badro et al., 2003; Goncharov et al., 2006; Tsuchiya et al., 2006; Fei et al., 2007; Crowhurst et al., 2008; Marquardt et al., 2009; Wu et al., 2009; Wentzcovitch et al., 2009; Antonangeli et al., 2011; Mao et al., 2011; Wu et al., 2013; Hsu and Wentzcovitch, 2014; Wu and Wentzcovitch, 2014).

In the case of iron-bearing bridgmanite, in spite of considerable progress of experimental measurements at high pressures and high temperatures (Badro et al., 2004; Frost et al., 2004; Li et al., 2004; Jackson et al., 2005; Li et al., 2006; Lin et al., 2008; Lundin et al., 2008; McCammon et al., 2008a,b; Dubrovinsky et al., 2010; Boffa Ballaran et al., 2012; Chantel et al., 2012; Fujino et al., 2012; Hummer and Fei, 2012; Lin et al., 2012; Dorfman et al., 2013; Lin et al., 2013; McCammon et al., 2013; Sinmyo et al., 2014; Mao et al., 2015), deciphering the valence and spin states of multivalent iron and its influence on the physical properties has been quite a formidable challenge due to complexity of the perovskite structure. Iron in bridgmanite may exists in ferrous (Fe^{2+}) and ferric (Fe^{3+}) states. Fe^{2+} occupies the A-site ($[Fe^{2+}]_{Mg}$), while Fe^{3+} can occupy A- ($[Fe^{3+}]_{Mg}$) and/or B-site ($[Fe^{3+}]_{Si}$) of the perovskite structure (Badro et al., 2004; Li et al., 2004; Jackson et al., 2005; Li et al., 2006; Stackhouse et al., 2007; Bengtson et al., 2009; Lin et al., 2008; Dubrovinsky et al., 2010; Hsu et al., 2010; Hsu et al., 2011;

* Corresponding author at: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.
E-mail addresses: shuk0053@umn.edu (G. Shukla), wentz002@umn.edu (R.M. Wentzcovitch).

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Fujino et al., 2012; Hummer and Fei, 2012; Lin et al., 2012; Lin et al., 2013; Tsuchiya and Wang, 2013; Caracas et al., 2014; Sinmyo et al., 2014; Mao et al., 2015). In the entire lower mantle pressure-range, $[Fe^{2+}]_{Mg}$ seems to remain in the HS state (S = 2) but to undergo a pressure induced lateral displacement resulting in the state with increased iron Mössbauer quadrupole splitting (QS) (McCammon et al., 2008a; Bengtson et al., 2009; Hsu et al., 2010; Lin et al., 2012; Lin et al., 2013; McCammon et al., 2013; Potapkin et al., 2013; Kupenko et al., 2014; Shukla et al., 2015a,b). By contrast, $[Fe^{3+}]_{Si}$ undergoes a crossover from HS (S = 5/2) to LS (S = 1/2) state, while $[Fe^{3+}]_{Mg}$ remains in the HS (S = 5/2) state (Catalli et al., 2010; Hsu et al., 2011; Lin et al., 2012; Lin et al., 2013; Tsuchiya and Wang, 2013; Mao et al., 2015; Xu et al., 2015; Shukla et al., 2016).

The onset of the HS to LS crossover of $[Fe^{3+}]_{Si}$ in Fe^{3+}-bearing bridgmanite (Fe^{3+}-br) is still much debated. For Fe^{3+}-br with 10 mol.% Fe_2O_3, Catalli et al. (2010) observed the crossover completion at 48 GPa by X-ray emission spectroscopy(XES), and a change in electronic configuration between 53 and 63 GPa by Synchrotron Mössbauer spectroscopy (SMS). These observations led them to conclude the crossover pressure range to be approximately ~48–63 GPa. Using SMS, Lin et al. (2012) found the crossover pressure range ~13–24 GPa for a sample containing about ~2.0–2.5% of Fe^{3+}. Lin et al. (2012) and Mao et al. (2015) further argued that the lower crossover pressure observed by them could be related to the smaller Fe^{3+} concentration in their samples. Using first-principles static LDA + U_{sc} and GGA + U_{sc} calculations for $(Mg_{1-x}Fe_x^{3+})(Si_{1-x}Fe_x^{3+})O_3$ with $x = 0.125$, Hsu et al. (2011) estimated the crossover pressure 41 GPa and 70 GPa, respectively, while Tsuchiya and Wang (2013) reported 44 GPa for $x = 0.0625$ using LDA + U calculations. A thermodynamic model by Xu et al. (2015) estimated the $Fe^{3+}/\sum Fe$ ratio under lower mantle conditions to be ~0.01–0.07 in Al-free bridgmanite. In an effort to understand and reconcile observations and results of these studies, we have investigated the effect of (1) disordered substitution of nearest neighbor Fe^{3+}—Fe^{3+} pairs, (2) Fe^{3+} concentration, and (3) vibrational effects on the HS to LS crossover of iron in Fe^{3+}-bearing bridgmanite.

2. Computational details and methodology

2.1. Computational details

Density functional theory (DFT) within the local density approximation (LDA) (Ceperley and Alder, 1980) has been used in this study. It is well known that standard DFT functionals do not capture strong correlation effects of 3*d* and 4*f* electrons properly. For this reason, standard DFT is augmented by the the self- and structurally consistent Hubbard U_{sc} (LDA + U_{sc} method) (Cococcioni and de Gironcoli, 2005; Kulik et al., 2006; Hsu et al., 2009). U_{sc} values reported by Hsu et al. (2011) using these methods have been used here for all iron concentration. Disordered substitution of Fe^{3+} in $(Mg_{1-x}Fe_x^{3+})(Si_{1-x}Fe_x^{3+})O_3$ bridgmanite with varying iron concentration has been investigated in 80- ($x = 0.125$), 40- ($x = 0.25$), and 20-atoms ($x = 0.50$) super-cells (Fig. 1). Ultrasoft pseudo-potentials (Vanderbilt, 1990) have been used for Fe, Si, and O. For Mg, a norm-conserving pseudo-potential, generated by von Barth-Car's method, has been used. A detailed description of these pseudo-potentials has been reported by Umemoto et al. (2008). The plane-wave kinetic energy and charge density cut-off are 40 Ry and 160 Ry, respectively. For 80-, 40-, and 20-atom super-cells, the electronic states were sampled on a shifted $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $6 \times 6 \times 4$ k-point grid, respectively. Structural optimization at arbitrary pressure has been performed using variable cell-shape damped molecular dynamics (Wentzcovitch, 1991; Wentzcovitch et al., 1993). Structures are optimized until the inter-atomic forces are smaller than 10^{-4} Ry/a.u. Vibrational density of states (VDOS) for Fe^{3+} concentration $x = 0.125$ has been calculated in a 40-atom super-cell using density functional perturbation theory (DFPT) (Baroni et al., 2001) within the LDA + U_{sc} functional (Floris et al., 2011). For this purpose, dynamical matrices on a $2 \times 2 \times 2$ q-point grid of a 40-atom cell were calculated and thus obtained force constants were interpolated on a $8 \times 8 \times 8$ q-point grid. High throughput calculations have been performed using the VLab cyberinfrastructure at the Minnesota Supercomputing Institute (da Silva et al., 2008).

2.2. Disordered substitution of Fe^{3+} and spin crossover

Disordered substitution of Fe^{3+} in $(Mg_{1-x}Fe_x^{3+})(Si_{1-x}Fe_x^{3+})O_3$ has been studied by replacing nearest neighbor Mg^{2+}–Si^{4+} pairs with $[Fe^{3+}]_{Mg}$—$[Fe^{3+}]_{Si}$ pairs and generating all possible atomic configurations consistent with super-cell size. The number of symmetrically inequivalent configurations, N_c, are 21, 13, and 5 in 80- ($x = 0.125$), 40- ($x = 0.25$), and 20-atom ($x = 0.50$) super-cells, respectively. Within the quasiharmonic approximation (QHA) (Umemoto et al., 2010), the partition function for disordered system with $[Fe^{3+}]_{Si}$ in a spin state σ is given by

$$Z_\sigma^{QHA}(T,V) = \sum_{i=1}^{N_c} g_i M_\sigma \exp\left\{-\frac{E_\sigma^i(V)}{k_B T}\right\} \times \prod_{j=1}^{N_{mode}}\left[\sum_{v_{i,j}=0}^{\infty} \exp\left\{-\left(v_{i,j}+\frac{1}{2}\right)\frac{\hbar\omega_{i,j,\sigma}(V)}{k_B T}\right\}\right], \quad (1)$$

where g_i is the multiplicity of symmetrically equivalent configurations and $E_\sigma^i(V)$ is the static energy of the *i*th inequivalent configuration at volume *V*. M_σ is the magnetic degeneracy of the system, which includes the spin and orbital degeneracies. $v_{i,j}$ and $\omega_{i,j,\sigma}(V)$ are the number of excited phonons and frequency of *j*th mode at volume *V* for *i*th configuration. k_B and $\hbar$ are Boltzmann and Planck constants, respectively. N_c and N_{mode} are the total number of configurations and vibrational modes of a given super-cell. After summing over $v_{i,j}$, the partition function is written as

$$Z_\sigma^{QHA}(T,V) = \sum_{i=1}^{N_c} g_i M_\sigma \exp\left\{-\frac{E_\sigma^i(V)}{k_B T}\right\} \times \prod_{j=1}^{N_{mode}}\left\{\frac{\exp\left(-\frac{\hbar\omega_{i,j,\sigma}(V)}{2k_B T}\right)}{1-\exp\left(-\frac{\hbar\omega_{i,j,\sigma}(V)}{k_B T}\right)}\right\}. \quad (2)$$

The computation of VDOS (i.e., phonon frequencies $\omega_{i,j,\sigma}(V)$) within DFPT + U_{sc} method (Floris et al., 2011) for every symmetrically inequivalent configuration is extremely challenging. To circumvent this difficulty, we approximate the partition function by assuming that VDOS for a given Fe^{3+} concentration *x* is same for all configurations. Within this approximation, the partition function becomes

$$Z_\sigma^{QHA}(T,V) = \left[\sum_{i=1}^{N_c} g_i M_\sigma \exp\left\{-\frac{E_\sigma^i(V)}{k_B T}\right\}\right] \times \left[\prod_{j=1}^{N_{mode}}\frac{\exp\left\{-\frac{\hbar\omega_{j,\sigma}(V)}{2k_B T}\right\}}{\left\{1-\exp\left(-\frac{\hbar\omega_{j,\sigma}(V)}{k_B T}\right)\right\}}\right]. \quad (3)$$

The Helmholtz free-energy for the system (the super-cell containing *N* formula units of Fe^{3+}-br) with $[Fe^{3+}]_{Si}$ in HS/LS state can be calculated as