Effect of anomalous compressibility on Fe diffusion in ferropericlase throughout the spin crossover in the lower mantle

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ABSTRACT

The transport of iron in the deep earth is important for understanding chemical equilibration between deep earth phases and between the core and mantle. However, iron transport modeling is complicated by its changes in spin state with pressure and temperature. Recent studies (Saha et al., 2011; Ammann et al., 2011) calculated the diffusivity of iron in ferropericlase as a function of iron's spin state but did not include the coupling of iron migration energetics to the observed anomalous bulk modulus softening associated with the spin transition (Wentzcovitch et al., 2009; Crowhurst et al., 2008). Here we calculate the diffusivity of iron in ferropericlase throughout the lower mantle using a model for both iron's spin and the anomalous bulk modulus softening to provide a complete model of iron diffusion in ferropericlase. Including the bulk modulus softening increases iron diffusivities by a factor of thirty relative to values without this effect at some depths on the geotherm.

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1. Introduction

Diffusion is a key transport mechanism in the Earth's lower mantle. Iron bearing ferropericlase (Fp) and silicate perovskite (Pv) are the two main constituents of the lower mantle. Iron diffusion in these minerals controls the Fe partitioning between the different phases and may play a role in the communication of Fe across the core–mantle boundary (Hayden and Watson, 2007). The recent discovery that iron's electronic and physical properties will change with pressure necessitates a new effort to determine the diffusion of Fe at all mantle pressures and temperatures.

In ferropericlase, Fe^{2+} undergoes a spin transition from a high spin (HS) state with four unpaired electrons in 3d orbitals to a low spin (LS) state with no unpaired electrons (Badro et al., 2003). The spin transition occurs within the pressure–temperature range extending from approximately 1000 km to 2200 km in depth and 1900 K to 2300 K in temperature in the lower mantle, where pressure varies from 40 to 70 GPa (Lin et al., 2007a; Tsuchiya et al., 2006; Speziale et al., 2005; Badro et al., 2003; Persson et al., 2006; Marquardt et al., 2009; Fei et al., 2007). The spin transition of Fe in this pressure–temperature range is not sharp (Sturhahn et al., 2005). Over the transition region the Fe spin is in a mixed spin (MS) state with a depth dependent fraction of HS and LS Fe (Lin et al., 2007a).

The spin transition has a significant effect on thermo-elastic properties of ferropericlase. Different research groups report the experimental observation of the effect of spin transition on the sound velocity (Lin et al., 2006; Crowhurst et al., 2008; Marquardt et al., 2009), electrical conductivity (Lin et al., 2007b), radiative conductivity (Goncharov et al., 2006) and thermal conductivity (Keppler et al., 2007) of ferropericlase. In particular, changes in bulk modulus and elasticity in ferropericlase have been measured by XES and XRD (Lin et al., 2005, 2009), acoustic velocities with impulsive stimulated scattering (Crowhurst et al., 2008), Brillouin spectroscopy (Marquardt et al., 2009) and inelastic X-ray scattering measurements (Antonangeli et al., 2011). These observations are consistent with the changes in density (Lin et al., 2005; Speziale et al., 2005; Fei et al., 2007; Zhuravlev et al., 2009) by XRD studies. Recent first principles studies have also found an anomalous increase in the thermal-expansion coefficient and thermal Gruneisen parameter, a noticeable change in specific heat, and a substantial softening of the bulk modulus as a consequence of spin crossover in ferropericlase (Wu et al., 2009; Wentzcovitch et al., 2009).

All studies, except one (by Antonangeli et al., 2011, discussed below), on ferropericlase elasticity to date suggest a dramatic reduction in bulk modulus associated with the spin transition (Lin et al., 2009; Crowhurst et al., 2008; Marquardt et al., 2009; Wentzcovitch et al., 2009). It is therefore important to explore how this softening might impact Fe diffusion. However, the recent inelastic X-ray scattering (IXS) research by Antonangeli et al. (2011) finds that the bulk modulus softening at $x = 0.17$ and room temperature is far less than expected from previous results. If the

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implications of this paper turn out to be completely valid for general ferropericlase samples it will imply that bulk modulus softening is very minor and, accordingly, that the softening enhanced diffusion described in this paper will be a small effect. Although the extent of softening is still a subject of active investigation, the model here provides a framework for understanding its impact on cation diffusion. At present, the only thermodynamically consistent and complete model for bulk modulus changes with the spin crossover comes from the work of Wentzcovitch et al. (2009) and we will use their values in the following study. Since the study of Wentzcovitch et al. (2009) predicts the most dramatic softening due to the spin crossover, the prediction from this study are the largest diffusivity changes consistent with the range of experimental data. A further source of enhanced effect in this study due to use of the elastic strain energy model (ESEM) (Sammis et al., 1981) is discussed below.

Prediction of the migration barrier and diffusivity of HS, LS, and MS Fe in feropericlase has also been made recently using density functional theory (Ammann et al., 2011; Saha et al., 2011). However, these studies were for dilute Fe concentrations, and therefore did not include coupling between Fe in the modeling of Fe diffusion. In particular, the collective effect of multiple Fe atoms undergoing spin crossovers leads to the predicted anomalous bulk modulus reduction (Wentzcovitch et al., 2009; Crowhurst et al., 2008; Marquardt et al., 2009) in the spin transition zone, and this effect was not included in previous diffusion studies. Here, we model the effect of bulk modulus softening on the diffusivity of Fe in ferropericlase at lower mantle pressures and temperatures using an elastic energy model (Sammis et al., 1981).

2. Methods

The thermodynamic model for the migration of Fe in feropericlase, including the spin transition and the mixed high- and low-spin state of Fe, was developed in Saha et al. (2011). According to this model the free energies of Fe at lattice sites, considering magnetic and electronic configuration degeneracy, can be written as

$$G^{OL} = -k_B T \ln \left[g_{LS} + g_{HS} \exp \left\{ -\frac{1}{k_B T} \left(E_{HS}^{OL} - E_{LS}^{OL} \right) \right\} \right], \tag{1}$$

and the free energies at the activated sites are

$$G^A = -k_B T \ln \left[g_{LS} \exp \left\{ -\frac{1}{k_B T} \left(E_{LS}^A - E_{LS}^{OL} \right) \right\} + g_{HS} \exp \left\{ -\frac{1}{k_B T} (E_{HS}^A - E_{LS}^{OL}) \right\} \right]. \tag{2}$$

The degeneracy due to magnetic and electronic configurations is given by $g = m(2S+1)$, where m is the electronic configuration degeneracy ($m=3$ for HS, $m=1$ for LS) and S is the quantum spin number for iron ($S=2$ for HS, $S=0$ for LS). OL denotes the on-lattice position and A denotes activated state. The effective migration free energy ΔG is then calculated as

$$\Delta G = G^A - G^{OL} \tag{3}$$

These migration energies can be determined as a function of temperature and pressure and used in statistical models to predict Fe diffusivity. However, such approaches are generally only rigorous diffusion models in the limit of dilute Fe (Ammann et al., 2011; Saha et al., 2011). The anomalous bulk modulus softening (Wentzcovitch et al., 2009; Crowhurst et al., 2008), which is likely to enhance diffusion, will increase with increasing Fe concentration. Since the effect is intrinsically due to Fe interactions, such an enhancement cannot be seen in a strictly dilute Fe model and has not been included in Fe diffusion models to date (Ammann et al., 2011; Saha et al., 2011). To assess the impact of bulk modulus softening on Fe

diffusion we extend the above model from Saha et al. (2011) with an elastic strain energy model (ESEM) (Sammis et al., 1981). Such an approach for understanding the coupling of lower mantle diffusion and the anomalous compressibility was recently proposed by Wentzcovitch et al. (2009).

In order to apply the ESEM, the key energies giving rise to the migration barrier for Fe are identified, then these energies are modified to incorporate changes due to the bulk modulus. It was shown by Ammann et al. (2011) and Saha et al. (2011) that, due to a high migration barrier, the probability of a LS Fe hopping from a lattice position to the activated state while remaining LS is very low. Hence, it can be assumed that the activated state is always HS. This approximation removes one of the terms from equation (2) which can then be simplified as

$$\begin{aligned} G^A &= -k_B T \ln g_{HS} + (E_{HS}^A - E_{LS}^{OL}) \\ &= -k_B T \ln g_{HS} + (E_{HS}^{OL} - E_{LS}^{OL}) + (E_{HS}^A - E_{HS}^{OL}) \end{aligned} \tag{4}$$

Now consider how the two key energy differences, $(E_{HS}^{OL} - E_{LS}^{OL})$ and $(E_{HS}^A - E_{HS}^{OL})$, depend on composition. First we denote the free energy associated with the HS jump as approximately

$$G^*(x, P, T) = (E_{HS}^A - E_{HS}^{OL}). \tag{5}$$

The previous model from Saha et al. (2011) allows evaluation of $G^*(x, P, T)$ for $x \approx 0$. In order to include the anomalous compressibility effects from the spin crossover, which are a strong function of x, the ESEM is used to find an expression for $G^*(x, P, T)$ for nonzero x. Assuming the distortion leading to the bulk modulus softening in Fp is predicted by a purely dilatational ESEM, then the energy associated with diffusive jump can be modeled as (Sammis et al., 1981)

$$G^*(x, P, T) = \frac{V(x, P, T) K(x, P, T)}{V(x, P_0, T) K(x, P_0, T)} \times G^*(x, P_0, T), \tag{6}$$

where $V(x, P, T)$ and $K(x, P, T)$ represent volume and bulk modulus at composition x, pressure P and temperature T, and where P_0 is a reference pressure. This model has been shown to work well with metals (Sammis et al., 1981) and high P and T Mg diffusion in MgO (Van Orman et al., 2003).

An additional assumption is made that G^* depends weakly on Fe concentration for pressures below the spin crossover. This assumption is supported by experiments at lower pressures showing that changes in composition impact the migration enthalpy weakly (Mackwell et al., 2005). Based on this assumption we can write a number of terms in Eq. (4) at $x \approx 0$. Specifically, this assumption implies $G^*(x, P_0, T) = G^*(x \approx 0, P_0, T)$, which yields

$$G^*(x, P, T) = \frac{V(x, P, T) K(x, P, T)}{V(x, P_0, T) K(x, P_0, T)} \times G^*(x \approx 0, P_0, T) \tag{7}$$

According to the elastic model, it should also be true that

$$G^*(x \approx 0, P, T) = \frac{V(x \approx 0, P, T) K(x \approx 0, P, T)}{V(x \approx 0, P_0, T) K(x \approx 0, P_0, T)} \times G^*(x \approx 0, P_0, T) \tag{8}$$

Combining Eqs. (7) and (8) yields

$$\frac{G^*(x, P, T)}{G^*(x \approx 0, P, T)} \approx \frac{V(x, P, T) K(x, P, T)}{V(x, P_0, T) K(x, P_0, T)} \times \frac{V(0, P_0, T) K(0, P_0, T)}{V(0, P, T) K(0, P, T)} \tag{9}$$

As will be shown below, this expression for $G^*(x, P, T)$ is now practical to evaluate under lower mantle conditions. However, to find G^A in Eq. (4) still requires evaluating $(E_{HS}^{OL} - E_{LS}^{OL})$.

The energy difference of $(E_{HS}^{OL} - E_{LS}^{OL})$ is the energy associated with the HS to LS transition for Fe on the lattice position. Previous studies of spin transition with Fe composition suggest that there is little change in the transition pressure for $X_{Fe} < 0.25$ (Persson et al., 2006; Tsuchiya et al., 2006). Therefore, for lower Fe concentrations the enthalpy differences between the LS and HS states $(E_{HS}^{OL} - E_{LS}^{OL})$ at the transition pressure can be assumed to be constant. For the present case a composition of $X_{Fe} \approx 0.18$ is