Melting temperature depression due to the electronic spin transition of iron

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ABSTRACT

The electronic spin transition of iron has been shown to strongly affect many thermoelastic properties of the host mineral. However, the response of melting temperatures to the spin transition remains largely unexplored. Here, we study the melting of lower mantle minerals, ferropericlase and bridgmanite, using Lindemann’s Law. This empirical law predicts a negligible melting temperature depression for Earth-relevant bridgmanite but a substantial depression for Earth-relevant ferropericlase across the spin transition of iron, consistent with extant experimental results. This melting depression can be explained within the framework of Lindemann’s Law for a Debye-like solid. The transition of iron from high- to low-spin configuration reduces the molar volume and the bulk modulus of the crystal, leading to a decrease in Debye frequency and consequently lowering the melting temperature. Thermodynamically, the melting depression likely derives from a more negative Margules parameter for a liquid mixture of high- and low-spin end-members as compared to that of a solid mixture. This melting depression across the spin transition of iron may be the process responsible for the formation of a deep molten layer during the crystallization of a magma ocean in the past, and a reduced viscosity layer at present.

Keywords: Melting, spin transition, ferropericlase, bridgmanite, lower mantle

INTRODUCTION

Many minerals in Earth’s mantle are believed to contain both ferrous and ferric iron. Specifically, for the lower mantle, the iron content of the two major constituents, (Mg,Fe)SiO3 bridgmanite and (Mg,Fe)O ferropericlase, are estimated to be 4–10 and 20–30 at%, respectively (Lee et al. 2004; Muir and Brodholt 2016). Both Fe2+ and Fe3+ are characterized by the partially filled 3d electron shells and thus multiple electronic spin states. The ionic radii and magnetic moments of iron ions with different electronic configurations in the same crystallographic site are intrinsically distinct. As such, the spin transition of iron is expected to affect the properties of lower mantle minerals. Indeed, recent experiments and first-principles simulations confirm that the spin transition of iron could result in substantial changes in physical (i.e., density and bulk modulus) (Tsuchiya et al. 2006; Crowhurst et al. 2008; Wentzcovitch et al. 2009; Liu et al. 2018), transport (i.e., diffusivity, viscosity, electrical/thermal conductivity) (Ohta et al. 2007; Saha et al. 2011), and chemical (e.g., element partitioning) properties of minerals (Badro et al. 2003; Shim et al. 2017).

Nevertheless, the effect of spin transitions on melting temperature, a fundamental thermodynamic property, remains poorly constrained. Intuitively, anomalous melting behavior is anticipated for a spin-crossover system like (Mg,Fe)O. This is because melting is essentially governed by the energetics of the solid and liquid phases that have been shown to strongly depend on the spin state of the system (Wentzcovitch et al. 2009; Holmstrom and Stixrude 2015; Ghosh and Karki 2016).

Recently, Deng and Lee (2017) observed a pronounced melting temperature depression of ferropericlase of Earth-relevant compositions at pressures greater than ~40 GPa where the spin transition of Fe2+ occurs, creating local minima in the solidus and liquidus fusion curves. To our knowledge, this is the first time the effects of spin transition on melting have been proposed.

To further explore the effects of the spin transition on the melting temperature, we utilize the semi-empirical Lindemann’s Law that states that melting occurs if the mean square amplitude of atomic vibrations exceeds a critical fraction $f$ of the interatomic distance in the crystal (Lindemann 1910; Gilvarry 1956b). As the properties of the liquid states are not explicitly considered, Lindemann’s Law lacks a legitimate physical basis as pointed out by many studies (e.g., Wolf and Jeanloz 1984; Wallace 1991). However, the applicability of the Lindemann’s Law has been well tested for many systems, and some general trends have emerged. Lawson (2009) demonstrated that Lindemann’s Law follows from straightforward thermodynamic considerations for elements of simple structure, although it does fail for others with more complicated structures (Wolf and Jeanloz 1984). Anderson (1995) concluded that Lindemann’s Law is applicable to densely packed (i.e., packing fraction is large) Debye-like solids for which a single value of Debye temperature would suffice to describe the thermoelastic properties. For example, MgO, FeO, and MgSiO3, bridgmanite are typical Debye-like solids (Anderson 1998), and the predicted melting curves based on Lindemann’s Law exhibit good agreement with the experiments and first-principles computations (Poirier 1989; Speziale et al. 2001; Fischer and Campbell 2010). In addition, bridgmanite with 10 at% iron is also characterized by Debye-like thermoelastic properties (Anderson and Hama 1999). Similarly, the (Mg,Fe)O solid solution may also be a Debye-like solid given its two Debye-like end-members (Anderson 1995). As a result, Lindemann’s Law is likely applicable to ferropericlase and bridgmanite of Earth-relevant compositions before the spin crossover. Upon the spin transition, components with different spin states are admixed, modifying the atomic vibrations and free energies