Volumes and spin states of FeHₓ: Implication for the density and temperature of the Earth’s core

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Abstract

Hydrogen is the most abundant element in the solar system and has been considered one of the main light elements in the Earth’s core. The hydrogen content in the Earth’s core is determined normally by matching the volume expansion caused by the incorporation of hydrogen into FeH, to the Earth’s core density deficit. The magnitude of this volume expansion at the pressure (P) and temperature (T) conditions of the Earth’s core is still unknown, and the effect of spin transition in FeH at high pressure is usually ignored. In this study, we simulate the Fe spin transition, equation of state, and hydrogen-induced volume expansion in Fe-H binaries at high P-T conditions using density functional theory (DFT) calculations. Our results indicate that hydrogen could stabilize the magnetic properties of fcc Fe from ~10 to ~40 GPa. A volume expansion induced by hydrogen is linear with pressure except at the Fe spin transition pressure, where it collapses significantly (~30%). The fcc FeH lattice is predicted to expand at an average rate of ~1.38 and 1.07 Å/ per hydrogen atom under the Earth’s outer and inner core P-T conditions, where the hydrogen content is estimated to be ~0.54–1.10 wt% and ~0.10–0.22 wt%, respectively. These results suggest that the Earth’s core may be a potentially large reservoir of water, with up to ~98 times as much as oceans of water being brought to the Earth’s interior during its formation. Based on our predicted hydrogen content in the Earth’s core, we propose that the presence of hydrogen would induce a relatively lower core temperature, ~300–500 K colder than it has been previously speculated.

Keywords: Hydrogen, iron hydride, spin transition, volume expansion, Earth’s core; Physics and Chemistry of Earth’s Deep Mantle and Core

Introduction

The Earth’s core comprises an iron-nickel alloy with some additional light elements such as Si, O, S, C, and H (Allegre et al. 1995; Ringwood 1984). Among these light elements, hydrogen has been proposed as an essential candidate in the Earth’s core (Poirier 1994). FeH adopts a face-centered cubic (fcc) structure that can exist stably under the conditions of the Earth’s core (Bazhanova et al. 2012; Kato et al. 2020). X-ray diffraction (XRD) and in situ neutron diffraction experiments are usually utilized to estimate the hydrogen content in the Earth’s core with a linear relation: \( x = (V_{FeH} - V_{Fe})/\Delta V_{H} \), where \( x \) is hydrogen concentration, \( V_{FeH} \) and \( V_{Fe} \) are the unit-cell volumes of iron hydride and pure iron, respectively, and \( \Delta V_{H} \) is the volume expansion caused by a single-formula unit of hydrogen. The values of \( \Delta V_{H} \) in the Fe-H system are crucial for acquiring the hydrogen content of the core. Previous studies have reported values ranging from 1.8 to 2.7 Å³ under relatively low P-T conditions (\( P = 4–82 \) GPa, \( T <2000 \) K) (Ikuta et al. 2019; Kato et al. 2020; Narygina et al. 2011; Pépin et al. 2014; Sakamaki et al. 2009; Thompson et al. 2018). These values are obtained under conditions far from the Earth’s core, however, and may underestimate the hydrogen content in the Earth’s core. Therefore, the value of \( \Delta V_{H} \) needs to be explored under the P-T conditions of the Earth’s core.

There is also considerable disagreement about the spin transition pressure of fcc FeH and its effect on volume and \( \Delta V_{H} \). The volume expansion of fcc FeH, is approximately linear with pressure at low P-T conditions (4–12 GPa, 750–1200 K) (Ikuta et al. 2019). However, the high-spin (HS) to low-spin (LS) transition in fcc FeH leads to a volume collapse and an anomaly in compression behavior (Kato et al. 2020), which will further affect the values of \( \Delta V_{H} \). Therefore, the pressure-driven HS to LS transition in fcc FeH needs to be considered to properly determine the hydrogen content in the Earth’s core. Narygina et al. (2011) suggested that at the pressure range of 26–47 GPa, the non-magnetic (NM) state of fcc FeH was observed in their Mössbauer spectroscopy experiments. Thompson et al. (2018) proposed that magnetic transition in fcc FeH is unlikely to occur at pressures up to 82 GPa. More recently, Kato et al. (2020) reported that the ferromagnetic (FM) to NM transition in fcc FeH happens at about 50–60 GPa based on their XRD measurements and theoretical calculations. Thus considerable discrepancies exist in predictions of where this transition occurs.

In this study, to examine the volume expansion \( \Delta V_{H} \) in iron hydride (FeH), we employed theoretical calculations to model FeH, at high P-T conditions. We calculated the volumes of FeH, as a function of pressure. The thermodynamic properties of FeH, were calculated using the lattice dynamics method with quasi-harmonic approximation. The spin transition in fcc FeH was determined to be at ~40 GPa. Before and after the spin transition point, the volume expansion induced by hydrogen is nearly linear...