The iron spin transition of deep nitrogen-bearing mineral Fe$_3$N$_{1.2}$ at high pressure

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**Abstract**

Nitrogen is a key probe to understanding the accretion and degassing of volatiles and the differentiation and evolution history of the Earth. However, it is one of the least studied elements under the Earth’s deep interior pressure and temperature ($P$-$T$) conditions. Surface and deep nitrogen are largely connected via subduction and volcanic degassing (Halama et al. 2014; Mao and Mao 2020; Halama and Bebout 2021). Notably, the nitrogen concentration in the present-day bulk silicate Earth may be only tens of parts per million, severely depleted with respect to other volatiles like carbon and sulfur (Marty 2012; Bergin et al. 2015; Yoshioka et al. 2018). Apart from volatile degassing during accretion, the metallic core has been considered a hidden reservoir to account for the missing nitrogen according to the siderophile nature of nitrogen as revealed in metal-silicate partition experiments (Hirschmann 2016; Li et al. 2016; Dalou et al. 2017, 2019). Up to 0.5 wt% nitrogen, together with other candidate light elements of Si, O, C, S, and H, has been suggested in the Earth’s core to interpret the core density deficit based on the global seismic models, e.g., the Preliminary Reference Earth Model (PREM) (Dziewonski and Anderson 1981; Sugiura 1998). In addition, the deep mantle becomes relatively reduced with the ~1 wt% metallic iron that is saturated at depths greater than 250 km (Rohrbach et al. 2007). Based on the presence of iron nitrides and carbonitrides in meteorites and deep diamond inclusions, nitrogen may be distributed heterogeneously and enriched in metal phases in the Earth’s interior (Li and Keppler 2014; Litasov et al. 2017; Rubin and Ma 2017; Huang et al. 2021).

Keywords: Spin transition, X-ray emission spectroscopy, high pressure, deep nitrogen; Physics and Chemistry of Earth’s Deep Mantle and Core

**Introduction**

Nitrogen is a key probe to understanding the accretion and degassing of volatiles and the differentiation and evolution history of the Earth. However, it is one of the least studied elements under the Earth’s deep interior pressure and temperature ($P$-$T$) conditions. Surface and deep nitrogen are largely connected via subduction and volcanic degassing (Halama et al. 2014; Mao and Mao 2020; Halama and Bebout 2021). Notably, the nitrogen concentration in the present-day bulk silicate Earth may be only tens of parts per million, severely depleted with respect to other volatiles like carbon and sulfur (Marty 2012; Bergin et al. 2015; Yoshioka et al. 2018). Apart from volatile degassing during accretion, the metallic core has been considered a hidden reservoir to account for the missing nitrogen according to the siderophile nature of nitrogen as revealed in metal-silicate partition experiments (Hirschmann 2016; Li et al. 2016; Dalou et al. 2017, 2019). Up to 0.5 wt% nitrogen, together with other candidate light elements of Si, O, C, S, and H, has been suggested in the Earth’s core to interpret the core density deficit based on the global seismic models, e.g., the Preliminary Reference Earth Model (PREM) (Dziewonski and Anderson 1981; Sugiura 1998). In addition, the deep mantle becomes relatively reduced with the ~1 wt% metallic iron that is saturated at depths greater than 250 km (Rohrbach et al. 2007). Based on the presence of iron nitrides and carbonitrides in meteorites and deep diamond inclusions, nitrogen may be distributed heterogeneously and enriched in metal phases in the Earth’s interior (Li and Keppler 2014; Litasov et al. 2017; Rubin and Ma 2017; Huang et al. 2021).

Iron nitrides have been widely suggested as the primary hosts of deep nitrogen in the reduced Earth’s interior; their thermostability and phase relations have attracted extensive attention. Among these Fe-N intermediates, orthorhombic $\zeta$-Fe$_x$N$_y$ (space group: $Pbcn$), cubic $\gamma$-Fe$_x$N (space group: $Pm\overline{3}m$), and nonstoichiometric siderazot $\varepsilon$-Fe$_x$N$_y$ (0.75 < $x$ < 1.5) are stable at ambient conditions (Nielsen and Burhwald 1981; Minobe et al. 2015; Litasov et al. 2017; Yoshioka et al. 2018). Under compression, $\varepsilon$-Fe$_2$N$_x$ forms from Fe$_3$N and Fe$_7$N at 9–15 GPa and 1400–1600 K (Schwarz et al. 2009; Guo et al. 2013). It has either a $P3\overline{1}2$ or $P6_322$ space group with hexagonal close-packed iron atoms, while nitrogen atoms occupy part of the octahedral voids (Sifkovits et al. 1999; Guo et al. 2013; Bette et al. 2021). The $\varepsilon$-Fe$_x$N$_y$ phase is the same as the $\varepsilon$-Fe-N$_p$ phase when $x$ is equal to ~1.3. Fe$_3$N$_x$ undergoes the pressure-induced phase transition from $\varepsilon$ to $\beta$ structures at pressures greater than 41 GPa and ~1000 K, while the $\beta$-Fe$_x$N$_y$ has been considered a candidate nitrogen-bearing phase in the Earth’s core (Minobe et al. 2015; Kusakabe et al. 2019). Additionally, previous studies reported that the $\varepsilon$-Fe$_x$N$_y$ phase is stable at least up to 60 GPa at room temperature (Lv et al. 2020; Huang et al. 2021). To date, the effects of nitrogen concentration on the stability and physical properties of nonstoichiometric $\varepsilon$-Fe$_x$N$_y$ have not been investigated.

The iron 3$d$ orbitals collapse under extremely high pressures of the deep Earth, leading to the high-spin to low-spin transition...