Measurements of the Lamb-Mössbauer factor at simultaneous high-pressure-temperature conditions and estimates of the equilibrium isotopic fractionation of iron

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Abstract

Isotopic fractionation has been linked to the lattice vibrations of materials through their phonon spectra. The Lamb-Mössbauer factor \( f_{LM} \) has the potential to provide information about the lattice vibrations in materials. We constrain the temperature evolution of the \( f_{LM} \) of \( \gamma \)- and \( \varepsilon \)-Fe at in situ high-\( P-T \) conditions between 1650 K and the melting point. We find that the vibrations of \( \gamma \)- and \( \varepsilon \)-Fe can be described using a quasiharmonic model with a pressure- and temperature-dependent Debye temperature computed from the measured \( f_{LM} \). From the Debye temperature, we derive the equilibrium isotopic fractionation \( \beta \)-factor of iron. Our results show that the quasiharmonic behavior of metallic iron would lower the value of \( \ln\beta^{57}_{54}Fe \) by 0.1‰ at 1600–2800 K and 50 GPa when compared to the extrapolation of room temperature nuclear resonant inelastic X-ray scattering data. Our study suggests that anharmonicity may be more prevalent in Fe metal than in lower mantle minerals at 2800 K and 50 GPa, a relevant condition for the core formation, and the silicate mantle may be isotopically heavy in iron.

Keywords: Iron isotope fractionation, high pressure-temperature, Mössbauer spectroscopy, anharmonicity

Introduction

Studies of the collective atomic oscillations in crystalline materials, or quantized lattice vibrations (phonons), are important for understanding and predicting the behavior of earth materials (e.g., Reynard et al. 2015). For example, acoustic phonons at the long-wavelength limit are intrinsically related to the elastic properties of minerals and affect seismic wave propagation within the Earth (Lin et al. 2005; Sturhahn and Jackson 2007; Zhang et al. 2013; Murphy et al. 2013; Chen et al. 2014; Wicks et al. 2017). Measurements of the phonon density of states as a function of pressure provide constraints on important thermodynamic parameters, including the vibrational free energy, entropy, and kinetic energy (e.g., Murphy et al. 2013; Morrison et al. 2019). Understanding phonon behavior in minerals provides estimates on the thermal budget of the Earth, as heat is mainly stored and transported via vibrational excitations (Chai et al. 1996; Jeanloz and Morris 1986; Jeanloz and Richter 1979; Kieffer 1979a, 1979b, 1979c, 1980, 1982). Studies of lattice vibrations have led to a better understanding of phase transitions (e.g., Wentzcovitch et al. 2010; Yu et al. 2008, 2010), including melting (Shen and Heinz 1998; Alfè et al. 1999, 2002, 2004; Vočadlo and Alfè 2002). Geochemical studies have demonstrated that mantle derived rocks are \(-0.1\)% heavier in \( ^{57}\)Fe than chondrite (Poitrasson et al. 2004; Sossi et al. 2016), and measurements of lattice vibrational properties of minerals and glasses are used to constrain whether the core formation would leave such isotopic signature to mantle rocks (Polyakov 2009; Shahar et al. 2016; Liu et al. 2017).

Lattice vibrations are determined by the interatomic potential (e.g., Reynard et al. 2015; Fultz 2010). In the harmonic approximation, the interatomic potential is quadratic in the vicinity of the atomic equilibrium positions (e.g., Dunitz et al. 1988; Trueblood et al. 1996; Sturhahn and Jackson 2007; Reynard et al. 2015). The harmonic approximation assumes that phonon spectra do not change with temperature. Although the harmonic approximation is used to explain selected physical properties of some solids under particular conditions (mostly at low temperatures), this model often fails to explain or predict material behavior under a wide range of conditions (Polyakov 1998; Fultz 2010; Wu 2010; Mauger et al. 2014). Several components contribute to the deviation from harmonicity in solids and are described by different physical models. Often-used models to describe nonharmonic lattice vibrations are quasiharmonic approximations, which allow temperature- and/or pressure-induced volume changes while assuming harmonic, non-interacting phonons (Polyakov 1998; Fultz 2010; Wu 2010; Mauger et al. 2014; Allen 2020).

Under some conditions, particularly at high temperatures, higher-order terms of the interatomic potential are required to describe the atomic displacements, and the anharmonicity is dominated by phonon-phonon interactions. These effects are sometimes named “intrinsic anharmonicity” (Polyakov 1998; Sturhahn and Jackson 2007; Fultz 2010; Reynard et al. 2015; Bansal et al. 2016; Allen 2020). In addition to phonon-phonon interactions, electron-phonon and magnon-phonon interactions might be included in the description of “intrinsic anharmonicity” (Fultz 2010; Mauger et al. 2014; Bansal et al. 2016). Anharmonicity is the origin of several important physical properties in solids, such as thermal expansion and lattice thermal conductivity (e.g.,...