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# Study of the thermodynamic stability of iron at inner core from first-principles theory combined with lattice dynamics

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ABSTRACT

The stability of iron has been reevaluated by a simple but accurate scheme. A combination of self-consistent *ab initio* lattice dynamics (SCAILD) and the long-wave limit approximation has been applied to investigate the elastic properties of iron at inner core conditions. We demonstrate that the vibrational contribution plays a crucial role to stabilize the systems with cubic symmetry. Especially, the fcc iron will be more stable than hcp iron at the temperature above 7200 K. As for the effect of the anharmonic part, in our calculation the smaller elastic constants are obtained at high temperature compared with previous calculations. Finally, applying our results to the seismological explorations, we find that the seismological data can be explained sufficiently when conglomerating the crystal of hcp and fcc iron with different orientation of fast crystallographic axes.



## 1. Introduction

The seismological exploration of the centre of Earth has shown a puzzling and complicating inner core. Especially, there is still a controversial issue about the strong seismic anisotropy that the longitudinal waves travel ~3% faster along the polar axis than in the equatorial plane (Creager, 1992; Tromp, 1993). As the main component of the Earth's inner core, iron at inner core conditions is usually used to explain seismological observations. The precise structure of iron at high pressure and high temperature is essential for modeling the geodynamo and building the theory of the geomagnetism. Though a large number of the researches have been performed to investigate iron under extreme conditions in theories and experiments (Belonoshko and Ahuja, 1997; Belonoshko et al., 2000, 2003, 2004, 2008, 2009; Stixrude and Cohen, 1995; Cohen et al., 1997; Vočadlo et al., 2003a,b; Vočadlo, 2007; Steinle-Neumann et al., 2001; Alfè et al., 2002; Gannarelli et al., 2005; Stixrude, 2012; Martorell et al., 2013a,b; Mao et al., 1998; Ma et al., 2004; Merkel et al., 2005; Boehler et al., 2008; Tateno et al., 2010; Takeshi et al., 2014; Laio et al., 2000; Anderson et al., 2001; Sha and Cohen, 2010; Luo et al., 2010; Chen et al., 2011; Pourovskii et al., 2013; Anzellini et al., 2013; Glazyrin et al., 2013; Cui et al., 2013; Neuhaus et al., 2014), the structure and properties of iron at the inner core conditions still remain an interesting debate, especially for the stability of cubic phase. If the cubic phase is the stable structure in the inner core, it will change our understanding about the inner core, such as, the explanation of the seismic anisotropy, the amount of light elements, and the anchor temperature of the inner core. Thus it is necessary for us to obtain a clear description about the stable phases of iron at inner core conditions. Unfortunately, it is difficult to produce the inner core condition in experiment due to the practical limits like extreme high pressure and temperature.

In principle, the First-principles calculations can yield a good description of the static equation of state and the low temperature phase diagram of iron by quasiharmonic approximation (QHA) Otero-de-la Roza et al., 2011. As we know, the quasiharmonic approximation is generally used to calculate the vibrational free energy. In this method, the lattice vibrations are harmonic at each volume and the phonon spectra only relate to the corresponding volume, not directly to the temperature. This will result in the lost of electron excitation and phonon interactions. Of course, the quasiharmonic approximation can yield reliable results at some situations where the intrinsic anharmonic effect is insignificant (Debernardi et al., 2001; Antonangeli et al., 2008). However, it fails to reproduce the thermodynamic properties of the cubic phase of iron at elevated temperatures due to the large anharmonic contribution originating from the high-temperature structure

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(Luo et al., 2010; Souvatzis et al., 2008). In order to overcome these disadvantages of quasiharmonic approximation and calculate thermodynamic properties, we use a method developed from SCAILD to calculate the free-energy for the different phases. For more details of this method, one can consult Section 2: The theoretical methods.

The effect of anharmonic part is important for understanding the equation of state (EOS) and the thermodynamic properties of cubic iron at the inner core conditions. To incorporate the effects of the anharmonic part, we need to introduce the higher-order anharmonic interactions into the Hamiltonian of lattice dynamical system and the interactions should be directly related to temperature. We realize this by an effective method named self-consistent *ab initio* lattice dynamics (SCAILD) Souvatzis et al., 2008, in which the phonon-dispersion relations can be obtained at a given temperature and volume. In this method the temperature dependence of phonon frequencies is introduced to simulate the phonon–phonon interactions. However, we must realize that the SCAILD method produces an effective harmonic Hamiltonian, which is a way to approximate the high temperature potential, but as such the method is not exact. Once the phonon dispersion relations are yielded at high temperatures and high pressures, we can obtain the corresponding elastic constants by the long-wave limit approximation without any artificial modification for the effect of temperature. Since we focus on iron properties at inner core, we perform nonmagnetic computations at extreme conditions. More detailed description of the basic theories of present scheme is presented in Section 2. We discuss our results in Section 3. Finally, a summary of our main results is given in Section 4.

## 2. The theoretical methods

### 2.1. The free energy with finite temperature

The free energy as a function of temperature and volume can be obtained from the following equation:

$$F(V,T) = U_0(V) + F_{el}(V,T) + F_{Vib}(V,T), \tag{1}$$

where $U_0(V)$ is the static energy with fixed ionic positions, $F_{el}(V,T)$ is the thermal free energy from the electronic excitations, and $F_{Vib}(V,T)$ is the vibrational free energy of the ions. The intrinsic anharmonic effects are included in the vibrational part, and it needs a further division for $F_{Vib}(V,T)$,

$$F_{Vib}(V,T) = F_h(V,T) + F_a(V,T). \tag{2}$$

The first part is the harmonic contribution in the right of equation, and the rest is the intrinsic anharmonic contribution. The effect of temperature on the volume and entropy are included in $F_a(V,T)$.

To get the accurate anharmonic contribution, The SCAILD method (Souvatzis et al., 2008) is used to measure the exact relationship between the phonon spectra and temperature at a fixed volume. In the means of the SCAILD method, the phonon frequency is temperature dependent, and the atomic movements at a supercell rely on all phonons with wave vectors $q$ commensurate. All of the excited phonons will result in the change of the entropy, which in turn influences the phonon frequencies. During the displacement calculation, the mode amplitude $A^{\sigma}_{ks}$ is calculated from different phonon frequencies:

$$A^{\sigma}_{ks} = \pm\sqrt{\frac{\langle D^{\sigma}_{ks} D^{\sigma}_{-ks}\rangle}{M_{\sigma}}} = \pm\sqrt{\frac{\hbar}{M_{\sigma}\omega_{ks}}\left[\frac{1}{2} + n\left(\frac{\hbar\omega_{ks}}{K_B T}\right)\right]}, \tag{3}$$

where $n(x) = 1/(e^x - 1)$, $M_{\sigma}$ is the mass of atoms of type $\sigma$, and $D^{\sigma}_{ks}$ is the canonic phonon operators. These operators appear along with the canonical phonon momentum $P^{\sigma}_{ks}$ in the harmonic Hamiltonian

$$H_h = \sum_{k,s,\sigma}\frac{1}{2}(P^{\sigma}_{ks}P^{\sigma}_{-ks} + \omega^2_{ks}D^{\sigma}_{ks}D^{\sigma}_{-ks}). \tag{4}$$

Once the relationship between the phonon spectra and temperature is obtained, we can take a series of calculations with different volume. Then, we can perform several calculations of Lagrangian finite difference to obtain the relationship between temperature, volume, and phonon frequencies. The internal energy $U$ is derived from following equation:

$$U = U(V,T) = F(V,T) + TS_{ph} \tag{5}$$

The temperature dependent parts of the free energy can be found as

$$F_{ph}(V,T) + F_{el}(V,T) = \frac{1}{N_I}\sum_{\{U_R\}}\Delta F^*(\{U_R\},V,T) + \frac{3}{2}k_B T - TS_{ph}(V,T) \tag{6}$$

Here $\Delta F^*$ is the change in free energy relative to the ground-state energy $U_0$, caused by the phonon-induced atomic displacements and thermal excitations of the electronic states. $N_I$ is the number of atomic configurations, used for each volume and temperature was typically 400. $TS_{ph}$ is the contribution of vibrational entropy. However, how to calculate the phonon entropy is an important problem. Since the same state phonons is the noninteracting bosons, it can be assumed that the entropy depends on the phonon occupation numbers $n_{qs}$:

$$S_{ph} = k_B\sum_{qs}[(1+n_{qs})\ln(1+n_{qs}) - n_{qs}\ln(n_{qs})]. \tag{7}$$

This equation also can be expressed from the phonon density of states $g(\omega)$,

$$S_{ph}(V,T) = \frac{1}{T}\int_0^{\infty} dwg(\omega,V,T)\hbar\omega\left[n\left(\frac{\hbar\omega}{k_B T}\right) - \frac{k_B T}{\hbar\omega}\ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right)\right]. \tag{8}$$

Here the phonon frequencies used to calculate the phonon density of states, $g(\omega)$, are the normal mode configurational mean values

$$\langle\hbar\omega\rangle = \frac{1}{N_I}\sum_{\{U_R\}}\frac{\delta E_{tot}(\{U_R\},V,T)}{\delta n_{qs}}. \tag{9}$$

It should be stressed that the partitioning of the free energy through Eqs. (1), (2), (6) and (8) has been chosen to maximize both the accuracy of the phonon potential energy, which in the form of Eq. (6) take into account anharmonicity up to infinite order, and

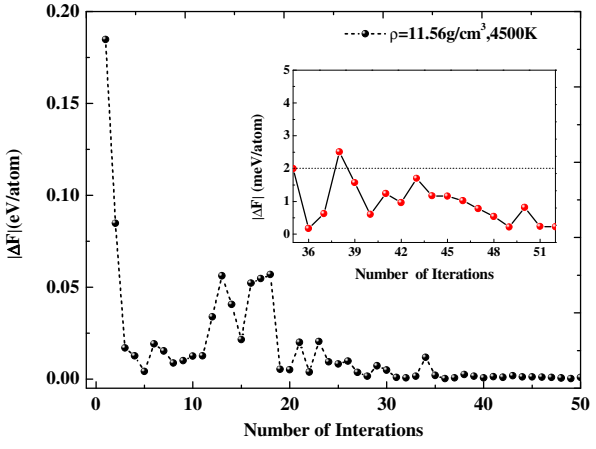


**Fig. 1.** The change in free energy between two consecutive iterations as a function of the number of iterations.

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