Dynamical stability of body center cubic iron at the Earth's core conditions

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Here, using self-consistent *ab initio* lattice dynamical calculations that go beyond the quasiharmonic approximation, we show that the high-pressure high-temperature bcc-Fe phase is dynamically stable. In this treatment the temperature-dependent phonon spectra are derived by exciting all the lattice vibrations, in which the phonon–phonon interactions are considered. The high-pressure and high-temperature bcc-Fe phase shows standard bcc-type phonon dispersion curves except for the transverse branch, which is overdamped along the high symmetry direction Γ -N, at temperatures below 4,500 K. When lowering the temperature down to a critical value T_C , the lattice instability of the bcc structure is reached. The pressure dependence of this critical temperature is studied at conditions relevant for the Earth's core.

ab initio | anharmonic lattice dynamics | high pressure and high temperature | inner core

The understanding of the Earth's core is one of the cornerstones of modern geophysics. The Earth's inner core, where the pressure is around 330–365 GPa, consists mainly of solid iron (1). The shock wave-derived melting curve (2–5) for Fe indicated that the melting temperature of Fe increased from 6,000 up to 8,000 K as the pressure is increased from 200 to 365 GPa, closely corresponding to the conditions for the Earth's core. Under laboratory conditions, one can presently achieve the Earth's outer core's pressures and temperatures to investigate the structure stability of iron. Recent experiments have shown that Fe doped with 10% Ni adopts the bcc structure at a pressure of 240 GPa and a temperature of 3,300 K (6). On the other hand, extrapolation of experimental results by Mao et al. (7) have suggested that a small doping of Ni does not stabilize the bcc phase over the hcp phase for pressures corresponding to the inner-core conditions.

Ab initio quantum mechanical calculations provide an alternative route to study these extreme conditions for iron. They usually have a sufficiently high accuracy for low temperatures. However, to describe properly the high-temperature thermal properties of materials, one must include the interaction between phonons that gives rise to the anharmonic effects in the lattice. There are two main theoretical methods that can be used, namely, molecular dynamics (MD) or quasiharmonic lattice dynamics. Belonoshko et al. have calculated the entropy (8) and mechanical properties of Fe (9) using classical as well as *ab initio* MD simulations, and found that the bcc phase is stabilized by entropy over the hcp phase and is dynamically stable at the Earth's inner-core conditions. The quasiharmonic lattice dynamics neglect anharmonicity; therefore the information on the temperature dependence of the vibrational modes and the interactions that are responsible for the high-temperature phase stability is lost. Information based on this approximation has ruled out that the bcc phase of pure Fe is stable in the inner core (10, 11), on the assumption that the anharmonic contribution is not enough to make up for the free energy difference between the bcc and hcp phase. However, for many transition metals it is shown that the phonon–phonon coupling stabilizes the high-tem-

perature bcc phase over the hcp phase, due to a large entropy relative to other lattice configurations (12–14).

At ambient pressure, iron takes various crystal phases depending on temperature: bcc α -Fe ($< 1,185$ K), fcc γ -Fe (1,185–1,667 K) and bcc δ -Fe (1,667–1,811 K, where the latter temperature is the melting point). The α -Fe phase is ferromagnetic at low temperatures. Above 1,185 K, iron is already paramagnetic (the Curie temperature of bcc-Fe is 1,044 K) until melting occurs (15, 16). Under the application of pressure at room temperature, α -Fe undergoes a transition at 13 GPa to the hcp structure, the so-called ϵ -phase (17), accompanied by a loss of the ferromagnetic order (18). At room temperature, the hcp phase is stable, at least up to 3,00 GPa (19).

Much less is known about the HP-HT Fe phase, an unfortunate fact given this material's great geophysical importance in the Earth's core regime. In the present work, we study the lattice dynamics stability of the bcc-Fe phase under the Earth's core conditions and we demonstrate that there is a firm region in the P-T phase diagram where bcc-Fe is dynamically stable.

Results and Discussion

Above the Curie temperature and at zero pressure, we find, according to our calculations, that the δ -Fe phase is stable for an antiferromagnetic state, whereas the nonmagnetic state is dynamically unstable. The calculated temperature-dependent phonon dispersion curves for α -Fe and δ -Fe at a temperature of 1,150 and 1,750 K are shown in Fig. 1, respectively.

The phonon dispersion of the α -Fe phase shows the typical phonon energy spectra of a bcc metal in high symmetry directions. For example one sees a dip of the longitudinal acoustic (LA) phonon branch at $k = 2/3$ [111], which is typical for bcc transition metals. However, it is observed that a few phonon softening branches appear in the dispersion curves for the δ -Fe phase. One softening branch exists around the high symmetry points H on the Brillouin zone boundary. The second one shows a deeper dip on the branch of the longitudinal mode along the direction of $[\xi\xi\xi]$. The third softening branch is the transverse acoustic mode TA2 along the high symmetry direction of N, which is due to the long range nature of the interatomic interaction. This means that the softening arises from the second neighbor force constant reduction.

As is well known, iron transforms to a non magnetic hcp phase, ϵ -Fe, at a pressure around 13 GPa and room temperature. At low temperature, the ϵ -Fe phase is dynamically stable up to the pressure in the Earth inner core. In sharp contrast to this, for a pressure interval of 200–450 GPa at 0 K, the phonon spectra of bcc-Fe contain imaginary dispersion curves (data not shown),

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Fig. 1. The phonon dispersion curves of bcc-Fe as a function of temperature. The green and yellow color lines give the simulation for low-temperature phase of α -Fe and high-temperature phase of δ -Fe, respectively, at ambient pressure. The red color lines show the simulation at high pressure with relative volume of $V/V_0 = 0.62$, where solid line indicates the phonon dispersion at a temperature of 4,500 K, and the dotted line presents the one at temperature of 5,000 K, respectively.

which means that the bcc phase is dynamically unstable. However, taking into account the temperature effects, as described in ref. 14, the bcc-Fe phase, according to our calculations, becomes dynamically stable at temperature above 4,500–5,500 K, depending on the pressure. Typical phonon dispersion curves of bcc-Fe with an atomic volume of $7.35 \text{ \AA}^3/\text{atom}$ ($V/V_0 = 0.62$) corresponding to a pressure of 235 GPa and temperature of 4,500 K and 5,000 K are shown in Fig. 1. The phonon dispersion curves show a similar behavior as for the high-temperature δ -Fe phase. The frequencies over the whole Brillouin zone are increased to higher values due to the high pressure, especially for the LA mode. The dynamic stability of the bcc-Fe phase at high pressures could only be driven by temperature. This temperature induced phase transformation is of great geophysical importance, because it means that iron in the interior of the Earth can be dynamically stable in the bcc phase.

As a result of the temperature effect at zero pressure, one can also see the bands of the phonon density of states (DOS) shifted to the low energy side and broadening in δ -Fe as shown in Fig. 2. Generally, the anharmonic effect is mainly responsible for the softening of the branch with the highest frequency. The result indicates a strong softening of the TA2 mode at a temperature of 1,750 K and ambient pressure, which should be partly related to the fact that the magnetic order transforms to a local order phase. For comparison, the phonon DOS of the high-pressure and high-temperature iron (HP-HT) bcc-Fe phase shows a similar distribution with the one of the δ -Fe phase and the frequencies have hardened due to the elevated pressure.

The TA2 branch damping originates from a local structural distortion of the cubic lattice, characterized by the shear strain of the (110) planes along the $[1\bar{1}0]$ direction, which is favored by a small elastic constant and by small TA2 $[\xi\xi0]$ phonon energies (21). The damping implies that the bcc phase may tend to be unstable toward the formation of a close-packed structure as the temperature is decreased (22). Hence, the HP-HT phase of Fe is dynamically stable in the bcc phase, and can therefore compete or coexist with other structures at the Earth's core conditions.

We now come to the central part of this communication, namely a pressure-temperature phase diagram of Fe where the bcc phase is dynamically stable. The phase diagram is based on self-consistent ab initio lattice dynamic (SCAILD) calculations, made in the region $150 \text{ GPa} < P < 380 \text{ GPa}$, and $3,000 \text{ K} < T < 7,500 \text{ K}$. If imaginary frequencies were found at the end of each self-consistent SCAILD calculation, the material was labeled as dynamically

Fig. 2. The temperature-dependent phonon DOS of bcc-Fe are simulated at ambient pressure and a pressure of 235 GPa (corresponding to the relative volume $V/V_0 = 0.62$), respectively. The green line represents ferromagnetic α -Fe at ambient pressure and a temperature of 1,150 K. [This gives a good agreement with experimental data on phonon DOS measured for α -Fe at a pressure of 6 GPa and temperature of 920 K (20)]. The orange line shows the δ -Fe at a temperature of 1,750 K. The red solid is obtained for a nonmagnetic bcc-Fe phase at a temperature of 4,500 K.

unstable; otherwise it is labeled as dynamically stable. In Fig. 3, we present the phase diagram, covering a pressure–temperature that is usually relevant for the Earth's inner core (a pressure ranging from 150 to 380 GPa and temperature from 3,000 to 7,500 K). It can be seen from the figure that above a certain temperature, bcc-Fe becomes lattice dynamically stable whereas below this temperature bcc-Fe is dynamically unstable (i.e., our phonon calculations result in one or several imaginary eigenvalues) and hence this phase must transform to another structure. The phase boundary describing this transition ranges from 150 GPa and approximately 3,000 K to 380 GPa and approximately 5,000 K (Fig. 3). It should be noted that the temperature needed to stabilize the bcc structure is increasing with increasing pressure. As a matter of fact, the general shape of this phase boundary follows

Fig. 3. The high-pressure and high-temperature (P–T) phase diagram indicates the lattice dynamical stability range of bcc-phase of pure iron at the Earth's core conditions. The red colored error bars are melting points from shock wave experiments of Yoo et al. (3). The orange error bar shows the melting data of Brown (2). The green error bar shows the bcc phase of Fe-10%Ni alloy from Dubrovinsky et al.'s static high-pressure experimental work using diamond anvil cell (6). The lattice dynamical stability of bcc-Fe is calculated below the experimental melting temperature for Earth's core pressure of 250 to 380 GPa. The green stars and the blue solid squares show the lattice dynamical stable and unstable points from this work, respectively. Red area indicates the inner core conditions.

the melting curve obtained from shock wave data (3) as well as from molecular dynamics simulations (8).

The SCAILD method, used here to calculate the dispersions of the HP-HT bcc-Fe and hcp-Fe phases, takes into account both a renormalization of the phonon frequency, due to the phonon-phonon interaction, and a broadening of the phonon dispersions. According to our results, the HP-HT bcc-phase exhibits a lattice dynamic stability at conditions of the Earth's inner-core; i.e., a temperature region about 2,000 K below the melting temperature, whereas the hcp phase is stable at lower temperature. We also observe that the HP-HT bcc phase has a very strongly damped transverse acoustic phonon branch along the $[\xi\xi0]$ direction, in which the crystal loses its shear resistance as the structural phase transition is approached. Hence, we have demonstrated that the transverse acoustic phonon mode of the bcc phase plays a dominant role in the anharmonic effects accounting for the lattice stability. The importance of anharmonic effects is shown to be very large from our calculations, and we argue that any microscopic model that attempts to describe the high-pressure high-temperature phase of Fe must take this effect into account.

The importance of our study can be summarised as follows. First, by means of finite temperature, lattice dynamical calculations, we have shown with fully ab initio calculations that the bcc phase is dynamically stable. Second, we suggest that the Earth's core is composed of bcc iron, therefore, the models based on the anisotropy of hcp iron to explain the seismic anisotropy of the Earth's inner core are not relevant. Third, consideration of the bcc phase, which is less dense than the hcp phase, might substantially diminish the amount of light elements in the Earth's inner core necessary to match its density. The establishment of

the HP-HT bcc structure will also have implications for the melting temperature, which in turn will put constraints on the temperature distribution inside the Earth.

Methods

We use the SCAILD method to study the influence of an anharmonic contribution to the lattice dynamics of the bcc phase, as a function of temperature, by exciting all the lattice waves with k-vectors commensurate to a supercell (14). As a result of the phonon-phonon interactions, the phonon frequencies are renormalized. When the quasiharmonic approximation is valid, the temperature dependence of the phonon spectrum may be calculated by including the temperature dependence of the lattice parameters. In the present work, we go beyond this approximation, by use of the SCAILD method. The calculations have been performed using the plane-wave based Vienna ab initio simulation package (23). For the exchange correlation functional the generalized gradient approximation (24) has been used.

Convergent calculations were performed with a Monkhorst-Pack $4 \times 4 \times 4$ k-point grid and a 345 eV plane-wave cutoff energy for a supercell 64 atoms. Selected atoms were displaced about 5% of the lattice constant away from equilibrium and the total force on each ion was converged to 0.001 eV/atom. The electron occupancy configurations were obtained from the Fermi-Dirac distribution function, which ensured a stable and rapid energy and force convergence. We have used projector augmented wave (PAW) potentials and we have also used pseudocore 3s and 3p electrons also as valence electrons apart from 3d and 4s electrons. We will also like to stress at this point that we have checked the convergence of K-points in all our results reported here. More details about the SCAILD method can be found in ref. 14.

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