

## The structure of iron under the conditions of the Earth's inner core

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**Abstract.** The inferred density of the solid inner core indicates that it is predominantly made of iron. In order to interpret the observed seismic anisotropy and understand the high pressure and temperature behaviour of the core, it is essential to establish the crystal structure of iron under core conditions. On the basis of extrapolated experimental data, a number of candidate structures for the high P/T iron phase have been proposed, namely, body-centred cubic (*bcc*), body-centred tetragonal (*bct*), hexagonal close-packed (*hcp*), double-hexagonal close-packed (*dhcp*) and an orthorhombically distorted *hcp* polymorph (Matsui, 1993; Stixrude and Cohen, 1995; Boehler, 1993; Saxena et al., 1996; Andrault et al., 1997). Here we present the results of the first fully *ab initio* free energy calculations for all of these polymorphs of iron at core pressures and temperatures. Our results show that *hcp*-Fe is the most stable polymorph of iron under the conditions of the Earth's inner core.

### Introduction

Since the density of the inner core is slightly lower than that inferred for pure iron, lighter alloying elements must be present. However, the high P/T phase diagram of pure iron itself presents major problems and it is essential to resolve these before trying to understand iron alloys. Direct experimentation on Fe at core conditions is extremely difficult, and there are major conflicts between the results of different groups. In particular, the existence of a solid-solid phase boundary between *hcp*-Fe and another undefined polymorph above ~200GPa and ~4000K has been suggested in order to reconcile data from static and shock experiments (Anderson and Duba, 1997); however, the results from the latest very high P/T shock experiments (Nguyen and Holmes, 1998) indicate that iron does not undergo any very high P/T phase change, as previously inferred by Brown and McQueen (1986). Such uncertainties can be resolved using *ab initio* calculations, which provide an accurate means of calculating the thermoelastic properties of materials at high P and T. Thermodynamic calculations on *hcp*-Fe and *fcc*-Fe at high P/T have already been reported (Stixrude et al. 1997; Wasserman et al., 1996) in which *ab initio* calculations were used to parameterise a tight-binding model; the thermal properties of this model were then obtained using the particle-in-a-cell method. The calculations presented here, using the Cray T3E at Edinburgh, are the first in which fully *ab initio* methods are used in conjunction with quasiharmonic

lattice dynamics to obtain free energies of all the candidate structures proposed for core conditions.

### Calculation Methodology

The calculations we shall present are based on density-functional theory (DFT) which is a widely used general scheme for using electronic structure calculations to obtain the total ground-state energy of a system as a function of atomic positions. More specifically, we use the pseudopotential approach in which only valence electrons are treated explicitly, with the interactions between these electrons and the ionic cores being described by an *ab initio* pseudopotential. The pseudopotential approach is an alternative to all-electron methods; it can be as accurate as these methods, while being computationally much less demanding (Vočadlo et al., 1997).

Our aim is to use the DFT pseudopotential method to study the relative thermodynamic stability of the proposed crystal structures at core conditions. We treat electronic exchange-correlation energy using the generalised gradient approximation (GGA), coupled with non-norm-conserving ultrasoft Vanderbilt pseudopotentials (Vanderbilt, 1990) as implemented in the VASP code (Vienna *ab initio* simulation package, Kresse and Furthmüller, 1996). Details of the construction of the pseudopotentials can be found in Kresse and Hafner (1994) and specific information about Fe pseudopotentials from Moroni et al. (1997). The results presented here were obtained using a pseudopotential with the *3p* electrons treated explicitly as valence electrons, i.e., with a  $[Ne]3s^2$  core, which we have previously found (Vočadlo et al., 1997; de Wijs et al., 1998) to be essential for the accurate description of the properties of solid and liquid iron at the high pressures of the Earth's core. The excellent quality of our pseudopotential DFT calculations is demonstrated by the accurate results we have found for the density and incompressibility of *bcc*-Fe, the *bcc*→*hcp* phase transition pressure (~10 GPa compared to an experimental value of 10-15 GPa), the magnetic moment of *bcc*-Fe (2.25  $\mu$ /atom compared to the experimental value of 2.12  $\mu$ /atom), and the elastic constants of *bcc*-Fe (a third order Birch-Murnaghan fit gives a value for the incompressibility, K, of 184 GPa compared to the experimental value of 173 GPa). These results are also in excellent agreement with those from the best all-electron first-principles methods currently available (Stixrude et al., 1994; Söderlind et al., 1996).

The most stable crystal structure at a given P and T is the one with the lowest Gibbs free energy, G, given by:

$$G = F + PV \quad (1)$$

where F is the Helmholtz free energy and V is the volume.

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Our strategy is to start by calculating  $F$  as a function of  $V$  and  $T$ , and to obtain  $P$  from the volume dependence of  $F$  by using the relation:

$$P = - \left( \frac{\partial F}{\partial V} \right)_T \quad (2)$$

we may then construct  $G$  from  $F$ ,  $P$  and  $V$ .

The Helmholtz free energy of a vibrating crystal can be expressed as:

$$F_{\text{total}}(V, T) = F_{\text{perf}}(V, T) + F_{\text{vib}}(V, T) \quad (3)$$

where  $F_{\text{perf}}$  and  $F_{\text{vib}}$  are the free energy of the rigid perfect lattice and the free energy due to atomic vibrations. At zero temperature,  $F_{\text{perf}}$  is just the total energy of the perfect lattice, but at the high  $T$  considered here, it must also contain the contribution to free energy from the electronic excitations. In DFT, this electronic contribution to  $F_{\text{perf}}$  is calculated by minimising the Mermin functional in the Kohn-Sham formalism (see, e.g., de Wijs et al, 1998).

To calculate the vibrational term, including the zero point energy, we use the harmonic approximation, in which  $F_{\text{vib}}$  is given by a standard formula involving a sum over the Brillouin zone of the free energy of each phonon mode. The phonon frequencies were obtained using the frozen-phonon technique: starting from the perfect lattice, an atom is displaced from equilibrium, and the resulting forces on all atoms are calculated. For a small displacement, the forces are proportional to the displacement, and the coefficients of proportionality constitute the force-constant matrix. The calculations of the phonon frequencies from the force-constant matrix is standard (e.g., Born and Huang, 1954). The *ab initio* calculation of the force-constant matrix was performed over the three densities 13.64, 13.44 and 13.00 gcm<sup>-3</sup> using supercells of 16 or 32 atoms (our current limit with available resources). The electronic k-point sampling (between 6 and 48 k-points in the irreducible Brillouin zone depending on symmetry) and plane-wave cutoffs were chosen to give a convergence in the energy difference between polymorphs of better than 0.004 eV/atom. As will be discussed later, such highly converged calculations are important since the free energy differences between the polymorphs becomes very small ( $\sim 0.05$  to 0.01 eV/atom) at core conditions.

It is possible that there will be a thermal contribution to the electron density and resulting interatomic forces due to electronic excitations which will affect the phonon frequencies. However, although it is relatively straightforward to calculate  $F_{\text{perf}}$  as a function of electronic temperature, it is impracticable to calculate phonon frequencies of large supercells as a detailed function of electronic temperature. Therefore, the supercell calculations were all performed with an electronic temperature of 6000K, which we consider to be representative of the possible range of temperatures to be found in the inner core.

In our calculations, the phonon frequencies were obtained from diagonalisation of the dynamical matrix which is the Fourier transform of the force constant matrix. Since this has been calculated to first nearest neighbours, the phonon frequencies are exact only at the gamma point and zone boundaries, the interpolation being performed throughout a 19x19x19 grid. The effect of supercell volume (e.g. 16 or 32 atoms for an *hcp* supercell) on the calculated vibrational

frequencies, and hence free energy, is small ( $< 0.3\%$ ); more importantly, this is a systematic effect with supercell size, and therefore its influence on the *difference* in free energy between polymorphs will be negligible.

## Results

Spin polarized simulations were initially performed on all the candidate phases at core pressures (which range from  $\sim 325$ -360 GPa). These revealed, in agreement with Söderlind *et al.*(1996), that under these conditions *bcc* and *bct*-Fe had only a small magnetic moment ( $\sim 1/2 \mu_B$ /atom) and all other phases had zero magnetic moment. We found that at these pressures the *bcc*, *bct* and the recently suggested orthorhombic polymorph of iron (Andraut et al., 1997) are mechanically unstable. The *bcc* and *bct* phases continuously transform to the *fcc* phase (confirming the findings of Stixrude and Cohen, 1995), while the orthorhombic phase spontaneously transforms to the *hcp* phase when allowed to relax to a state of isotropic stress. In contrast, *hcp*, *dhcp* and *fcc* Fe remain mechanically stable at core pressures, and we were therefore able to calculate their phonon frequencies and free energies.

Although no experimental data exist for phonons at high  $P$ , the quality of our calculations can be gauged by comparing the calculated phonon dispersion for *bcc*-Fe (done using fully spin polarised calculations), at ambient pressure, where experimental data do exist. Figure 1 shows the phonon dispersion curve for magnetic *bcc*-Fe at ambient conditions compared with inelastic neutron scattering experiments (see Gao et al., 1993); the calculated frequencies are in excellent agreement with the experimental values which further confirms the quality of the pseudopotential used in this study.

The temperature dependence of the Helmholtz free energy and the thermal pressure (i.e.  $P_{\text{total}}(V, T) - P_{\text{perfect}}(V, T=0)$ ) are shown in Figures 2 and 3. The thermal pressure at core conditions has been estimated to be 58 GPa (Anderson, 1995) and  $\geq 50$  GPa (Stixrude et al., 1997); this is in excellent agreement with our calculated thermal pressure for the *hcp* and *dhcp* structures (58 GPa and 49 GPa respectively at 6000K); however, the calculated thermal pressure is considerably higher for *fcc*-Fe, and we find that this thermodynamically destabilises this phase at core conditions with respect to *dhcp* and *hcp*-Fe.

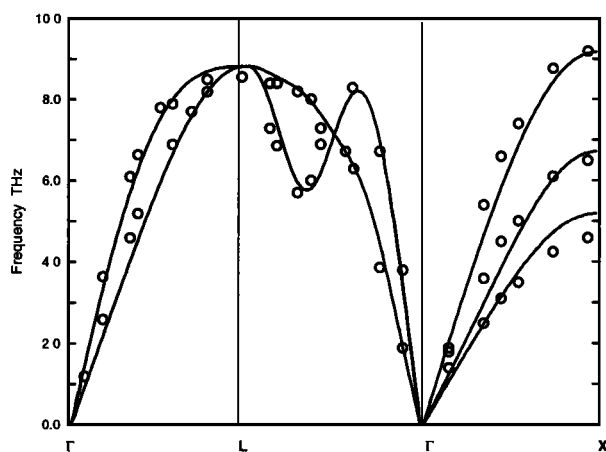


Figure 1. Calculated phonon dispersion curve for magnetic *bcc*-Fe under ambient conditions compared with inelastic neutron scattering experiments (see Gao et al., 1993) (open circles).

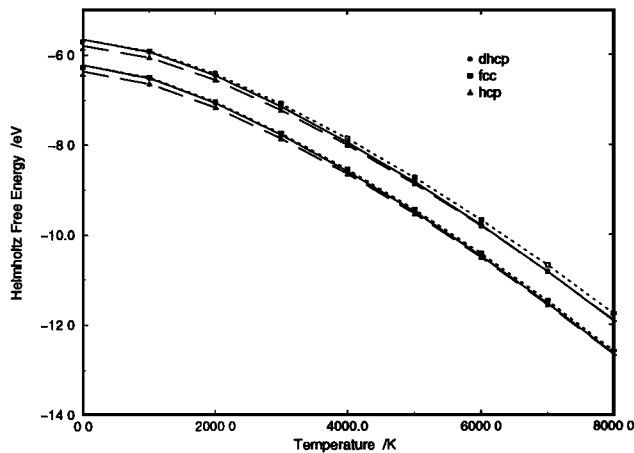


Figure 2. Calculated temperature dependence of the Helmholtz free energy as a function of temperature at  $V=7.134\text{\AA}^3$  (lower curve) and  $V=6.8\text{\AA}^3$  (upper curve).

Thus far we have obtained  $G(V,T)$ , but in order to make any predictions about the relative stability of the *dhcp* and *hcp* phases at core conditions, we require  $G(P,T)$ . By analysing the total pressure as a function of temperature obtained from our calculations for these two phases, we are able to ascertain the temperature for each of the three volumes considered at which  $P=325\text{GPa}$  and  $P=360\text{GPa}$  - pressures spanning the inner core range of pressures - and therefore determine the Gibbs free energy at those  $T$  and  $P$ . Figure 4 shows the Gibbs free energy as a function of  $T$  for these two phases at 325 GPa and 360 GPa; these were fitted to an exponential function satisfying the entropic requirement that  $(\partial G/\partial T)_{T=0}=0$  and  $(\partial G/\partial T)_{T\neq 0}=(S_{\text{total}})_{\text{calculated}}$ . Over the whole  $P$ - $T$  space investigated the *hcp* phase has the lower Gibbs free energy and is therefore predicted to be the stable structure at core conditions.

## Discussion

The validity of this important result depends upon three key issues which we discuss below: (i) the convergence criteria used in the calculations, (ii) the use of a fixed electronic temperature, and (iii) the affect of anharmonicity at these high  $P/T$  conditions.

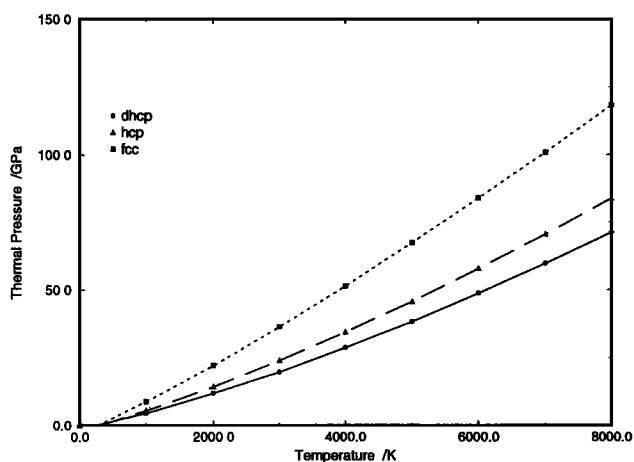


Figure 3. Calculated thermal pressure as a function of temperature; *fcc*-Fe is thermodynamically destabilised with respect to the other two phases due to its relatively high thermal pressure.

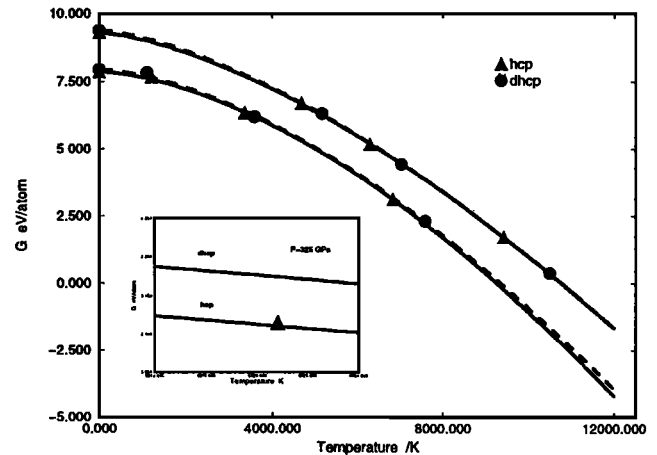


Figure 4. Calculated Gibbs free energy for *hcp*-Fe and *dhcp*-Fe as a function of temperature at  $P=325\text{GPa}$  (lower curves) and  $P=360\text{GPa}$  (upper curves); *hcp*-Fe is more stable throughout the whole  $P/T$  space shown.

(i) The results show that the free energy difference between the *hcp* and *dhcp* phases is small, as we would expect for two very similar close packed isochemical structures. We calculate  $\Delta G \sim 0.05\text{eV/atom}$  at  $P=325\text{GPa}$ , and ranges from  $\Delta G \sim 0.05\text{eV/atom}$  at  $P=360\text{GPa}$  and  $T=4000\text{K}$  to  $\Delta G \sim 0.01\text{eV/atom}$  at  $P=360\text{GPa}$  and  $8000\text{K}$ . Although these differences are small, they are significantly larger than the  $0.004\text{eV/atom}$  precision of our calculations limited by  $k$ -point sampling and plane-wave cut off discussed earlier. In addition, although we expect the effect of supercell size to be systematic between the two phases, it would be desirable to sample the phonon spectrum more effectively by performing calculations on significantly larger supercells.

(ii) As mentioned earlier, the phonon frequencies were calculated using a fixed electronic temperature of  $6000\text{K}$ . In order to determine the validity of this constraint, we performed indicative calculations on the effect of electronic temperature on phonon frequencies. We found that the effect of electronic temperature on free energy in the expected range of core temperatures ( $4000$  to  $8000\text{K}$ ) is generally significantly smaller than the free energy differences between the phases (a maximum of  $16\%$  of these differences between  $4000\text{K}$  and  $7000\text{K}$ ), and only becomes comparable in magnitude to the calculated free energy difference between the *dhcp* and *hcp* polymorphs as the temperature approaches  $8000\text{K}$  at  $P=360\text{GPa}$ .

(iii) As indicated above, these calculations do not take into account possible anharmonic effects. Over much of the  $(P,T)$  range investigated, we believe that we are justified in assuming that the motion of the atoms can be treated as harmonic vibrations, and that all thermodynamic properties can reasonably be calculated from the energy of the static perfect crystal and the harmonic lattice vibrational frequencies (Matsui et al., 1994). This assumption is validated by our calculated thermal expansion coefficient for *hcp*-Fe at  $\sim 5100\text{K}$  and  $325\text{GPa}$  of  $\sim 0.96 \times 10^{-5}\text{K}^{-1}$ , in excellent agreement with the values inferred from shock experiments (Duffy and Ahrens, 1993) and thermoelasticity calculations (Wasserman et al., 1996) of  $\sim 0.9 \times 10^{-5}\text{K}^{-1}$ . At the highest temperatures, however, anharmonic effects may become significant, but given the structural similarity of *hcp* and *dhcp* Fe, we would expect anharmonic effects on both phases

to be comparable and we suggest that they would have a small, or even negligible, effect on the relative stability of these two polymorphs.

Finally, it has been suggested (Matsui and Anderson, 1997) that although not mechanically stable at zero Kelvin, the *bcc* phase could be entropically stabilised at high T in the inner core, since *bcc* retains some magnetic moment at core pressures (Söderlind et al., 1996), and it is therefore conceivable that magnetic entropy effects may be non-negligible. However, Moroni et al. (1996) have estimated that the maximum contribution of magnetic entropy at core conditions is of the order of 0.3R per mole at 6000K. The maximum likely contribution to vibrational entropy is comparable to the melting entropy (Stixrude et al., 1994), which tends to  $R \ln 2$  for close-packed metals at high pressures (see Poirier, 1991). Therefore, the total maximum entropic contribution is  $\sim R$ . We calculate that the metastable enthalpy difference between *bcc*-Fe and *hcp*-Fe at a density of 13 g/cc is  $\sim 1.1eV$ . For this lattice energy difference to be overcome, the entropy difference between the phases would need to exceed  $\sim 2R$ , and it is therefore improbable that the magnetic and vibrational entropy could overcome this at core conditions.

In conclusion, therefore, our calculations, combined with other evidence, indicate that *hcp* is the thermodynamically most stable phase of Fe at the conditions believed to exist in the Earth's inner core. Our work has established the essential basis for a further study which is now needed to establish the equations of state and thermodynamic stability of alloys of Fe to establish which phase and which light alloying elements are indeed present in the Earth's core.

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