

## Constraints on the crystalline structure of the inner core: Mechanical instability of BCC iron at high pressure

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**Abstract.** We examine the energetics of close-packed phases of iron (bcc, fcc, hcp) throughout the pressure regime of the earth with elaborate first principles electronic structure calculations. The calculations reproduce the relevant experimental observations including the equation of state to over 300 GPa and the pressure of the bcc to hcp phase transition. The bcc structure is found to be energetically unfavorable and mechanically unstable with respect to a tetragonal strain at high pressure ( $P > 150$  GPa). This phase is thus highly unlikely to exist in the earth's inner core as has frequently been proposed.

### Introduction

The earth's inner core is composed primarily of iron, but exists at such extreme conditions of pressure (330-360 GPa) and temperature that its crystalline structure remains essentially unknown. As a result, the elastic anisotropy of the inner core, recently observed seismologically [Morelli *et al.*, 1986; Woodhouse *et al.*, 1986; Tromp, 1993], is difficult to interpret, and its cause remains unknown. Though plausible models for the formation of anisotropy exist, these rely heavily on assumptions about the type of crystalline structure in the inner core [Jeanloz and Wenk, 1988; Karato, 1992]. The crystalline structure of the inner core will largely determine its electromagnetic properties, and thus its influence on the geometry of the geomagnetic field, which recent modeling results indicate is substantial [Hollerbach and Jones, 1993]. The inner core also represents a major energy source for the geomagnetic field, as its continued formation, through freezing of the overlying liquid outer core, releases latent heat [Merrill and McElhinny, 1986]. The magnitude of this energy source will depend on the crystalline structure of the frozen material.

Despite much recent experimental progress, the sub-solidus phase diagram of iron above 200 GPa, remains essentially unconstrained. Structural determinations are difficult and have not yet been attempted in this pressure regime, so that the structures involved in the phase transitions observed dynamically [Brown and McQueen, 1986] and statically [Boehler, 1993; Saxena *et al.*, 1993] are unknown. All observed phases of iron: body-centered cubic (bcc), face-centered cubic (fcc),

and hexagonal close-packed (hcp), have been considered as the crystalline structure of the inner core [Anderson, 1986; Ross *et al.*, 1990; Jeanloz, 1990]. Recent attention has focused on the bcc structure [Ross *et al.*, 1990; Bassett & Weathers, 1990], but all three are permitted by current experimental data. Our ignorance of the sub-solidus phase diagram also multiplies current uncertainties in the iron melting curve. These uncertainties are directly reflected in the very large range of current estimates for the temperature of the inner core (4000-8000 K) [Williams *et al.*, 1987; Boehler, 1993; Saxena *et al.*, 1993; Yoo *et al.*, 1993]. Constraints on the high pressure sub-solidus phase diagram of iron are desperately needed.

First principles density functional theory (DFT) represents an ideal complement to high pressure experimental techniques and, as we show here, provides some of the first constraints on the crystalline structure of the inner core. DFT is a very powerful way of predicting the behavior of nearly all types of solids with high accuracy, independently of experimental data and without recourse to free parameters. We have applied this theoretical method to the prediction of the energetics of the three observed structures of iron (bcc, fcc, hcp) throughout the pressure regime of the earth. Our results reveal a mechanical instability in the bcc phase of iron at high pressure which leads to the conclusion that this phase is highly unlikely to exist in the inner core.

### Method

Density functional theory, and the Linearized Augmented Plane Wave Method (LAPW), which is used to solve the equations, are fully described elsewhere [see e.g. Pickett, 1989; Singh, 1994]. Only a brief description will be given here. The important points are that our calculations are 1) first principles - they are parameter-free and completely independent of experimental data 2) state-of-the-art in the sense that more exact ways of solving Schrödinger's equation for solids are not currently available and 3) a highly accurate way of predicting solid state properties, as has been demonstrated for essentially all types of materials, including silicates and metals.

In density functional theory, one solves self-consistently the equation for the charge density together with the Schrödinger-like Kohn-Sham [1965] equations

$$\rho(\vec{r}) = \sum n_i \psi_i^*(\vec{r}) \psi_i(\vec{r}) \quad (1)$$

$$\left\{ T_i + \int \rho(\vec{r}') V_{ee}(\vec{r}, \vec{r}') d\vec{r}' + V_{en}(\vec{r}) + V_m + V_{xc}[\rho(\vec{r})] \right\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (2)$$

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where  $\psi$  and  $\epsilon$ , are the one-electron wave-function and eigenvalue respectively,  $\rho$  is the charge density,  $T$ , the one-electron kinetic energy operator, and the potential ( $V$ ) is composed, from left to right, of electron-electron, electron-nucleus, nucleus-nucleus, and exchange-correlation terms. All terms but the many-body exchange correlation potential,  $V_{xc}$ , are readily evaluated - the remaining potential terms are simply Coulomb potentials. Because the exact exchange correlation potential is unknown, the solution is necessarily approximate. However, simple approximations to this term have proved very successful. The most widely used, the Local Spin Density Approximation (LSDA) [von Barth and Hedin, 1972] uses information about the charge density at every point to approximate the local value of the exchange correlation terms. Recently, a new approach, the Generalized Gradient Approximation (GGA), has been developed which takes into account not only the local charge density but also includes terms up to 6th order in the charge density gradient [Perdew *et al.*, 1992]. The advance represented by the GGA is particularly important in the case of iron, as it correctly recovers the ferromagnetic bcc structure as the global ground state [Bagno *et al.*, 1989]. For the energetics of the tetragonally strained lattice, we consider both approximations.

The equations (1-2) are solved with the LAPW method [Wei and Krakauer, 1985]. This is an all electron method - all core and valence electrons are fully included - which makes no approximations to the shape of the charge density or the potential. There are no approximations to the nature of bonding (ionic, covalent, metallic). Within the LSDA or GGA, essentially fully converged solutions of the Khon-Sham equations are achieved. The details of the calculations for iron are discussed in Stixrude *et al.* [1994]. Briefly, we include 100-200 LAPW basis functions per atom and sample the Brillouin zone on a  $16 \times 16 \times 16$  special  $k$ -point mesh for hcp, bcc and fcc calculations while a  $12 \times 12 \times 12$  mesh is used for tetragonally strained calculations. Total energies are converged to better than a few tenths of a mRy. Hcp and fcc calculations are non-magnetic, bcc and tetragonal calculations are ferromagnetic.

## Results

We have previously shown [Stixrude *et al.*, 1994] that the GGA approximation yields excellent agreement with experimental observations of 1) the equation of state of iron from 0 to 300 GPa (maximum deviation less than 1% above 100 GPa) corresponding to a more than two-fold range of compression 2) the pressure of the bcc-hcp phase transition (11 GPa theoretical vs. 10-15 GPa experimental) 3) the minimum energy  $c/a$  ratio of the hcp structure (1.58-1.59 increasing slightly with pressure) and 4) the zero pressure magnetic moment of the bcc phase.

Both GGA and LSDA calculations predict the hcp phase to be the equilibrium structure at low temperatures everywhere above 11 GPa. This is illustrated in Fig. 1 where GGA total enthalpies of fcc and bcc phases relative to the hcp phase are shown as a function of pressure. Hcp and fcc phases have similar total enthalpies over the entire volume range. A determination of their relative stability at inner core conditions is beyond the scope of the present calculations which are athermal (zero temperature) and will require a careful treatment of the thermal contributions to their respective free energies. The bcc phase however, has an enthalpy much higher than either fcc or hcp phases at high pressures. The energy required to

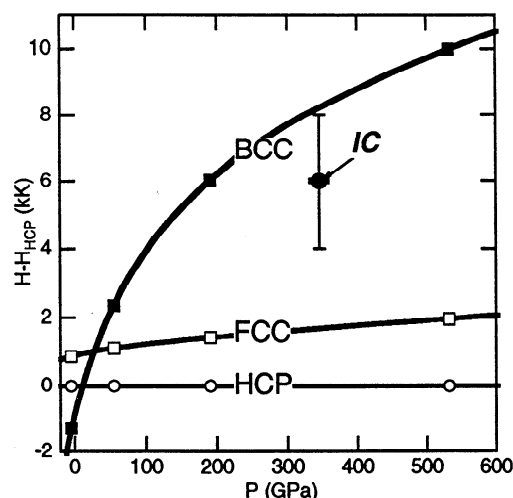
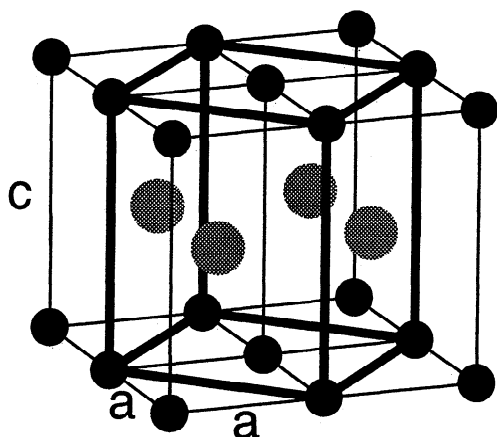


Figure 1. Total enthalpy per atom of bcc (solid squares) and fcc (open squares) structures relative to that of hcp (open circles) in the GGA approximation calculated with the LAPW method. Relative enthalpies are expressed as  $\Delta H/k_B$  giving temperature in units of Kelvin. The conditions of the inner core (solid circle) are indicated by its seismologically determined pressure range (horizontal bar) and its estimated temperature (error bar). The comparison of the bcc-hcp enthalpy difference with inner core temperatures indicates thermodynamic instability of bcc (see text). Total energy differences are converged to better than a few tenths of a mRy ( $\approx 50$  K).

transform hcp to bcc at inner core pressures exceeds the highest estimates of the thermal energy available in the inner core. For bcc to be stable, its molar entropy must exceed that of hcp by approximately  $1.4R$ , where  $R$  is the gas constant. This value exceeds typical high pressure entropies of melting [Stishov, 1969] and is larger than the sum of estimated magnetic, electronic and vibrational contributions to the bcc-hcp entropy difference [Sherman, 1994]. These results make the bcc phase an unlikely constituent of the inner core.

The bcc phase is not only energetically unfavorable but mechanically unstable. We have found that the bcc phase is elastically unstable with respect to a tetragonal strain at high pressure [Stixrude *et al.*, 1994]. The body-centered tetragonal structure is shown in Fig. 2. It relates the bcc structure ( $c/a=1$ ) to the fcc structure ( $c/a=\sqrt{2}$ ). The change in energy produced by this strain is related to the combination of elastic constants  $C_{11}-C_{12}$  which is positive for stable crystal structures.

Both bcc and fcc phases are found to be elastically stable at low pressure in both GGA and LSDA approximations, in agreement with experiment (Fig. 3). Fcc displays normal behavior as the density increases: the energy changes more rapidly with strain at high density, corresponding to a pressure induced increase in  $C_{11}-C_{12}$ . The bcc structure, however, displays the opposite behavior, the strain-induced energy change becomes smaller as the density increases. The bcc lattice becomes mechanically unstable at a volume between 50 and 60 Bohr<sup>3</sup> ( $P=85-220$  GPa), i.e. beginning at pressures much smaller than those of the inner core. The total energy of the bcc lattice decreases as the tetragonal strain is applied;  $C_{11}-C_{12}<0$  so that the lattice is mechanically unstable and will spontaneously distort to the fcc structure.



**Figure 2.** The body-centered tetragonal structure. Four body-centered unit cells are shown (light lines) The face-centered unit cell is shown in bold lines. The shaded atoms can be regarded as either body-centered or face-centered. The bcc structure corresponds to  $c/a=1$ ; the fcc structure to  $c/a=\sqrt{2}$ .

## Discussion

Previous results that argued for the stability of the bcc phase at inner core conditions were based on either pair potential parameterizations of the total energy or extrapolation of experimental thermodynamic properties [Ross *et al.*, 1990; Matsui, 1994; Bassett & Weathers, 1990]. The fact that our calculations disagree with these approximate treatments indicates on the one hand the importance of many body terms in iron-iron interactions in the solid state, and, on the other, the existence of higher order terms in the volume dependence of the thermodynamic properties of bcc iron which are not probed by existing data. Neither of these inferences are surprising. Many body terms are well known to be important in understanding the relative stability of transition metal structures [e.g. Carlsson, 1990]. In the case of thermodynamic extrapolation, the existence of higher order terms are expected because the pressure-temperature regime over which the bcc phase is experimentally accessible is small compared with inner core pressures and temperatures.

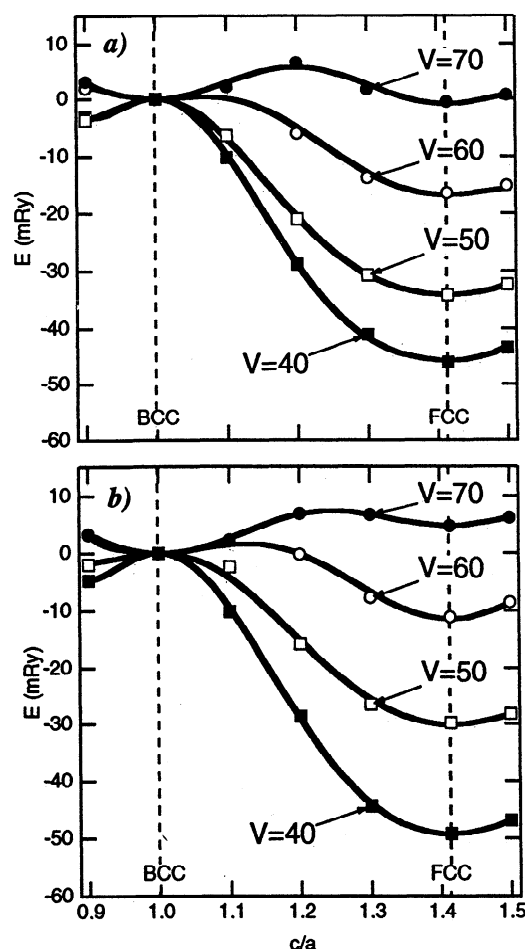
Two factors which could in principle restabilize the bcc structure, but which are unlikely to, are temperature and the presence of an alloying constituent in the inner core. Zirconium is an example of a material in which the bcc structure is quasiharmonically unstable but restabilized by high temperature anharmonic effects. However, the instability in bcc iron is qualitatively different from that observed in Zr, where only a portion of one phonon branch is quasiharmonically imaginary and  $C_{11}-C_{12}$  remains positive [Willaime & Massobrio, 1989]. In the case of iron the magnitude of the instability is large: at inner core pressures, the strain energy associated with a small change in  $c/a$  is comparable in magnitude to that of the stable bcc lattice at zero pressure. The small amount of light element (e.g. O, S, Si) permitted in the inner core by seismological data [Jephcoat and Olson, 1987] is also unlikely to overcome the energetically substantial effect of mechanical instability found here.

High pressure phase transitions in iron represent an important test of experimental techniques which are used to address the melting curve of iron. The bcc phase is a highly unlikely

candidate for participation in phase transitions recently observed experimentally in the 150 GPa range [Boehler, 1993; Saxena *et al.*, 1993]. Assuming these phase transitions are confirmed by structural measurements, they must involve either the fcc or hcp phases of iron, or some as yet unobserved new phase. If a new phase of iron exists, it is not likely to be body-centered tetragonal. We find no local minima in the dependence of the energy on tetragonal strain (Fig. 3) which would suggest the existence of such a phase at any pressure.

## Conclusions

State of the art density functional calculations are a powerful way of predicting the behavior of materials high pressures. These methods are completely independent of experimental data and thus represent the ideal complement to high pressure laboratory approaches. We have used the LAPW method to



**Figure 3.** Total energy as a function of  $c/a$  ratio for the tetragonal structure shown in Fig. 2 at four different atomic volumes (indicated in units of Bohr<sup>3</sup>).  $V=70$  a.u. is similar to the GGA zero pressure volume of fcc [Stixrude *et al.*, 1994];  $V=48$  a.u. is the atomic volume of iron corresponding to the mean density of the inner core. a) LSDA approximation b) GGA approximation. The lines are polynomial fits to guide the eye. At high pressure ( $V < 60$  Bohr<sup>3</sup>), the energy of bcc is lowered by small changes in the  $c/a$  ratio, i.e. the structure is elastically unstable and will spontaneously distort to fcc.

show that the close-packed structures of iron (fcc and hcp) have similar energies throughout the pressure regime of the earth while the bcc phase is highly unfavorable energetically at core pressures. We predict a mechanical instability with respect to a tetragonal strain in the bcc phase which makes this structure highly unlikely to exist in the earth's core.

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