Volume 268, Issues 3–4 30 April 2008 ISSN 0012-821X

ELSEVIER

EARTH
& PLANETARY
SCIENCE LETTERS

Available online at www.sciencedirect.com

ScienceDirect

Earth and Planetary Science Letters 268 (2008) 444–449

EPSL

www.elsevier.com/locate/epsl

Ab initio calculations on the free energy and high *P*–*T* elasticity of face-centred-cubic iron

Lidunka Vočadlo [a,]*, Ian G. Wood [a], Dario Alfè [a,b,c], G.D. Price [a]

[a] *Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK*
[b] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*
[c] *London Centre for Nanotechnology, 17-19 Gordon Street, London WC1H 0AH, UK*

Received 31 October 2007; received in revised form 18 December 2007; accepted 22 January 2008
Available online 16 February 2008
Editor: R.D. van der Hilst

Abstract

Ab initio finite temperature molecular dynamics simulations have been used to calculate the free energy and elasticity of face-centred cubic (fcc) iron at a state point representative of the Earth's inner core. Whilst the free energy of this phase is found to be higher than that of hexagonal-close-packed (hcp) iron, the difference is only 14 meV/atom. It is possible that this difference might be overcome by the presence of light elements, as previous calculations at zero Kelvin have shown that the addition of elements such as silicon stabilise fcc-Fe with respect to hcp-Fe by at least 40 meV/atom. The calculated elastic constants at core pressures and temperatures of pure fcc-Fe, and of alloys of Fe with sulphur and nickel (Fe_3S and Fe_3Ni) derived from the fcc structure, lead to average shear wave velocities that are considerably higher than those inferred from seismology; however, these mineralogical and seismological results could be reconciled by the presence of partial melt in the inner core. The calculated P-wave anisotropy of fcc-Fe is comparable with the seismological values, but only if there is a high degree of crystal alignment, although the necessity for alignment can be reduced if a layered model for the inner core is invoked. The results presented in this paper therefore suggest that fcc-Fe cannot be ruled out as a candidate for the dominant phase of the Earth's inner core.

Keywords: inner core; phase of iron; ab initio calculations; free energy; elasticity; iron alloys

---

1. Introduction

It is generally assumed that the Earth's inner core is made of iron alloyed with ~5 wt.% nickel and a few percent light elements such as sulphur or silicon (Birch, 1964), yet the structural state of iron in the Earth's inner core is still unknown. Until recently the hexagonal-close-packed (hcp) phase of iron has been favoured because experiments have shown it to be the stable phase at relatively modest pressure and temperature conditions (e.g., Nguyen and Holmes, 2004) and theoretical calculations from both quasi-harmonic lattice dynamics (Vočadlo et al., 2000) and finite temperature molecular dynamics (Vočadlo et al., 2003a,b,) have shown it to have the lowest free energy at core conditions with respect to other candidate phases. However, the free energy difference between hcp-Fe and the body-centred-cubic (bcc) phase of iron is very small (~35 meV) when compared to the thermal energy at core conditions (~500 meV) and so it is plausible that this difference might be overcome by the presence of alloying elements. It has been shown both experimentally (Lin et al., 2002a) and theoretically (Vočadlo et al., 2003a,b; Côté et al., 2008, in press) that the presence of light elements stabilises bcc-structured phases with respect to hcp-structured phases and, on the basis of these results, evidence has recently been mounting for an inner core made predominantly of iron in the bcc structure. However, very recently, calculations at core pressures and temperatures of the elasticity of the hcp and bcc phases of iron, together with the light element end members, FeS and FeSi (Vočadlo, 2007),

---

* Corresponding author.
E-mail address: l.vocadlo@ucl.ac.uk (L. Vočadlo).

0012-821X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2008.01.043

showed that while the predicted compressional wave velocities were in excellent agreement with those extrapolated from experiments (Badro et al., 2007), the shear wave velocities of all of the phases studied were significantly higher than those inferred from seismology. Indeed, Vočadlo (2007) suggested that the mineralogical model could only match the seismic model if the inner core was partially molten, containing ~8% liquid.

Another possible explanation for the discrepancy between the observed shear wave velocities and those predicted from calculations is that the structural state of the inner core is a different phase from those previously studied and, in view of the factors discussed with regard to the relative stability of the hcp and bcc phases, it is logical to investigate also the face-centred cubic (fcc) phase of iron. Although naive arguments might suggest the fcc structure to be a likely candidate (being the closest packed structure of highest symmetry), it has, until now, received little attention. The fcc phase is a particularly attractive candidate as experiments show that nickel crystallises in the fcc structure and stabilises fcc-Fe–Ni alloys relative to pure Fe (e.g., Huang et al., 1988, 1992; Lin et al., 2002b; Mao et al., 2006); furthermore, both Lin et al. (2002b) and Mao et al. (2006) have found regions of fcc and hcp phase coexistence in Fe–Ni alloys at high pressures and temperatures. In order to establish whether the fcc phase is a viable candidate for the structure of iron in the inner core, we present here the first ab initio calculations performed at inner core conditions to obtain both the free energy and elastic properties of fcc-Fe, Fe_3Ni and Fe_3S for comparison both with previous calculations and with seismological observations.

2. Calculation methodology

The calculations presented here are based on Density Functional Theory (DFT) (Hohenberg and Kohn, 1964) within the Generalised Gradient Approximation (Wang and Perdew, 1991) implemented in the code VASP (Kresse and Furthmüller, 1996), with the Projected Augmented Wave method (Blöchl, 1994) used to calculate the total energy of each system The main advantage of this code is that the ab initio energy of the system can be combined with molecular dynamics methods to simulate simultaneously the high pressure and temperature properties of iron. In ab initio molecular dynamics, the ions in the system are treated as classical particles and, for each set of atomic positions, the electronic energy and forces on the ions are calculated, within the DFT approximation, which includes the thermal excitations of the electrons. The calculations were performed without spin polarisation as fcc iron has no magnetic moment at the pressures and temperatures of the inner core.

2.1. Free energy calculations

The free energy of the fcc phase was obtained using the method of thermodynamic integration which allows us to calculate the difference in free energy, $F-F_0$, between our ab initio fcc system and a reference system whose potential energies are U_1 and U_0 respectively. Adopting the dynamical method described by Watanabe and Reinhardt (1990), a mixing parameter λ, which depends on time, is slowly (adiabatically) switched from 0 to 1 during a single simulation. The switching rate has to be slow enough so that the system remains in thermodynamic equilibrium and adiabatically transforms from the reference system to the ab initio system. The change in free energy is then given by:

$$\Delta F = \int_0^T dt \frac{d\lambda}{dt}(U_1 - U_0) \qquad (1)$$

where T is the total simulation time; $\lambda(t)$ is an arbitrary function of t with the property of being continuous and differentiable for $0<t<1$, $\lambda(0)=0$, and $\lambda(T)=1$.

We have successfully used this method to calculate ab initio the melting behaviour of iron (Alfè et al., 1999) and aluminium (Vočadlo and Alfe, 2002) as a function of pressure, and have also reported results for the free energies of bcc and hcp-Fe at core conditions (Vočadlo et al., 2003a,b). Following the methodology described previously (Alfè et al., 1999, 2001; Vočadlo and Alfe, 2002; Vočadlo et al., 2003a,b) we use as a reference system a simple inverse power potential which takes the form $U=4\varepsilon(\Gamma/r)^{\alpha}$, where $\varepsilon=1$ eV, $\Gamma=1.77$ Å and $\alpha=5.86$. The final result is totally independent of the choice of reference system, but it is desirable to choose a reference system as close to the ab initio system as possible in order to maximise the efficiency of the calculation. To be directly comparable to the free energy calculations presented before (Vočadlo et al., 2003a,b) the present calculations were performed on a 64 atom supercell ($4\times4\times4$ primitive cells) with a $3\times3\times3$ k-point grid with a volume of 7.2 Å^3 per atom and at a temperature of 6000 K. The error in free energies is calculated to be <10 meV per atom.

2.2. Elasticity calculations

The elasticity calculations were performed with 1 k-point in the Brillouin zone on a 108-atom supercell of fcc-Fe, Fe_3Ni and Fe_3S; the Fe_3Ni and Fe_3S structures were produced by substituting Ni/S for the Fe atom at 0,0,0 in the fcc cubic subcell, leading to a primitive cubic structure. For fcc-Fe and Fe_3Ni the unit cell volumes were chosen so that the calculations were performed at a density of 13,155 kg m^{-3} so as to be directly comparable with the results presented previously for hcp and bcc Fe (Vočadlo, 2007). Similarly, in all cases a temperature of 5500 K was used to ensure comparability with previous results for hcp-Fe, bcc-Fe, FeS and FeSi (Vočadlo, 2007). The elastic constants were determined from the calculated equilibrated stresses associated with strains applied to the supercells. To obtain the three non-zero elastic constants of the cubic cells (namely, c_{11}, c_{12} and c_{44}) the deformation matrix shown below was applied with distortions, δ, of ±2% and ±4%:

$$\begin{pmatrix} 1+\delta & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Simulation times of ~7.5 ps were used, allowing (after equilibration) a statistical analysis over 5–6 ps. Using the time averaged stresses from the calculations, the elastic constants were then obtained by the standard relations $\sigma_{ij}=c_{ijkl}\varepsilon_{kl}$. From these elastic constants it is straightforward to determine the isothermal incompressibility, K_T, for a polycrystalline aggregate by using the Voigt average for a cubic crystal, given by:

$$K_T = \frac{c_{11} + 2c_{12}}{3}$$

The adiabatic incompressibility can then be obtained from:

$$K_\mathrm{S} = K_T(1 + \alpha\gamma T)$$

The necessary values of the volumetric thermal expansion coefficient and of the Grüneisen parameter were taken from earlier calculations on the hcp phase of iron (Vočadlo et al., 2003b: $\alpha=1\times10^{-5}$ K^{-1} and $\gamma=1.5$).

The Voigt average for the shear modulus of the cubic system is given by:

$$G = \frac{c_{11} - c_{12} + 3c_{44}}{5}$$

The P-wave velocity, V_P, shear wave velocity, V_S, and bulk sound velocity, V_Φ, are then readily obtained from standard relations.

3. Results

The free energies for the hcp and bcc phases of Fe (at a density of 13,155 kg m^{-3} and a temperature of 5500 K) calculated previously (Vočadlo et al., 2003a,b) are $F_\mathrm{hcp}=-10.668$ eV, $F_\mathrm{bcc}=-10.633$ eV; thus, $\Delta F_\mathrm{bcc-hcp}=35$ meV. For the fcc phase of Fe the calculations in the present work result in $F_\mathrm{fcc}=-10.654$ eV and therefore $\Delta F_\mathrm{fcc-hcp}=14$ meV. While it is clear, therefore, that the hcp phase remains the most stable structure in an inner core made of *pure* iron, the free energy difference between this and the other two phases is very small. Through calculations at zero Kelvin, Vočadlo et al. (2003a,b) and Côté et al. (2008, in press) have already suggested that the free energy difference between hcp and bcc iron could be overcome with the addition of light elements such as silicon; the free energy difference between hcp and fcc iron is even smaller. Indeed, very recently, indicative calculations at zero K (Côté, 2007) at the same volume (7.2 Å^3 per atom) have shown that the addition of 8 at.% silicon to the fcc phase increases its stability with respect to the hcp phase by 40 meV per atom, an amount almost three times greater than that required to overcome the free energy difference at core conditions.

The calculated elastic properties for the fcc phase of iron are shown in Table 1 together with those at high density and the same temperature for the bcc-Fe, hcp-Fe, FeS and FeSi phases calculated previously (Vočadlo, 2007). Since we know that the Earth's inner core contains some nickel as well as light elements, we have also calculated the elastic properties of $\mathrm{Fe_3Ni}$ and $\mathrm{Fe_3S}$, both of which have topologically equivalent structures to fcc-Fe. For comparison with these mineralogical results, selected values of V_P and V_S from PREM (Dziewonski and Anderson, 1981) are also shown in the table. It is clear that for all phases studied, the calculated average shear wave velocities are considerably higher than the seismologically determined values. There are a number of mechanisms by which the mineralogical and seismological results might be reconciled. Firstly, in an earlier paper (Vočadlo, 2007), the effects of anelasticity were considered but it was shown that this should result in a decrease in the shear wave velocity of only 0.5–1.5%, much less than that required; a similar reduction would obtain here. Secondly, there is evidence from laboratory work on olivine which suggests that grain size may be an important factor in determining seismic velocity; it was found that reduction in grain size reduced the shear wave velocity (Faul and Jackson, 2005). However, ab initio calculations on mantle phases (e.g. Oganov et al., 2001) do not show large discrepancies between the predicted velocities and those from seismic reference models. If grain size was a large factor, it might be expected that its effect should be even more apparent in the mantle. The fact that we do not see this therefore suggests that this mechanism cannot be invoked for the shear wave velocity disparity seen in the core. Thirdly, it has been suggested previously that the discrepancy could be explained by melt pockets in the inner core (Vočadlo, 2007). The amount of melt can be estimated by taking the Hashin–Shtrikman bound for the effective shear

Table 1

Isothermal (*adiabatic*) elastic constants and sound velocities of fcc-Fe (this work), hcp-Fe and bcc-Fe (Vočadlo, 2007), together with those of $\mathrm{Fe_3S}$, $\mathrm{Fe_3Ni}$ (this work), FeSi and FeS (Vočadlo, 2007); also shown are values taken from PREM at the core–mantle boundary and at the centre of the inner core (Dziewonski and Anderson, 1981)

	ρ (kg m^{-3})	T (K)	c_{11} GPa	c_{12} GPa	c_{44} GPa	c_{23} GPa	c_{33} GPa	V_P km s^{-1}	V_S km s^{-1}
fcc	13155	5500	1397 (*1499*)	1247 (*1349*)	423			11.64	4.64
hcp	13155	5500	1631 (*1730*)	1232 (*1331*)	159	983 (*1074*)	1559 (*1642*)	11.14	4.01
bcc	13155	5500	1505 (*1603*)	1160 (*1258*)	256			11.29	4.11
FeSi	10212	5500	1643 (*1732*)	1030 (*1119*)	462			13.53	6.26
FeS	10353	5500	1294 (*1371*)	1050 (*1127*)	257			12.02	4.43
$\mathrm{Fe_3S}$	12097	5500	1377 (*1478*)	1281 (*1382*)	321			11.87	4.18
$\mathrm{Fe_3Ni}$	13155	5500	1296 (*1386*)	1175 (*1265*)	406			11.28	4.51
PREM	12760							11.02	3.5
	13090							11.26	3.67

To obtain the adiabatic elastic constants, the isothermal elastic stiffnesses (c_{ij}) were first converted into isothermal compliances (s_{ij}) and then transformed into adiabatic compliances (as described in Nye, 1985) using a linear thermal expansion coefficient of $(1/3)\times10^{-5}$ K^{-1} and a heat capacity of 5 $\mathrm{k_B}$/atom (Vočadlo et al., 2003b); these compliances were then transformed back into elastic stiffnesses. Uncertainties in V_P and V_S are ~1%.

modulus of two-phase media (Hashin and Shtrikman, 1963); in Vočadlo (2007) the minimum amount of melt in the inner core for either an hcp or bcc-structured phase was estimated to be $\sim$8%. The results from this present work, using a similar analysis, suggest that a much greater melt fraction for fcc-Fe (>25%) is required and that the amount of melt is not significantly reduced by the presence of either nickel or sulphur.

In order to be a viable candidate for the inner core phase, the fcc structure must also be consistent with the observed P-wave anisotropy of $\sim$3% (Creager, 1992; Song, 1997; Ouzounis and Creager, 2001). Fig. 1a shows the P-wave velocities, calculated from the elastic constants of fcc-Fe as a function of propagation direction; for comparison, the corresponding figures for bcc-Fe and hcp-Fe are also given in Fig. 1b and c respectively. The equivalent plots for the fcc-derived alloys, Fe$_3$Ni and Fe$_3$S, are very similar to that for pure fcc-Fe, and are therefore not shown. For fcc-Fe, Fe$_3$Ni and Fe$_3$S the maximum P-wave anisotropy is 10–15% (as indicated in Fig. 1a) but this degree of anisotropy cannot be achieved through two mutually perpendicular directions. If it is assumed that the P-wave anisotropy in the Earth's inner core is due to crystal alignment then, by inspection of Fig. 1, we can examine the degree of anisotropy between polar and equatorial directions for different crystal orientations. Fig. 1a indicates that, for fcc-Fe, the anisotropy will be <1% for crystals aligned along <110>, $\sim$3% for crystals aligned along <111> and as much as 6% for crystals aligned along <100>; for <110> and <100> the anisotropy is such that the velocity along the alignment axis is lower than the average velocity in the plane perpendicular to it. Alignment of fcc-Fe with <111> parallel to the polar axis can, in principle, give values comparable with the observed anisotropy, but would require full crystal alignment in the inner core; alternatively, the observations could be explained by crystals oriented with <100> in the equatorial plane, this arrangement requiring a lesser degree of alignment. It should be noted, however, that for the case in which <111> is aligned parallel to the polar axis, an increase in anisotropy, therefore requiring less preferential orientation, can be achieved by assuming the inner core is layered (Ouzounis and Creager, 2001) in such a way that a central, cylindrical (co-axial with the rotation axis) portion of the inner core is aligned. Since the average velocity perpendicular to <111> is faster than the average velocity for randomly oriented crystals, this layering has the effect of reducing the aggregate equatorial velocity, whilst keeping the polar velocity the same (and hence increasing the anisotropy); in the case in which <100> lies in the equatorial plane, the opposite is true and the anisotropy would be reduced. For comparison with the results for fcc-Fe, we note that for bcc-Fe (Fig. 1b) the P-wave anisotropy is similar in form but smaller in magnitude; the maximum anisotropy that can be achieved through mutually perpendicular directions is never more than $\sim$2%; for the hcp-Fe phase (Fig. 1c) a $\sim$3% anisotropy can be achieved through mutually perpendicular directions whereby, for the polar P-wave velocity to be faster, the *c*-axis of the crystals would lie in the Earth's equatorial plane. Thus, for the bcc phase of iron, the observed seismic anisotropy in the Earth's inner core cannot be achieved by alignment alone, while for the hcp phase it is just possible to achieve the required degree of anisotropy by alignment but, as for the <111> orientation of fcc-Fe, the degree of alignment required would need to be very high.

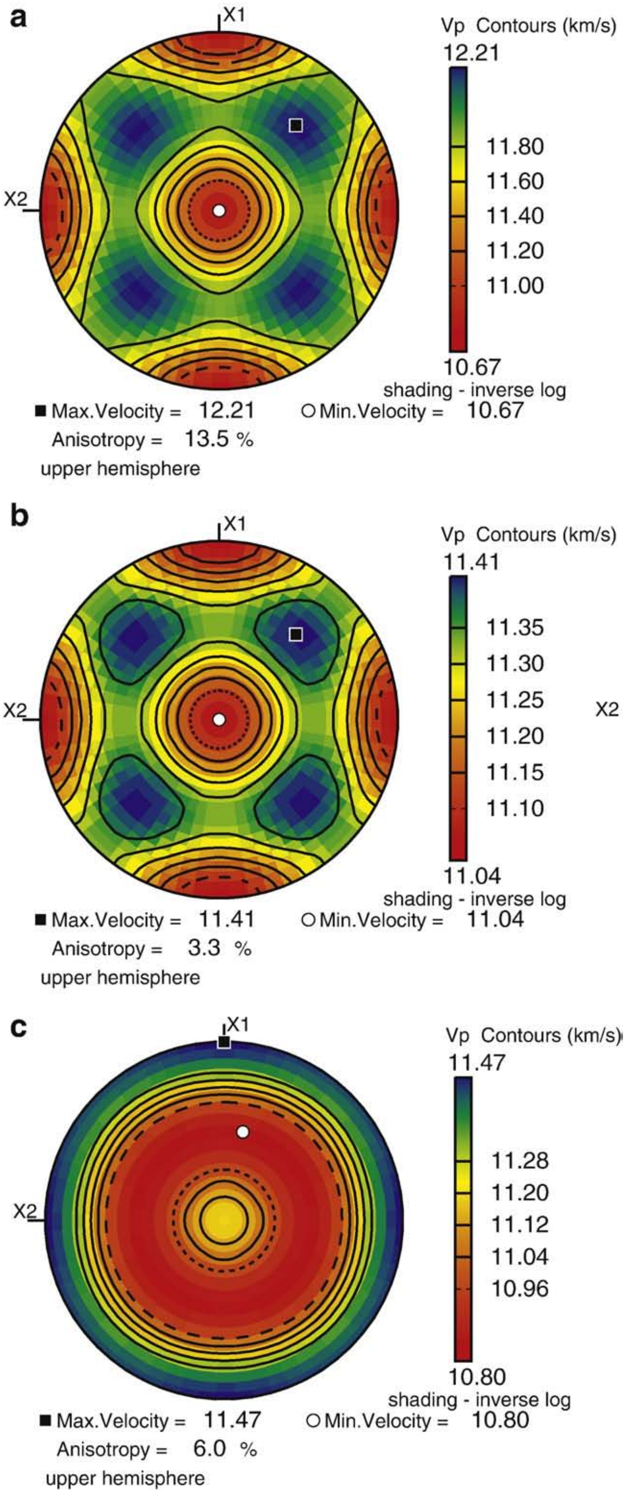

Fig. 1. Single crystal P-wave velocities for a) fcc-Fe, b) bcc-Fe and c) hcp-Fe at inner core conditions as a function of propagation direction. Figure generated by Unicef Careware (Mainprice, 1990).

Finally, any model for the inner core incorporating crystal alignment capable of explaining the observed P-wave anisotropy must also be compatible with the shear wave anisotropy required in seismic models (e.g., Tromp, 1993; Beghein and Trampert, 2003). In Fig. 2 we show the two shear wave velocities (Fig. 2a and b), and the difference between them (Fig. 2c), in fcc-Fe as a function of propagation direction. The degree of shear wave anisotropy shown by fcc-Fe is striking and is much larger than that found for either bcc- or hcp-Fe, both in terms of the difference in wave velocities for a given propagation direction and for the variation of the velocity with direction for a given polarisation. For example, it can be seen from Fig. 2c that for <110> directions the difference in shear wave velocity for the two polarisations is very large, with the anisotropy (defined here by the quantity $2(V_{S1}-V_{S2})/(V_{S1}+V_{S2})$) as high as ~80%. In contrast, the maximum value for this anisotropy is ~20% along <110> for bcc-Fe and the maximum for hcp-Fe is ~26% for directions inclined at ~40° to the *c*-axis (the values for both bcc- and hcp-Fe have been derived from the elastic constants given in Vočadlo, 2007). Similarly, when V_{S1} and V_{S2} are considered separately as a function of propagation direction, their anisotropy values $2(V_{\max}-V_{\min})/(\mathrm{V}_{\max}+\mathrm{V}_{\min})$ are ~35% and ~80% respectively for fcc-Fe, but only ~10% and ~20% for bcc-Fe and ~30% and ~10% for hcp-Fe. However, as discussed above for the case of P-waves, when discussing crystal alignment in the Earth, mutually perpendicular propagation directions must be considered. From the results shown in Fig. 2a and b, we find that for fcc-Fe: (i) the average values of V_{S1} and V_{S2} in the plane perpendicular to <111> are ~40% faster and ~20% slower respectively than the velocity along <111>, and (ii) for<100> alignment, V_{S1} is unchanged while the average value of V_{S2} in the plane perpendicular to <100> is ~30% slower than the velocity along <100>.

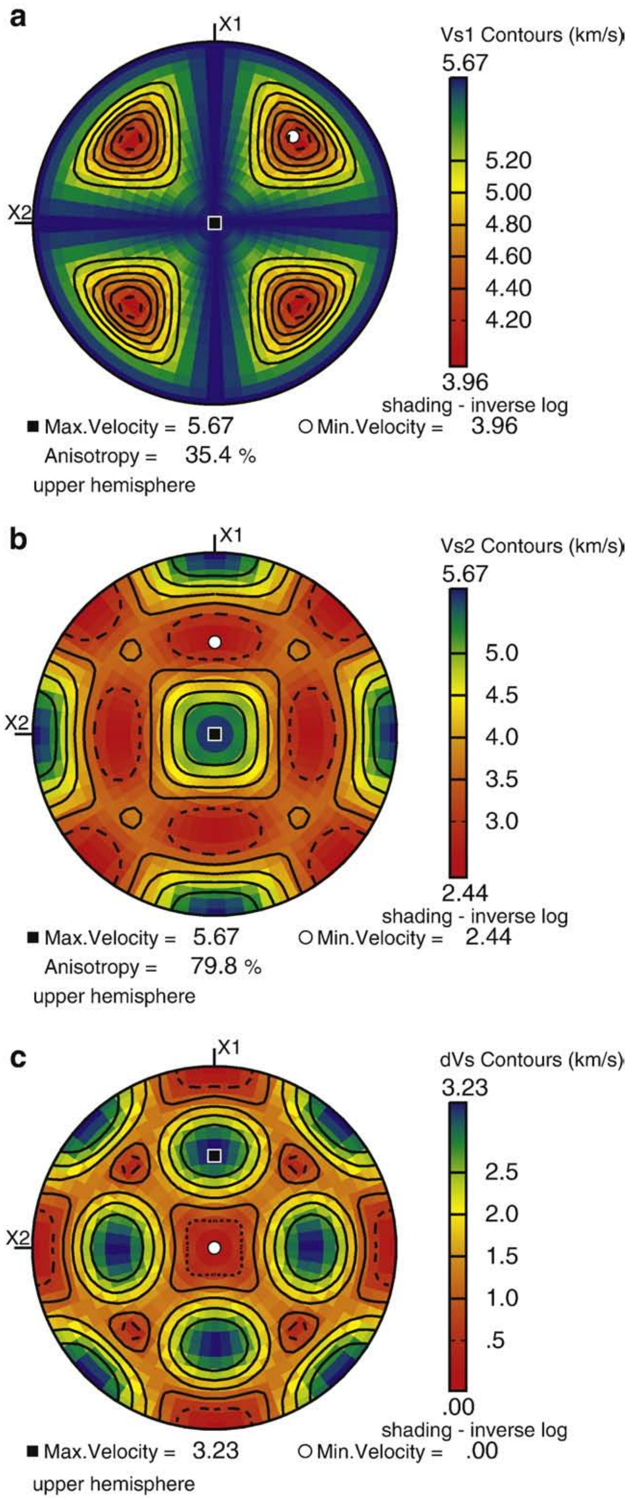

Fig. 2. Single crystal S-wave velocities as a function of propagation direction: a) V_{S1} and b) V_{S2}, together with the difference between them, $\mathrm{d}V_S$ (c). Figure generated by Unicef Careware (Mainprice, 1990).

4. Conclusions

Ab initio finite temperature calculations using the technique of thermodynamic integration to calculate free energies presented both previously (Vočadlo et al., 2003a,b) and here show that the thermodynamically stable phase of pure iron at core conditions is the hexagonal-close packed phase. However, the free energy differences between hcp-Fe and either bcc-Fe or fcc-Fe are very small (35 meV for bcc-Fe and 14 meV for fcc-Fe). Previous calculations performed at zero Kelvin suggest that such small free energy differences could easily be overcome by the addition of light elements (Vočadlo et al., 2003a,b; Côté et al., 2007, 2008, in press). The calculated elastic properties of fcc-Fe, Fe_3Ni and Fe_3S presented here show behaviour similar to that seen for hcp-Fe, bcc-Fe and their alloys (Vočadlo, 2007), namely that the average shear wave velocities are considerably higher than those determined from seismology. One way of reconciling this difference is to invoke a model for the inner core that includes some molten material; however, for fcc-Fe the amount of melt required is considerably greater than for either bcc-Fe or hcp-Fe. Finally, the observed P-wave anisotropy in the inner core could be accounted for if the solid phase were fcc-Fe, provided there was a high degree of crystal alignment or layering present. In conclusion, our results show that the fcc phase of iron should not be ruled out as a viable candidate for the major phase present in the Earth's inner core.

Acknowledgements

LV wishes to thank the Royal Society for their continued support. The work of DA was conducted as part of a EURYI scheme award as provided by EPSRC. This work was first presented at a meeting in honour of Professor David Gubbins' 60th birthday. He may or may not recall that it was presented under a considerably different title.

References

Alfè, D., Gillan, M.J., Price, G.D., 1999. The Melting curve of Iron at Earth's core pressures from ab-initio calculations. Nature 401, 462–464.

Alfè, D., Price, G.D., Gillan, M.J., 2001. Thermodynamics of hexagonal close packed iron under Earth's core conditions. Phys. Rev. B 64 (045123), 1–16.

Badro, J., et al., 2007. Effect of light elements on the sound velocities in solid iron: implications for the composition of Earth's core. Earth Planet. Sci. Lett. 254, 233.

Beghein, C., Trampert, J., 2003. Robust normal mode constraints on inner-core anisotropy from model space search. Science 299, 552–555.

Birch, F., 1964. Density and composition of the mantle and core. J. Geophys. Res. 69, 4377–4388.

Blöchl, P.E., 1994. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979.

Côté AS. 2007 Pers. Comm.

Côté, A.S., Vočadlo, L., Brodholt, J., 2008. Light 372 elements in the core: effects of impurities on the phase diagram of iron. Geophys. Res. Lett. 35, LXXXXX. doi:10.1029/2007GL032788.

Côté, A.S., Vočadlo, L., Brodholt, J., in press. The effect of silicon impurities on the phase diagram of iron and possible implications for the Earth's core structure. J. Chem. Phys.

Creager, K.C., 1992. Anisotropy of the inner core from differential travel times of the phases PKP and PKIKP. Nature 356, 309–314.

Dziewonski, A.M., Anderson, D.L., 1981. Preliminary reference Earth model. Phys. Earth Planet. Int. 25, 297–356.

Faul, U.H., Jackson, I., 2005. The seismological signature of temperature and grain size variations in the upper mantle. Earth Planet. Sci. Lett. 234, 119–134.

Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. Phys. Rev. 136, B864–B871.

Huang, E., Bassett, W.A., Weathers, M.S., 1988. Phase relationships in Fe–Ni alloys at high pressures and temperatures. J. Geophys. Res. 93, 7741.

Huang, E., Bassett, W.A., Weathers, M.S., 1992. Phase diagram and elastic properties of Fe 30% Ni alloy by synchrotron radiation. J. Geophys. Res. 97, 4497.

Hashin, Z., Shtrikman, S., 1963. A variational approach to the theory of the elastic behaviour of multiphase materials. J. Mech. Phys. Solids 11, 127.

Kresse, G., Furthmüller, J., 1996. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186.

Lin, J.F., Heinz, D.L., Campbell, A.J., Devine, J.M., Shen, G.Y., 2002a. Iron–silicon alloy in the Earth's core? Science 295, 313–315.

Lin, J.F., Heinz, D.L., Campbell, A.J., Devine, J.M., Mao, W.L., Shen, G.Y., 2002b. Iron–nickel alloy in the Earth's core. Geophys. Res. Lett. 29, 1471 (art. no.).

Mainprice, D., 1990. A Fortran program to calculate seismic anisotropy from the lattice preferred orientation of minerals. Computers and Gesosciences 16, 385 (ftp://www.gm.univ-montp2.fr/mainprice//CareWare_Unicef_Programs/).

Mao, W., Campbell, A.J., Heinz, D.L., Shen, G., 2006. Phase relations of Fe–Ni alloys at high pressure and temperature. Earth Planet. Sci. Lett. 155, 146–151.

Nguyen, J.H., Holmes, N.C., 2004. Melting of iron at the physical conditions of the Earth's core. Nature 427, 339–342.

Nye, J.F., 1985. Physical Properties of Crystals. Oxford University Press.

Oganov, A.R., Brodholt, J.P., Price, G.D., 2001. The elastic constants of $MgSiO_3$ perovskite at pressures and temperatures of the Earth's mantle. Nature 411, 934–937.

Ouzounis, A., Creager, K.C., 2001. Isotropy overlying anisotropy at the top of the inner core. Geophys. Res. Lett. 28, 4331.

Song, X., 1997. Anisotropy of the Earth's inner core. Rev. Geophys. 35, 297–313.

Tromp, J., 1993. Support for anisotropy of the Earth's inner core from free oscillations. Nature 366, 678–681.

Vočadlo, L., 2007. Ab initio calculations of the elasticity of iron and iron alloys at inner core conditions: evidence for a partially molten inner core. Earth Planet. Sci. Lett. 254, 227.

Vočadlo, L., Alfe, D., 2002. Ab initio melting curve of the fcc phase of aluminium. Phys. Rev. B 65 (214105), 1–12.

Vočadlo, L., Brodholt, J.P., Alfe, D., Gillan, M.J., Price, G.D., 2000. Ab initio free energy calculations on the polymorphs of iron at core conditions. Phys. Earth Planet. Int. 117, 123–137.

Vočadlo, L., Alfe, D., Gillan, M.J., Wood, I.G., Brodholt, J.P., Price, G.D., 2003a. Possible thermal and chemical stabilisation of body-centred-cubic iron in the Earth's core. Nature 424, 536–539.

Vočadlo, L., Alfe, D., Gillan, M.J., Price, G.D., 2003b. The properties of iron under core conditions from first principles calculations. Phys. Earth Planet. Int. 140, 101–125.

Wang, Y., Perdew, J., 1991. Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling. Phys. Rev. B 44, 13298–13307.

Watanabe, M., Reinhardt, W.P., 1990. Direct dynamical calculation of entropy and free energy by adiabatic switching. Phys. Rev. Lett. 65, 3301–3304.