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Earth and Planetary Science Letters 254 (2007) 227–232
EPSL
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Ab initio calculations of the elasticity of iron and iron alloys at inner core conditions: Evidence for a partially molten inner core?

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Received 21 June 2006; received in revised form 29 September 2006; accepted 29 September 2006
Available online 15 November 2006
Editor: R.D. van der Hilst

Abstract

Ab initio finite temperature molecular dynamics simulations have been used to calculate the elasticity of hcp-Fe, bcc-Fe, FeS and FeSi at core conditions. The calculated compressional wave velocities are in excellent agreement with the most recent experimental data. However, the calculated shear wave velocities of all phases studied are significantly higher than those inferred from seismology. This discrepancy can only be explained if the inner core is partially molten containing more than ~8% liquid.

Keywords: iron; iron alloys; Earth's inner core; ab initio calculations; elastic properties

There are many unresolved problems concerning our understanding of the Earth's inner core; even fundamental properties, such as its internal structure and exact composition, are poorly known. Although it is well established that the inner core is made of iron with some alloying element(s) [1], the structural state of the iron and the nature of the light element(s) involved remain controversial [2–4]. Furthermore, seismically observed P-waves show the inner core to be anisotropic and layered [5–7], but the origins of this are not understood; seismically observed S-waves add to the complexity as they have unexpectedly low velocities [8]. Seismic interpretation is hampered by the lack of knowledge of the physical properties of core phases at core conditions. Experimental and theoretical groups have put an enormous effort into obtaining the properties of pure iron at simultaneously elevated pressures and temperatures, but above relatively modest conditions of pressure and temperature much uncertainty still remains [2–4]. Nevertheless, in the past, the general consensus seems to have been that the hexagonal-close-packed (hcp) phase of iron is the most likely stable phase in the inner core. However, this has been recently challenged, with the suggestion that the presence of lighter elements may stabilise a body-centred-cubic (bcc) phase [3,9] at inner core conditions. A fundamental step towards resolving the structure and composition of the Earth's inner core is to obtain the elastic properties of the candidate phases that could be present. Previous work has already suggested that oxygen [10] and carbon [11] are unlikely to be the light element in the inner core, while the presence of hydrogen seems questionable as the quantities needed to produce the required density deficit are improbably high [12]. In this study, therefore, we concentrate on the properties of the two other candidate alloys of sulphur and silicon. From experimental and theoretical work we already know that the shear wave velocities of hcp iron at

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doi:10.1016/j.epsl.2006.09.046

high pressures are significantly higher than those of the inner core as inferred from seismology [13,14]. One of the primary motivations for the present study was to see if results obtained from calculations on the bcc phase of iron and iron alloys could reconcile the differences between theory, observations and the experiments. In this paper we present the very first ab initio molecular dynamics results for the elastic properties, at core conditions, of the bcc and hcp phases of iron, as well as on two end-members of candidate light element-bearing alloys, the CsCl structured phases [15,16] of FeSi and FeS.

It is well established that, at zero Kelvin, ab initio calculations give an acceptably accurate description of all the key properties, including elastic constants, of Fe and its alloys [2,14,17]. The ab initio methodology used in this work is based on density functional theory (DFT) [18] within the generalised gradient approximation (GGA) [19]. The calculations were performed using the VASP [20] code with the projected-augmented wave (PAW) [21] method to calculate the total energy of each system; they were run on the UK high-performance computers (CSAR and HPC-X). 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 and its alloys. 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 with 4 irreducible k-points in the Brillouin zone on a 54-atom (64-atom) supercell of bcc-Fe, FeSi, FeS, (hcp-Fe) atoms, at a range of densities (7000–14,000 kg m^{-3}) and temperatures (1000–6000 K); convergence tests in k-point sampling, cell-size and simulation time were carried out to ensure that the uncertainties in the wave velocities were within 1%. Each system was analysed throughout the simulations to ensure

Table 1
Isothermal (*adiabatic*) elastic constants and sound velocities of hcp-Fe, bcc-Fe, FeSi and FeS at different densities and temperatures, together with values taken from PREM [26]

	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})
hcp	11,628.1	4000	1129 (*1162*)	736 (*769*)	155	625 (*658*)	1208 (*1240*)	9.91	4.15
	13,155	5500	1631 (*1730*)	1232 (*1311*)	159	983 (*1074*)	1559 (*1642*)	11.14	4.01
bcc	11,592.91	750	1100 (*1106*)	712 (*718*)	287			10.11	4.64
	11,592.91	1500	1066 (*1078*)	715 (*727*)	264			9.98	4.44
	11,592.91	2250	1011 (*1029*)	740 (*758*)	250			9.88	4.20
	13,155	5500	1505 (*1603*)	1160 (*1258*)	256			11.29	4.11
	13,842	2000	1920 (*1967*)	1350 (*1397*)	411			12.22	5.1
	13,842	4000	1871 (*1966*)	1337 (*1431*)	167			11.66	3.87
	13,842	6000	1657 (*1795*)	1381 (*1519*)	323			11.83	4.24
FeSi	6969.44	1000	488 (*489*)	213 (*214*)	125			8.32	4.32
	6969.44	2000	425 (*428*)	238 (*241*)	150			8.29	4.28
	8199.34	1000	938 (*842*)	413 (*417*)	263			10.74	5.66
	8199.34	2000	863 (*871*)	431 (*439*)	263			10.58	5.45
	8199.34	3500	788 (*803*)	469 (*484*)	250			10.42	5.11
	10,211.74	5500	1643 (*1732*)	1030 (*1119*)	462			13.53	6.26
	10,402.15	1000	2025 (*2043*)	1007 (*1025*)	625			14.34	7.46
	10,402.15	2000	1909 (*1944*)	1029 (*1064*)	583			14.08	7.11
	10,402.15	3500	1904 (*1972*)	1117 (*1185*)	603			14.36	7.06
	10,402.15	5000	1780 (*1874*)	1132 (*1226*)	563			14.12	6.71
FeS	8587.14	1000	788 (*793*)	531 (*536*)	213			10.03	4.56
	8587.14	2000	763 (*772*)	519 (*528*)	175			9.79	4.23
	10,353	5500	1294 (*1371*)	1050 (*1127*)	257			12.02	4.43
	10,894.13	1000	1513 (*1533*)	1400 (*1420*)	575			13.38	5.81
	10,894.13	2000	1571 (*1613*)	1386 (*1428*)	532			13.43	5.72
	10,894.13	3500	1545 (*1617*)	1360 (*1432*)	492			13.34	5.52
	10,894.13	5000	1558 (*1666*)	1379 (*1487*)	458			13.41	5.34
PREM [26]	12,760							11.02	3.5
	13,090							11.26	3.67

Isothermal elastic constants were converted into compliances and then transformed into adiabatic compliances (using an average thermal expansion of 1×10^{-5} K^{-1} and heat capacity of 5 k_B [17]); these were then transferred back into elastic constants (as described in [31]). Uncertainties in V_P and V_S are ~1%.

that no melting had occurred. The elastic constants were determined from the calculated stresses associated with strains applied to hydrostatically equilibrated supercells. A deformation matrix was applied to enable distortions, δ, of ±2% and ±4% to be applied to each phase, as shown below. Simulation times from 3 ps to 6.5 ps were used, allowing (after equilibration) a statistical analysis over 2.5–6 ps. The deformation matrix required to obtain the three non-zero elastic constants of the cubic cells (namely, c_{11}, c_{12} and c_{44}) is given by:

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

Two deformation matrices are required in order to obtain the five elastic constants of the hexagonal phase, and, for convenience, in order to follow the standard convention for representing the elastic constant tensor [22], the hexagonal structure is represented using a C-centred orthogonal unit cell, as follows:

$$\begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & \sqrt{3} & \delta\sqrt{3} \\ 0 & \delta(c/a) & (c/a) \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \sqrt{3} & 0 \\ 0 & 0 & (c/a)(1+\delta) \end{pmatrix}$$

When calculating elastic constants it is essential that the simulated box is in hydrostatic equilibrium before any strain matrix is applied. Of particular importance is the use of the correct equilibrium c/a ratio in hcp-Fe; indeed, there has been an evolving story in the literature just on this property of iron alone, as it has a significant effect on the nature of the elastic anisotropy [23,24]. In their work on the high-pressure, high-temperature elastic properties of hcp-Fe, Steinle-Neumann et al. [23] reported an unexpectedly large c/a ratio of almost 1.7. However, the work of Gannarelli et al. [24] casts doubt on the robustness of these calculations; they found that the c/a ratio ranges from 1.585 at zero pressure and temperature to 1.62 at 5500 K and 360 GPa. These lower values for the c/a ratio are confirmed in our calculations, and also by [31].

Using the time averaged stresses from the calculations, the elastic constants were obtained by the standard relation $\sigma_{ij}=c_{ijkl}\varepsilon_{kl}$ (Table 1). From the elastic constants it is straightforward to determine the isothermal incompressibility, K_T, for a polycrystalline aggregate by using the Voigt average, which, for the cubic and hexagonal crystals respectively, is given by:

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

$$K_T = (2/9)(c_{11}+c_{12}+2c_{23}+(1/2)c_{33})$$

The use of the Voigt, rather than the Reuss, average is appropriate when calculating seismic wave properties as the former assumes constant strain consistent with the propagation of plane–waves, while the latter is derived under conditions of constant stress; these uses of the averages are discussed further in the final

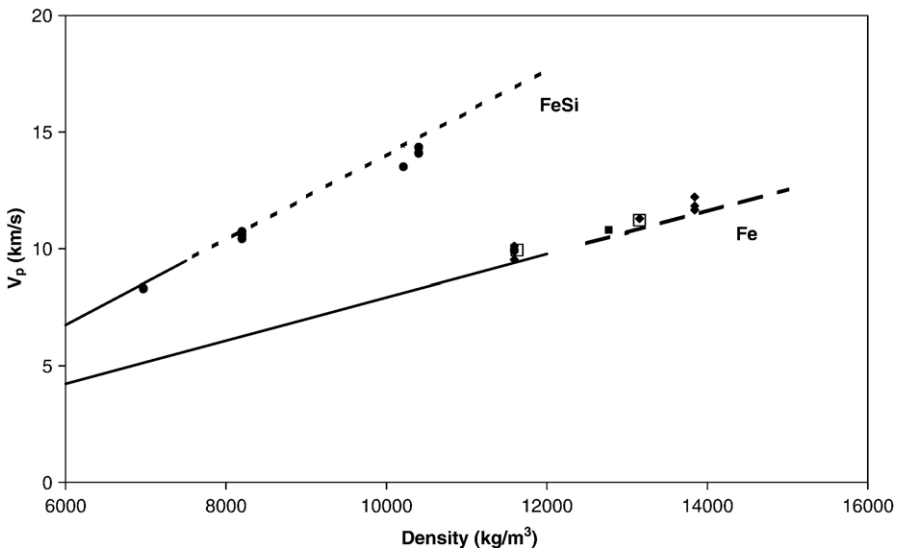

Fig. 1. P-wave velocity as a function of density compared with the high-P ambient-T DAC experiments of Badro et al. [25]. Circles: calculated FeSi-V_p at different temperatures; diamonds: calculated bcc-Fe V_p at different temperatures; squares: calculated hcp-Fe at different temperatures; black filled square: shock datum of Brown and McQueen [32].

paragraph of this paper. The adiabatic incompressibility was obtained from:

$$K_S = K_T(1 + \alpha\gamma T)$$

where the volumetric thermal expansion coefficient $\alpha = 1 \times 10^{-5}$ K^{-1} and the Grüneisen parameter $\gamma = 1.5$ [17].

The Voigt average for the shear modulus of the cubic and hexagonal systems respectively is given by:

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

$$G = \frac{2(c_{11} + c_{33})}{15} - \frac{c_{12} + 2c_{23}}{15} + \frac{3(2c_{44} + (1/2)(c_{11} - c_{12}))}{15}$$

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

In the past, Birch's law has been used to make inferences about the elastic properties of the inner core. Birch's law suggests a linear relationship between V_Φ and ρ, and in the absence of reliable experimental data at very high pressures and temperatures, it has been assumed that this linearity may be extrapolated to the conditions of the inner core. In their very recent work, Badro et al. [25] used inelastic X-ray scattering in a diamond-anvil-cell at high pressures, but ambient temperatures, to demonstrate a linear relationship between V_p and ρ for a number of systems including hcp-Fe and FeSi. Fig. 1 shows the fit to their results extrapolated to core conditions, together with the results from the present work (where the uncertainties lie within the symbols). The agreement is generally outstandingly good; it is noteworthy that the calculated bcc-Fe and hcp-Fe velocity–density systematics are indistinguishable, although this is not so surprising as Birch's Law does not discriminate between different crystal structures. Fig. 2 shows how V_Φ varies with density for both athermal and hot calculations (present work), together with values from PREM [26] and from a previous computational study [23]. It is clear that Birch's Law holds for all the systems studied in the present work, and that the velocities at constant density are almost temperature independent. The calculated elastic constants from the present study are shown in Table 1. At a given density, within the precision of the calculation, they show no significant variation with temperature; similar behaviour has also been found for magnesium silicate perovskite [27].

The calculated P-wave anisotropy for the hcp and bcc phases of Fe at core conditions is ~6% and ~4% respectively, the former being close to the experimentally determined value of 4–5% [13]; for both FeS and FeSi, it is ~6%. The seismically observed anisotropy (3–5% [6]) and layering in the inner core could, therefore, be accounted for by any of the phases studied if the crystals were randomly oriented in the isotropic upper layer and partially aligned in the anisotropic lower layer. The fundamental conclusion of the present work, however, is that, for all candidate core phases, V_S at

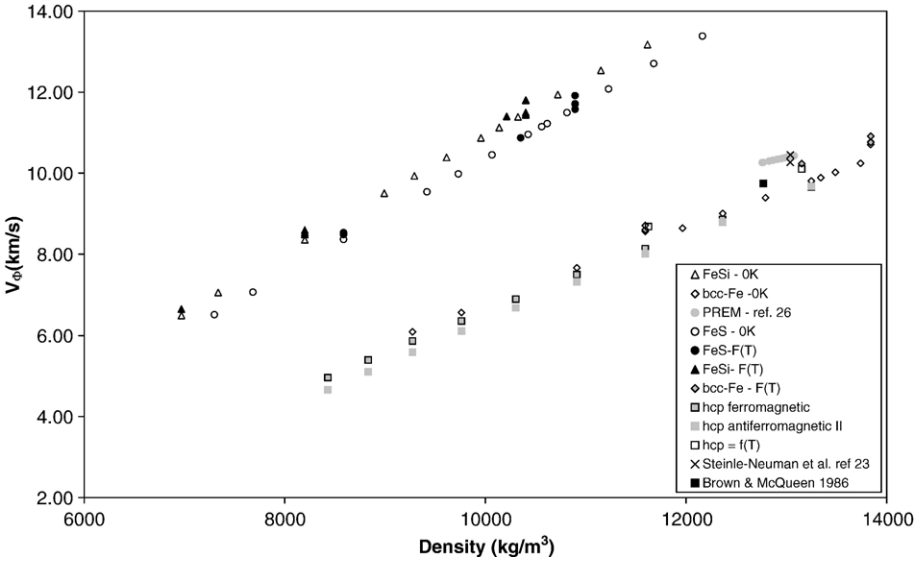

Fig. 2. Bulk sound velocity as a function of density compared with PREM [26].

viable core temperatures (i.e., >5000 K) is more than 10% higher than that inferred from seismology (PREM values between 3.5 and 3.67 km s^{-1} [26]). Table 1 shows that the calculated values of V_S for pure iron phases are >4.0 km s^{-1} (in agreement with inferences drawn from the extrapolation of lower pressure experimental data [13] and also with the value of 4.04 inferred from shock experiments at a density of 12,770 kg m^{-3} [32]), while the effect of light elements is to increase the shear wave velocities to over 5 km s^{-1}. If the uncertainties in the seismological values are well constrained, the difference between these observations and the results from both theory and experiment suggest that a simple model for the inner core based on the commonly assumed phases is wrong.

Firstly, however, it is important to assess whether this difference could be accounted for by anelasticity. The reduction in shear wave velocity due to shear wave attenuation is given by:

$$V(\omega,T) = V_0(T)\left(1-\frac{1}{2}\cot\left(\frac{\pi\alpha}{2}\right)Q^{-1}(\omega,T)\right)$$

Where $V(\omega,T)$ and $V_0(T)$ are the attenuated and unattenuated shear wave velocities respectively, Q is the quality factor and α is the frequency dependence of Q. For the inner core $Q \sim 100$ [28] and $\alpha \sim 0.2$–0.4 [29], which results in a decrease in the shear velocity of only 0.5–1.5%, nowhere near the >10% difference between the seismological observations and the calculated materials properties. It is important to note that the above analysis is necessarily approximate; anelasticity is a very complex issue that requires material data at the conditions of the Earth's inner core in order to draw irrefutable conclusions — clearly such data are unavailable at present.

Another possible explanation for the difference between the observations and the results from both theory and experiment is that parts of the inner core may be partially molten, with solute rich liquid pockets trapped between solid grains. The amount of melt can be estimated by taking the Hashin–Shtrikman bound for the effective shear modulus of two-phase media [30]. In the present study, the shear modulus of the solid phases is greater than 200 GPa in all cases; using this minimum value (i.e., that closest to the seismological result) the minimum amount of melt in the inner core is estimated to be ~8%. Note that use of the Reuss average rather than the Voigt average for the elastic moduli results in melt estimates that are very slightly higher (by 1–2%). These liquid pockets are not necessarily concentrated in the upper part of the inner core; the observed PKJKP waves go right through the centre of the Earth [8] so the difference in V_S between seismology and theory suggest that melt may exist throughout the inner core. However, more detailed models involving liquid inclusions can only be tested when more exact, spatially resolved seismological data become available. Whatever the reason for the discrepancy, having shown that attenuation is likely to be very small (~1%), the current seismological and standard mineralogical models cannot, at present, be reconciled.

Acknowledgements

LV wishes to thank the Royal Society for their continued support. LV also wishes to acknowledge the enormous efforts of Ian Wood, who, despite indispensable input, continues to refuse co-authorship. John Brodholt and David Dobson gave very helpful suggestions to the text. Frederik Simons played the role of the friendly seismologist.

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