The effect of ferromagnetism on the equation of state of Fe$_3$C studied by first-principles calculations

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Abstract

First-principles calculations have been used to determine the equation of state of Fe$_3$C in both its low-pressure magnetically ordered and high-pressure non-magnetically ordered states; at 0 K the ferromagnetic transition was found to occur at about 60 GPa. In the high pressure, non-magnetically ordered regime at 0 K the material may be described by a Birch–Murnaghan third-order equation of state with $V_0 = 8.968(7)$ Å^3 per atom, $K_0 = 316.62(2)$ GPa and $K' = 4.30(2)$. At atmospheric pressure the ferromagnetic phase transition in Fe$_3$C occurs at ~ 483 K; preliminary measurements of the thermal expansion by powder neutron diffraction show that this transition produces a large effect on thermoelastic properties. The volumetric thermal expansion coefficient in the paramagnetic phase was found to be 4.34×10^{-5} K^{-1} at $T \sim 550$ K. By applying a thermal expansion correction to the calculated equation of state at 0 K, predicted values for the density and adiabatic incompressibility of this material at core pressures and temperatures were obtained. These results appear to be sufficiently different from seismological data so as to preclude Fe$_3$C as the major inner core-forming phase.
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1. Introduction

Wood [1] proposed that iron carbide (Fe$_3$C) might be the major phase crystallising to form the Earth's inner core. He based this suggestion on cosmic abundances, thermodynamic calculations and on an equation of state of Fe$_3$C which led to a density at an average inner core pressure (338 GPa) in excellent agreement with the probable range of density determined from seismic data. The equation of state used by Wood [1] was based on values of the incompressibility, K_0, and its first derivative with respect to pressure, K', at ambient pressure and temperature, which he estimated to be 174.0 GPa and 5.1 respectively. Two subsequent measurements of these parameters [2,3], by high-pressure X-ray powder diffrac-

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tion, are in exact agreement with each other and with his estimates ($K = 175 \pm 4$ GPa, $K' = 5.2 \pm 0.3$ and $K = 174 \pm 6$ GPa, $K' = 4.8 \pm 0.8$, respectively). It might, therefore, be considered that the case for Wood's proposal is significantly strengthened by these recent measurements. However, there is, in principle, a significant shortcoming in using these equation of state parameters to determine inner core properties, which we shall demonstrate in this letter, and which we believe may weaken the argument for Fe_3C as the major inner core phase. This weakness arises because the values of K_0 and K' were determined for ferromagnetically ordered Fe_3C, but it is readily apparent from recent thermal expansion measurements (see below) that the physical properties of Fe_3C can be significantly affected by the state of magnetisation. Measurements of incompressibility made on ferromagnetically ordered Fe_3C will therefore not necessarily be representative of the properties of the material under core conditions where high pressures and temperatures will ensure that there will be no magnetic ordering.

The purpose of this letter is three-fold. Firstly, we present preliminary neutron diffraction data to demonstrate the effect of the magnetic phase transition on the thermal expansion of Fe_3C. Secondly, we then use first-principles calculations to determine the magnetic transition pressure and the equations of state in both the magnetically ordered and non-magnetic configurations. Thirdly, we use the results of our first-principles calculations to examine the likelihood of Fe_3C as a major core-forming phase by estimating the expected values of its density and incompressibility under core conditions.

2. The effect of magnetism on thermal expansion

Fe_3C adopts the cementite structure (cohenite in its mineral form); it is orthorhombic, space group Pnma, with $Z = 4$. The structure consists of pleated layers of Fe atoms, derived from an h.c.p. structure, with C atoms occupying interstitial sites [4]. At room pressure and temperature the material is metallic and magnetically ordered [5,6]. The spontaneous magnetisation may be de-

stroyed either by temperature, $T_c = 483$ K [5], or by pressure, $P_c \sim 60$ GPa (see below). Recently, we have carried out a pilot study of the structure of Fe_3C as a function of temperature by time-of-flight neutron powder diffraction using the PO-LARIS diffractometer at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, UK [7]. The sample used was prepared from mixtures of 90 wt% Fe, 10 wt% C, following the procedure of Tsuzuki et al. [6]. The mixtures were pelleted under 50 MPa pressure and packed in pyrex glass capsules which were then loaded into 3/4-inch talc-pyrex piston-cylinder assemblies and sintered at 1.5 GPa and 1200–1250°C for 30 min. Each synthesis experiment yielded approximately 0.85 g of Fe_3C plus a small excess of graphite, which was separated after grinding. Representative diffraction patterns at room temperature (ferromagnetic phase) and 550 K (paramagnetic phase) are shown in Fig. 1. Unit cell dimensions were obtained by simultaneous Rietveld refinement of the data from all three detector banks on the POLARIS instrument using the program GSAS [8]. Graphite and iron impurities, where present in the sample, were also included in the refinement model. Fig. 2 shows how the cell volume of Fe_3C varies with temperature between 300 and 650 K. Even with the relatively low resolution of the POLARIS diffractometer, it is clear that the magnetic transition at ~ 483 K greatly affects the thermal expansion coefficient of the material. There is no a priori reason to suppose that other physical properties will not be similarly affected by the state of magnetisation. In particular, the question of whether the application of pressure produces commensurately large changes in K_0 and K' needs to be addressed. First-principles calculations provide an excellent tool with which to investigate this aspect of the material's behaviour since the pressure required to destroy magnetic order is expected to be sufficiently high to make experimentation extremely difficult.

In the remaining sections of this letter, we present the results of first-principles pseudopotential calculations on Fe_3C in both the magnetically ordered and non-magnetic states. We find that there is indeed a significant difference in the elastic properties of the non-magnetic and ferromag-
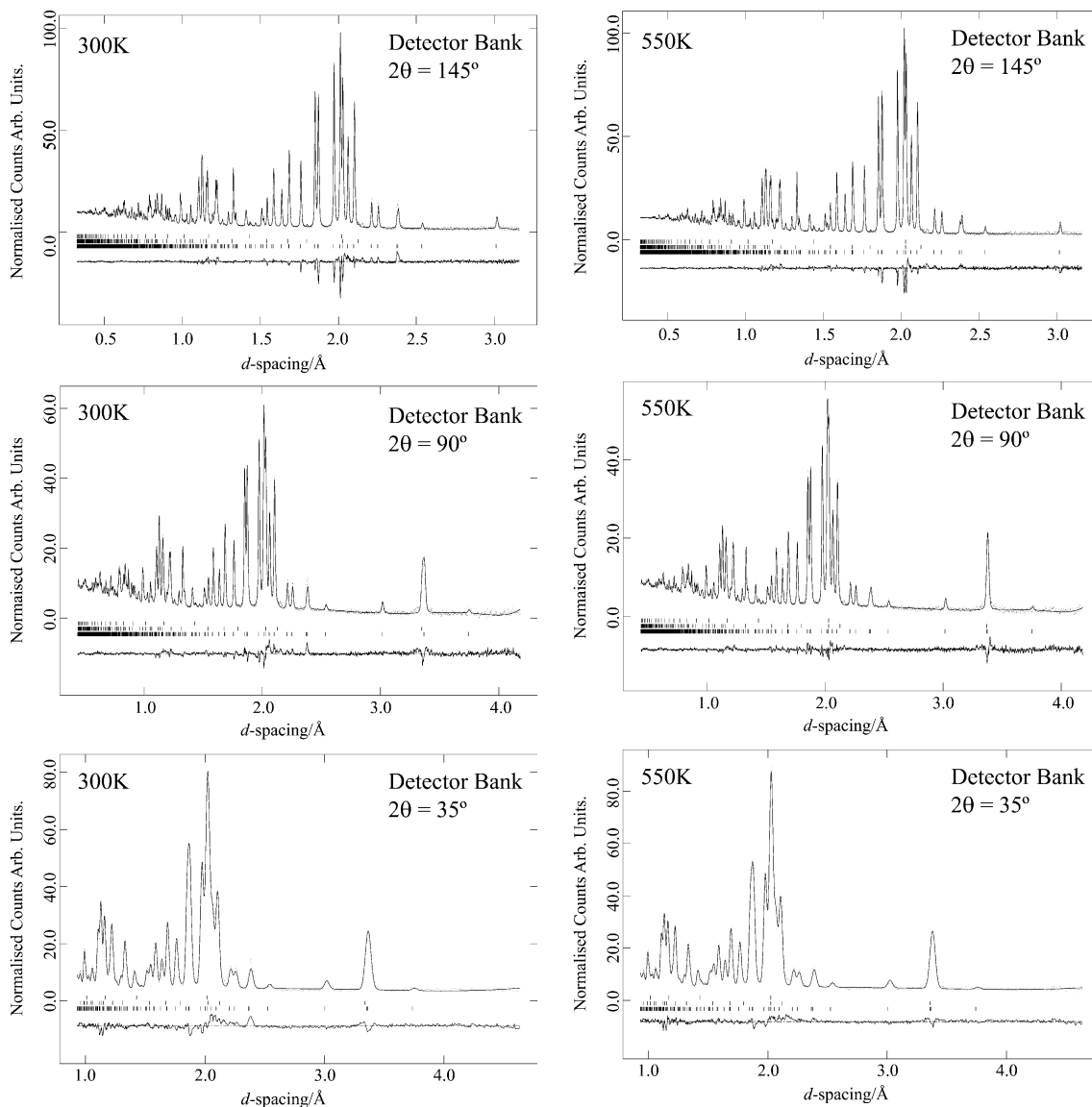
Fig. 1. Neutron powder diffraction patterns of Fe_3C at 300 and 550 K (ferromagnetic and paramagnetic phases respectively). Experimental data are shown as points, the line giving the calculated pattern from the Rietveld refinement. The lower trace shows the difference between the observed and calculated values, and the tick marks (from bottom to top) give the expected positions of the Bragg reflections from Fe_3C, C (graphite) and Fe. The 2θ values shown (35°, 90° and 145°) refer to the 'low', '90°' and 'high' angle detector banks respectively.

netic material. We then apply a thermal expansion correction to the 0 K equation of state and calculate density and incompressibility values for a range of pressures and temperatures to re-examine Wood's suggestion [1] that the properties of Fe_3C are consistent with those observed for the Earth's inner core.

3. Computational methodology

First-principles calculations now provide a well-established methodology for the accurate prediction of thermoelastic properties of materials well beyond the pressures achieved by experimentation. The calculations presented here are based
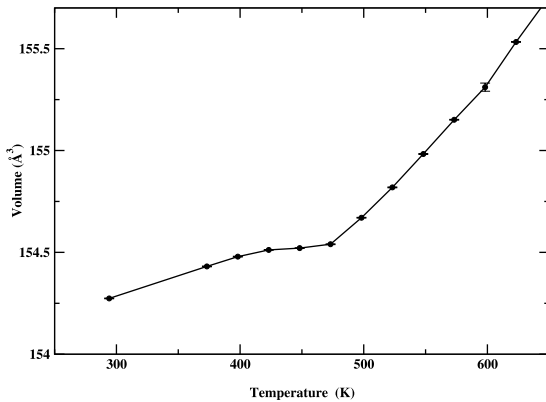
Fig. 2. Unit cell volume of Fe_3C as a function of temperature, obtained by time-of-flight neutron powder diffraction with the POLARIS diffractometer at the ISIS spallation neutron source. The error bars (in V) are typically smaller than the symbols. The line is merely a guide to the eye.

on density functional theory within the generalised gradient approximation using ultrasoft non-norm-conserving Vanderbilt pseudopotentials, implemented in the computer program VASP (Vienna ab initio simulation package; [9,10]). In this method, the valence orbitals are expanded as plane waves and the interactions between the core and valence electrons are described by pseudopotentials. When using VASP, the ground state ($T = 0$) is calculated exactly for each set of ionic positions and the electronic free energy is taken as the quantity to be minimised. Calculations may be performed either non-spin-restricted (NSR), where the occupation numbers for electrons with up and down spins are allowed to vary independently (i.e. the atoms are allowed to have a net magnetic moment if that corresponds to the minimum energy state) or spin-restricted (SR), where the occupation numbers of every electronic orbital are equal for up and down spins (i.e. the net magnetic moment is constrained to be zero). In addition to variation in the magnetisation, relaxation of atomic coordinates and axial ratios is allowed during the simulation; these parameters are changed iteratively so that the sum of the lattice energy and electronic free energy converges to a minimum value. It has been suggested [11] that, for some materials, the use of pseudopotentials to describe magnetic ordering may lead to slightly inaccurate results. However, we do not believe

that this presents a problem in the present study, since it is the properties of the material in its non-magnetically ordered state which are of interest when considering the properties of the inner core.

The calculations were carried out using a $3 \times 3 \times 3$ *k*-points sampling grid, equivalent to eight *k*-points in the symmetry-irreducible volume of the Brillouin zone. Any further increase in the number of *k*-points led to negligible differences in energy (less than 1 meV per atom). Convergence in the atomic motions was assumed to have occurred when the energy differences between subsequent iterations were less than 10^{-6} eV per cell. We used VASP to determine the equations of state by calculating the internal energy (E) of the crystal at a set of chosen volumes (V). The resulting E–V data were then fitted to an integrated third-order Birch–Murnaghan equation of state (see, e.g. [12] for details).

4. Results and discussion

4.1. The magnetic transition

Fig. 3 shows the calculated variation of magnetisation with volume. It can be seen that there is a magnetic phase transition at a volume, V_c, of approximately 7.9 $Å^3$ per atom, corresponding to a pressure of ~ 60 GPa. There are no experimental data available with which to compare this pre-
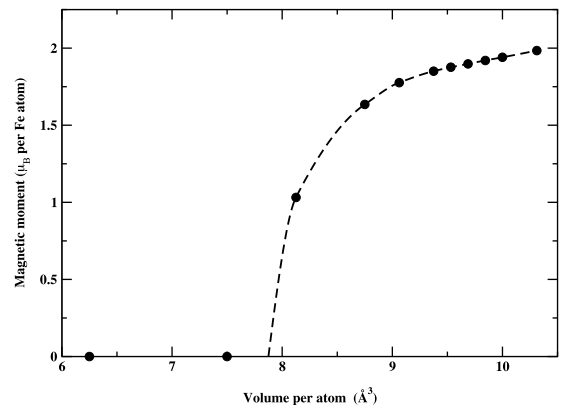

Fig. 3. Spontaneous magnetisation of Fe_3C as a function of unit cell volume. The dashed line is merely a guide to the eye.

dicted transition pressure. However, our calculated magnetic moment at V_0 of ~ 1.88 μ_B per Fe atom is in reasonable agreement with experimental values of 1.72–1.78 μ_B [13,14] and with the value from previous calculations of 1.82 μ_B [5].

4.2. Equations of state

Fig. 4 shows how the energy varies with volume for both non-spin-restricted (NSR) and spin-restricted (SR) calculations. For $V < V_c$, the calculated points are effectively identical (although it appears that the method stabilises the SR results relative to the NSR results by about 10 meV/atom); for $V > V_c$, the imposition of spin restriction allows us to calculate the energy of the non-magnetised material in a pressure region where this phase does not actually exist. Formally, the behaviour of the actual material cannot be represented by a single equation of state such as the third-order Birch–Murnaghan equation (BM3) since a second-order magnetic phase transition requires that there is a discontinuity in the second derivative of the Gibbs free energy. At constant temperature, $\partial^2 G / \partial P^2 = \partial V / \partial P$; however, a discontinuity in $\partial V / \partial P$ is incompatible with the BM3, in which $\partial V / \partial P$ is a continuous function. A consequence of this is that if the BM3 is fitted to either experimental data or to the results of calculations, the resulting EOS parameters will vary according to the pressure range used. We illustrate this point by comparing the parameters obtained using a BM3 for both SR and NSR states of Fe_3C (shown as lines in Fig. 4), together with the values from recent experimental work (Table 1).
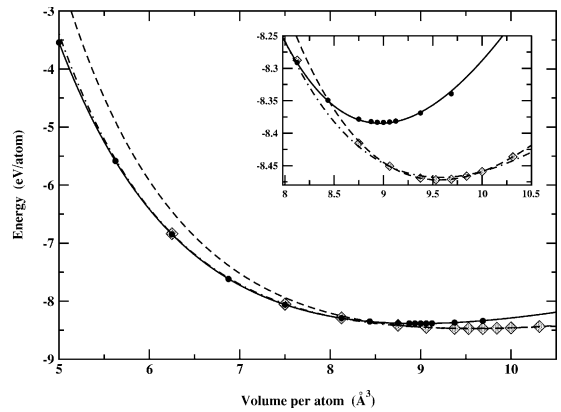

Fig. 4. Energy–volume curves for spin-restricted (solid symbols) and non-spin-restricted (stippled symbols) calculations. The lines correspond to BM3 fits as listed in Table 1: SR (solid line), NSR: $6.25 \leq V \leq 10.31$ Å^3 (dot-dashed line), NSR: $9 \leq V \leq 10.31$ Å^3 (dashed line). The inset shows the low-pressure region in more detail (see text).

It can be seen from Table 1 that the parameters obtained by fitting the BM3 to the calculations depend significantly on both the magnetisation of the material and the volume range over which the fit has been made. In particular, EOS parameters obtained by fitting in the low-pressure, magnetised state may well be unrepresentative of the properties of the material in its high-pressure, non-magnetised state. This point is illustrated by the dashed line in Fig. 4, which corresponds to extrapolation of an EOS fitted to the low-pressure region of the NSR graph, where the spontaneous magnetisation changes by only a small amount; it can be seen that the agreement of this EOS with the calculated $E–V$ points at high pressures is extremely poor. Similarly, although an EOS fitted to

Table 1
Equation of state parameters for Fe_3C

	V_0 Å^3/atom	K_0 GPa	K'
NSR: $6.25 \leq V \leq 10.31$ Å^3	9.578(37)	173.02(8)	5.79(41)
NSR: $9 \leq V \leq 10.31$ Å^3	9.565(4)	228.55(1)	5.36(64)
SR: $5 \leq V \leq 9.69$ Å^3	8.968(7)	316.62(2)	4.30(2)
Li et al. [3]	9.705	174(6)	4.8(0.8)
Scott et al. [2]	9.704(9)[a]	175.4(35)	5.1(3)
Jephcoat [15][b]		162	6.4

NSR, non-spin-restricted calculations; SR, spin-restricted calculations.
[a] Experimental volume not necessarily derived from the fit.
[b] Data fitted to a Vinet equation of state.

the NSR results over the full volume range appears to be in good agreement with the calculated points and lies very close to the fitted SR EOS at high pressures, a more detailed examination of the graph (see inset) shows, in fact, that there is poor agreement with the calculated E–V points at low pressure. Conversely, the EOS for the SR results fits the calculations well throughout.

With regard to fitting of experimental data, the values of the parameters obtained and the accuracy to which the resulting EOS represents the true behaviour of the material are likely to be pressure dependent. The large pressure range ($P < 73$ GPa) used by Scott et al. [2] suggests that their P–V curve may, in fact, give a reasonable representation of the density at high pressure, possibly as a consequence of their highest pressure data point being above the magnetic phase transition. However, our argument above then implies that their EOS may not necessarily be accurate at low pressures. The former point is well illustrated in Fig. 5 which shows the P–V curves predicted by both their EOS and that from our SR calculations. It can be seen that the curves are in exact agreement at about 120 GPa and differ by only 1% at 300 GPa. It should be noted that, since at low pressures the SR calculations do not represent a physically real material, we would not expect the curves to agree in this region. Our NSR calculations, however, give values of V_0 which are in good agreement with experimental values (see below).

4.3. Implications for the Earth's core

It is of interest to use our calculated EOS to re-examine the analysis made by Wood [1] of the viability of Fe_3C as a major component of the inner core. We do this firstly by calculating the density at his chosen representative state point of 338 GPa and 5300 K. We then extend this analysis, including also estimation of incompressibility, over the inner core pressure range given by PREM [16] and its likely temperature range of 4000–6000 K.

4.3.1. Density at 338 GPa and 5300 K
Wood [1] derived the density at 338 GPa and

5300 K in the following way. Using values of $V_0 = 9.644$ Å^3/atom, $K_0 = 174.0$ GPa and $K' = 5.1$, and assuming an average pressure for the inner core of 338 GPa, he obtained a density of 12.94 Mg m^{-3} at 298 K. He then applied a correction for thermal expansion to 5300 K, which gave a final density of 12.74 Mg m^{-3}, which he considered to be in agreement with the density range obtained from seismological data.

A similar analysis based on our results leads to rather different conclusions. We firstly calculate the volume at 0 K and 338 GPa from our EOS based on the SR results (Fig. 5). This leads to a value of V/V_0 of 0.6542 and a density of 12.71 Mg m^{-3} at $T = 0$ K which, even without correction for thermal expansion, is already below the range of densities for the inner core given by PREM [16] of 12.76–13.09 Mg m^{-3}.

To obtain a numerical estimate for the discrepancy between our predicted density for Fe_3C at core conditions and the PREM values, some form of thermal expansion correction is necessary. Although in principle possible, the cost of finite-temperature quantum-mechanical methods for a material such as Fe_3C, with 16 atoms in the primitive unit cell, is currently prohibitively high, and, given our conclusion that the density of Fe_3C is
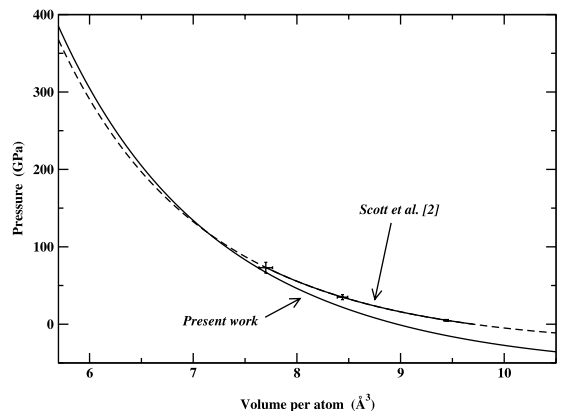

Fig. 5. Birch–Murnaghan third-order EOS for Fe_3C corresponding to (i) the results of Scott et al. [2] and (ii) the present work, SR calculations at 0 K. For the P–V range covered in the experiments of Scott et al., the EOS is shown as a solid line, with its extension to higher and lower pressures shown as a dashed line; the three sets of error bars do not correspond to data points, but merely indicate typical uncertainties in the experimental data [2].

lower than that of the inner core is inescapable, this was not considered an appropriate use of resources. We therefore simply correct for thermal expansion using the method suggested by Wood in eq. 2 of his paper [1], which may be written as:

$$\ln\left(\frac{\alpha}{\alpha_0}\right) = \frac{6.5}{1.4}\left(\left[\frac{V}{V_0}\right]^{1.4}-1\right)$$

where α_0 is the thermal expansion at $P = 0$ and α is that at $P = 338$ GPa, and where V_0 is the volume at $P = 0$ and V is the volume at $P = 338$ GPa (see [1] for details of the values of the coefficients used in the equation).

Our value for α_0 for the paramagnetic state of Fe$_3$C, obtained from the data shown in Fig. 2, is 4.34×10^{-5} K^{-1} at $T \sim 550$ K. Using the above equation, this leads to a value for α of 5.42×10^{-6} K^{-1}, which, in turn, leads to a density of 12.35 Mg m^{-3} at 5300 K and 338 GPa. This density value is 3–5% lower than that determined from seismology [16] and 3% lower than that reported by Wood [1]. It should be noted that we have not included in this analysis any terms to describe the variation of thermal expansion coefficient with temperature; however, such an effect would only serve to reduce the density still further.

As a test for the sensitivity of our method to the chosen EOS, we repeated the analysis but, in this case, fitted the SR E–V points in the high-pressure region ($V < V_c$) to a fourth-order polynomial so as to obtain the pressure via $P = -\partial E/\partial V$ ($T = 0$). This led to a density at 338 GPa and 0 K of 12.70 Mg m^{-3}. Applying the correction for thermal expansion as before gives a final value for the density at 5300 K of 12.34 Mg m^{-3}, almost identical to that which we obtained using the BM3.

It is clear, therefore, that our method for determining the volume at 338 GPa is not sensitive to the detailed EOS employed. This is attributable to the pressure range accessible in our calculations, which allows us to interpolate between successive points rather than being forced to extrapolate from low-pressure data. The only sources of inaccuracy, apart from the correction for thermal expansion, therefore lie in the limitations of the

first-principles calculations themselves. Some indication of the magnitude of any systematic error may be obtained by comparing the value of V_0 from our NSR calculations with those determined experimentally. With a thermal expansion correction to 300 K applied to the average of our values for V_0 from Table 1 (9.572 Å^3), we obtain a value for V at 300 K of 9.697 Å^3, which differs by only 0.1% from that obtained by X-ray diffraction experiments [2,3] and by 0.5% from the results of our neutron diffraction experiment (Fig. 2). Furthermore, since $-\partial E/\partial V$ is much greater at high pressures, it is not unreasonable to expect that our calculations will become more accurate as the pressure increases. It would, therefore, appear that the difference in density between our calculated values and those determined from seismology may be regarded as significant.

In their discussion, Scott et al. [2] considered extrapolation of experimental results to inner core conditions to be highly premature. Nevertheless, it is of interest to repeat the above analysis using their experimental EOS, which leads to a density of 12.78 Mg m^{-3} at 338 GPa and 300 K. Incorporating our correction for thermal expansion then gives a value for the density at 5300 K of 12.53 Mg m^{-3}, which again is somewhat below the allowable range of core density values.

4.3.2. Incompressibility and density at inner core conditions

A further constraint on the viability of Fe$_3$C as a major phase in the inner core can be obtained by comparison of its expected incompressibility values with those derived from seismological data [16]. We derived equations of state at 4000, 5300 and 6000 K by applying the pressure-dependent thermal expansion coefficient (calculated using the equation in the previous section) to our 0 K BM3 EOS. We then fitted the BM3 EOS to these modified P–V curves, obtaining values of $V_0 = 10.520$, 11.092 and 11.417 Å^3, $K_0 = 154.7$, 125.1 and 111.9 GPa, and $K' = 4.74$, 4.81 and 4.84 respectively at 4000, 5300 and 6000 K. The resulting values of $\Delta K_0/\Delta T$ are in the range -0.02 to -0.04 GPa K^{-1}, in line with those previously estimated for other iron alloys (-0.01 to -0.03 GPa K^{-1} [17]). At high pressures the values of

these coefficients are reduced (e.g. $\Delta K/\Delta T =$ -0.026 GPa K^{-1} for $P = 338$ GPa and $T =$ 5300 K). Although the method used to estimate the effect of temperature is approximate, we believe it to be sufficiently reliable for the present purpose since it gives reasonable values for $\Delta K/\Delta T$, possibly producing, if anything, an overestimate of the decrease in K at high temperature.

In order to make a comparison with PREM, values for the adiabatic incompressibility, K_S, must be obtained from our isothermal value, K. The quantities K and K_S are related by $K_S = (1+\alpha\gamma T)K$, where γ is the Grüneisen parameter. Calculating the thermal expansion coefficient, α, as before, and making an assumption that γ in the inner core lies between 1 and 2, allows us to estimate the expected density, ρ, and adiabatic incompressibility as a function of temperature. The resulting values are shown in Fig. 6 for both $\gamma = 1$ and $\gamma = 2$. In this figure, the three isotherms are truncated at the upper and lower pressures given by PREM for the inner core (329 GPa $< P <$ 364 GPa) and the shaded region indicates the K_S–ρ range for PREM. It is clear that the isotherms for Fe$_3$C all lie well outside the acceptable range of inner core values. For example, at 338 GPa and 5300 K ($\rho = 12.35$ Mg m^{-3}), K_S is 1440 and 1480 GPa for $\gamma = 1$ and 2 respectively, which is 5–8% greater than that ex-

pected from PREM ($K_S \sim 1365$ GPa). There does not appear to be any way in which the agreement between our estimated values for Fe$_3$C and the PREM results can be improved by an alternative choice of thermal expansion coefficient since a lower value for α will give better agreement in density, but will increase the discrepancy in incompressibility, and vice versa.

In conclusion, therefore, our calculations show that both the density and incompressibility of Fe$_3$C differ from the expected values for the inner core observed by seismology. Although this does not preclude the possibility of other carbides being present in the core, or of Fe$_3$C as a minor constituent, it does suggest that Fe$_3$C is unlikely to be the predominant inner core-forming phase.
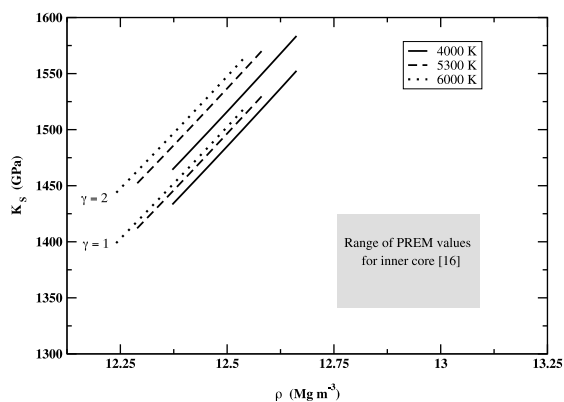
Acknowledgements

Fig. 6. Predicted adiabatic incompressibility, K_S vs. density, ρ, of Fe$_3$C at 4000 K (solid line), 5300 K (dashed line) and 6000 K (dotted line) in the pressure range 329–364 GPa. The upper set of lines are for $\gamma = 2$, the lower set are for $\gamma = 1$. The shaded region shows the range of values given by PREM for the Earth's inner core [16].

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