Thermodynamic stability of Fe/O solid solution at inner-core conditions

D. Alfè, G. D. Price

Research School of Geological and Geophysical Sciences Birkbeck College and University College London
Gower Street, London WC1E 6BT, UK.

M. J. Gillan

Physics and Astronomy Department, University College London Gower Street, London WC1E 6BT, UK.

Abstract. We present a new technique which allows the fully *ab initio* calculation of the chemical potential of a substitutional impurity in a high-temperature crystal, including harmonic and anharmonic lattice vibrations. The technique uses the combination of thermodynamic integration and reference models developed recently for the *ab initio* calculation of the free energy of liquids and anharmonic solids. We apply the technique to the case of the substitutional oxygen impurity in h.c.p. iron under Earth's core conditions, which earlier static *ab initio* calculations indicated to be thermodynamically very unstable. Our results show that entropic effects arising from the large vibrational amplitude of the oxygen impurity give a major reduction of the oxygen chemical potential, so that oxygen dissolved in h.c.p. iron may be stabilised at concentrations up a few mol % under core conditions.

The thermodynamic stability of oxygen dissolved in iron is a key factor in considering the physics and chemistry of the Earth's core. We present here a new technique which allows the *ab initio* calculation of the chemical potential of an impurity in a high-temperature solid solution, including harmonic and anharmonic lattice vibrations. We report the application of the technique to substitutional oxygen dissolved in hexagonal close-packed (h.c.p.) iron at Earth's core conditions, and we show that the Fe/O solid solution is thermodynamically far more stable than expected from earlier work. The new technique should find wide application to a range of other earth-science problems.

It has long been recognised that the liquid outer core must contain a substantial fraction of light impurities, since its density is $6 - 10$ % less than that estimated for pure liquid Fe (Birch 1964, Poirier 1994); similar arguments suggest that the inner core contains a smaller, but still appreciable impurity fraction (Stixrude et al. 1997, Jephcoat and Olson 1987). The leading impurity candidates are S, Si and O, and arguments have been presented for and against each of them (Poirier 1994). Ringwood (Ringwood 1977) and others (Dubrovskiy and Pan'kov 1972) have argued strongly on grounds of geochemistry that oxygen must account for a large part of the impurity content. However, it has proved difficult to assess these ideas, because the Fe/O phase diagram is so poorly known at Earth's core conditions. (For

reference, we note that the pressures at the core-mantle boundary, the inner-core boundary (ICB) and the centre of the Earth are 136, 330 and 364 GPa respectively; the temperatures at the core-mantle boundary and the ICB are poorly established, but are believed to be in the region of 4000 and 6000 K respectively.)

The thermodynamic stability of dissolved oxygen is governed by the free energy change in the reaction

$$(n - 1)\mathrm{Fe(solid)} + \mathrm{FeO(solid)} \rightarrow \mathrm{Fe}_n\mathrm{O(solid\ solution)} \quad (1)$$
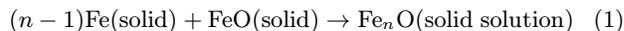
Let ΔG be the increase of Gibbs free energy as this reaction goes from left to right, excluding the configurational contribution associated with the randomness of the lattice sites occupied by dissolved O. Then the maximum concentration (number of O atoms per crystal lattice site) at which dissolved O is thermodynamically stable with respect to precipitation of FeO is $c_{\max} = \exp(-\Delta G/k_{\mathrm{B}}T)$. (At equilibrium the Gibbs free energy (G) of the left-hand-side (lhs) of Eq. (1) must be equal to that of the right-hand-side (rhs). On the rhs $G = k_B T \ln c + \tilde{G}$, where c is the O concentration and the $k_B T \ln c$ term is the configurational contribution. The configurational term is absent in the lhs because Fe and FeO are separated perfect crystals.) Several years ago, Sherman (Sherman 1995) used *ab initio* calculations based on density functional theory (DFT) to calculate the zero-temperature limit of ΔG, i.e. the enthalpy ΔH of reaction (1). He found that ΔH is very large (~ 5 eV at the ICB pressure of 330 GPa), and concluded that the concentration of dissolved O in the inner core must be completely negligible. His argument has been widely cited. However, these were static, zero-temperature calculations, which entirely ignored entropic effects. We shall show here that the high-temperature entropy of dissolved O produces such a large reduction of free energy that Sherman's argument should be treated with caution when considering core temperatures.

Our *ab initio* calculations are based on the well established DFT methods used in virtually all *ab initio* investigations of solid and liquid Fe (Stixrude et al. 1994, Soderlind et al. 1996, de Wijs et al. 1998a, Alfè et al. 1999a, 2000a), including Sherman's (Sherman 1995). We employ the generalised gradient approximation for exchange-correlation energy, as formulated by Perdew *et al.* (Perdew et al. 1992), which is known to give very accurate results for the low-pressure elastic, vibrational and magnetic properties of body-centred cubic (b.c.c.) Fe, the b.c.c. $\rightarrow$ h.c.p. transition pressure, and the pressure-volume relation for h.c.p. Fe up to over 300 GPa (Stixrude et al. 1994, Alfè et al. 2000a). We use the ultra-soft pseudopotential implementa-
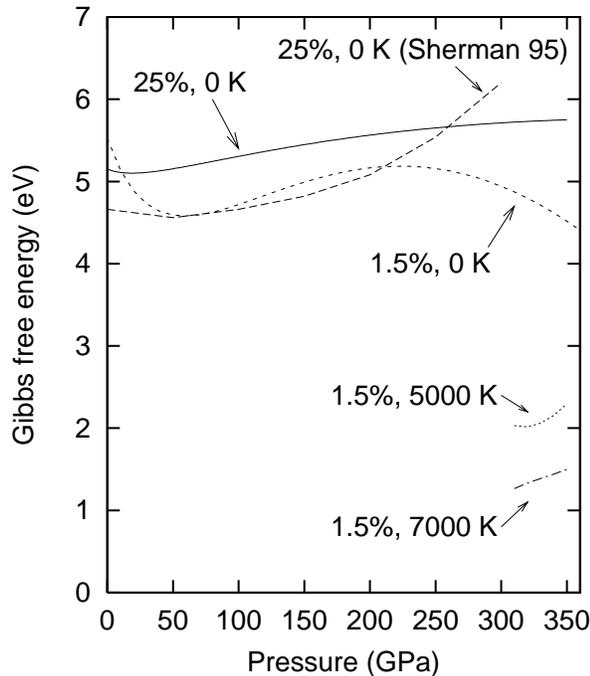
Figure 1. Gibbs free energy ΔG of the reaction $(n - 1)$Fe(solid) + FeO(solid) $\rightarrow$ Fe$_n$O (solid) from *ab initio* calculations. Upper curves show zero-temperature values (i.e. enthalpies) for 25 mol % concentration from Refs. (Alfè et al. 1999b) (solid curve) and (Sherman 1995) (long dashes) and for 1.5 % concentration (short dashes) from present work. Short lower curves show high-temperature results for ΔG from present work at 5000 K (dots) and 7000 K (chain line).

tion (Vanderbilt 1990) of DFT with plane-wave basis sets, an approach which has been demonstrated to give results for solid Fe that are virtually identical to those of all-electron DFT methods (Alfè et al. 2000a). Our calculations are performed using the VASP code (Kresse and Furthmüller 1996), which is exceptionally stable and efficient for metals. The technical details of pseudopotentials, plane-wave cutoffs, etc. are the same as in our previous work on the Fe/O system (Alfè et al. 1999b).

We first report static zero-temperature results for the enthalpy ΔH of the reaction (1). Sherman's results (Sherman 1995) later confirmed by the present authors (Alfè et al. 1999b), were obtained for the high O concentration of 25 mol %, corresponding to $n = 3$, but here we wish to focus on the dilute limit, and we take $n = 63$, which gives a mole fraction of 1.5 %. To do this, we treat a 64-atom supercell with the h.c.p. structure containing a single O substitutional, and we calculate the total ground-state energy and pressure for a sequence of atomic volumes, with all atoms relaxed to their equilibrium positions at each volume. The enthalpy of the pure iron system is obtained from total-energy and pressure calculations for a single unit cell of the h.c.p. crystal. For the FeO crystal, we obtain the enthalpy from total-energy and pressure calculations on a unit cell of the NiAs structure. (The high-pressure stable structure of FeO is believed to be either NiAs or inverse-NiAs; the relative stability of the two structures has been controversial (Fei and Mao 1994, Cohen at al. 1997, Fang et al. 1999), but our own *ab initio* calculations indicate

that the NiAs structure is slightly more stable at pressures above *ca.* 145 GPa. Our calculations also indicate that at high pressure and temperature FeO in this structure is non-magnetic.) The enthalpy ΔH is reported as a function of pressure in Fig. 1, where we also show Sherman's results and our own for the 25 mol % case. We see that ΔH at 1.5 mol % is between 0.5 and 1.0 eV lower than at 25 mol %, having a value of *ca.* 4.7 eV at 330 GPa, but this is still very large and Sherman's arguments would remain valid if this represented a good estimate of the free energy of reaction (1) at Earth's core temperatures.

To get an idea of the freedom of movement of the substitutional O atom, and hence its vibrational entropy, we now perform a series of calculations in which the O atom is displaced by different amounts from its equilibrium site, with all other atoms held fixed at the equilibrium positions they have when the O atom is at its own equilibrium position. Results for the energy variation with displacement along the *c*-axis and in the basal plane for the crystal volume of 6.97 Å^3/atom are shown in Fig. 2. Since we are interested in core temperatures, we also mark the energy $k_B T$ for $T = 6000$ K. We see that in the energy range set by this T the energy surface is extremely anharmonic, with almost vanishing curvature at the equilibrium site and large curvatures for large displacements. The curve of Fig. 2 leads one to expect a vibrational-root-mean-square displacement (rmsd) of ~ 0.45 Å, and our direct *ab initio* molecular-dynamics calculations confirm this value. (We note that for an isotropic harmonic oscillator the rmsd is $(3/2)^{1/2} r_0$, where r_0 is the displacement at which the vibrational potential is equal to $k_B T$, while for a hard-wall potential of radius r_0, the rmsd is $(3/5)^{1/2} r_0$; our anharmonic potential should lie somewhere between the two.) For comparison, we estimate the rmsd O in FeO at the same P and T to be
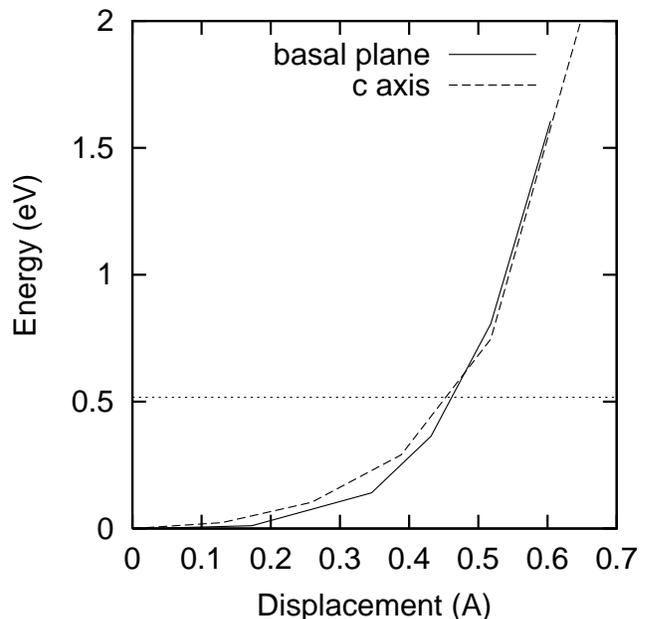
Figure 2. Calculated energy (eV units) as function of displacement (Å units) of O impurity from its equilibrium site in basal plane (solid curve) and along *c*-axis (dashed curve). Results are for crystal volume of 6.97 Å^3/atom. The energy $k_B T$ corresponding to T = 6000 K is marked with a dotted line.

~ 0.23 Å. This implies a substantial vibrational entropy for the O impurity, because it fits so loosely into the Fe lattice. For the same reason, the vibrations of the 12 Fe neighbours of the O impurity will be softened, and this will also increase the entropy.

To make quantitative statements about high-temperature behaviour, we need to calculate the *ab initio* Gibbs free energies, rather than zero-temperature enthalpies. The *ab initio* calculation of the Helmholtz free energies F of the Fe and FeO perfect crystals is straightforward in the harmonic approximation, since this requires only the energy of the static lattice and the *ab initio* lattice vibrational frequencies, which we calculate by the small-displacement method, as discussed in several previous papers (Alfè et al. 1999a, Kresse et al. 1995, Vočadlo at al. 1999, 2000) From F, we then directly obtain the Gibbs free energy $G = F + PV$, by calculating the pressure P as $-(\partial F/\partial V)_T$, with V the volume. The only difficult part of the present problem is therefore the calculation of F (and hence G) for the Fe_nO crystal containing the substitutional O atom. This free energy must include the vibrations of many shells of neighbours of the O impurity. The harmonic approximation will clearly not suffice. We meet this challenge by drawing on recently developed *ab initio* methods for calculating the free energies of liquids and anharmonic solids (Alfè at al. 1999a, 2000b, de Wijs at al. 1998b). These methods rely on two things: empirical reference models, parameterised to accurately mimic the *ab initio* energies; and the technique of 'thermodynamic integration', used to determine free energy differences. Our overall strategy will be to obtain the *ab initio* free energy $F_{Fe/O}^{AI}$ of the O-substitutional system by starting from the *ab initio* free energy F_{Fe}^{AI} of pure Fe and using thermodynamic integration to compute the free energy change $F_{Fe/O}^{AI} - F_{Fe}^{AI}$ that results from converting a single Fe atom into an O atom.

We recall briefly that thermodynamic integration (Frenkel and Smit 1996) is a general technique for calculating the difference of free energies $F_1 - F_0$ of two systems containing the same number N of atoms but having different total-energy functions $U_0(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and $U_1(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$, with $\mathbf{r}_i (i = 1, 2 \ldots N)$ the atomic positions. The technique relies on the equivalence between the free energy difference and the reversible work done on switching the total energy function continuously from U_0 to U_1. The work done is:

$$F_1 - F_0 = \int_0^1 d\lambda \langle U_1 - U_0 \rangle_\lambda , \qquad (2)$$

where the thermal average $\langle \cdot \rangle_\lambda$ is evaluated in the canonical ensemble generated by the switched energy function U_λ defined by:

$$U_\lambda = (1 - \lambda)U_0 + \lambda U_1 . \qquad (3)$$

To apply this in practice, we use molecular dynamics simulation to evaluate the average $\langle U_1 - U_0 \rangle_\lambda$ at a sequence of λ values and we perform the integration over λ numerically.

In principle, we could calculate $F_{Fe/O}^{AI} - F_{Fe}^{AI}$ by identifying U_0 and U_1 as the *ab initio* total energy functions U_{Fe}^{AI} and $U_{Fe/O}^{AI}$ of the pure-Fe and O-substitutional systems, but this brute-force approach is computationally prohibitive at present. It is also unnecessary, since exactly the same result can be achieved much more cheaply by using empirical reference models. In our recent work on liquid Fe (Alfè et al. 2000a), we have found that a simple inverse-power pair potential $\phi(r) = A/r^\alpha$ reproduces the *ab initio* total energy very accurately; for the anharmonic high-temperature

Fe crystal, a linear combination of this pair-potential model with an *ab initio* harmonic description has been very effective (Alfè et al. 1999a) We denote the total energy of this latter anharmonic model by $U_{Fe}^{ref}(\mathbf{r}_1, \ldots \mathbf{r}_N)$, where $\mathbf{r}_i$ are the atomic positions.

In order to make a reference system for the Fe/O system containing a single substitutional O atom, whose total energy is $U_{Fe/O}^{ref}(\mathbf{r}_1, \ldots \mathbf{r}_N)$ ($\mathbf{r}_1$ is the position of the O atom), we simply delete all terms in U_{Fe}^{ref} involving atom 1 and replace them with a pair interaction potential $\chi(r) = B/r^\beta$. All parts of $U_{Fe/O}^{ref}$ involving the $N - 1$ Fe atoms $2, 3, \ldots N$ remain precisely as they are in U_{Fe}^{ref}. Our procedure for determining B and β starts by requiring that the pair potential $\chi(r)$ should reproduce as well as possible the dependence of the total energy on position of the O atom with all Fe atoms held fixed, i.e. the curves shown in Fig. 2. The values for B and β thus obtained give us an initial form for $U_{Fe/O}^{ref}$. This initial $U_{Fe/O}^{ref}$ is then used in a classical MD simulation to generate a long trajectory at the temperature of interest, from which we take 100 statistically independent configurations. The full *ab initio* energies are calculated for these configurations, and the B and β parameters are readjusted to give a least squares fit to these energies. Finally, the $U_{Fe/O}^{ref}$ obtained from the new B, β is used to generate a further 100 statistically independent configurations, and B and β are adjusted once more to fit the *ab initio* energies of these configurations. The B and β produced by this final step are found to be essentially identical to those in the previous step, and we accept them as the optimal values for the assumed form of $\chi(r)$.

The free energy difference $F_{Fe/O}^{AI} - F_{Fe}^{AI}$ between the Fe/O and pure Fe systems is now expressed as the sum of three contributions: the difference $F_{Fe/O}^{ref} - F_{Fe}^{ref}$ between the reference systems, and the two differences $F_{Fe/O}^{AI} - F_{Fe/O}^{ref}$ and $F_{Fe}^{ref} - F_{Fe}^{AI}$ between the *ab initio* and reference systems. All three of these differences are calculated by thermodynamic integration. We emphasise that, although the reference systems play a vital role, the final result for $F_{Fe/O}^{AI} - F_{Fe}^{AI}$ does not depend on how they are chosen.

Thermodynamic integration to get $F_{Fe/O}^{ref} - F_{Fe}^{ref}$ is easy and rapid, since only simple potential models are involved. We have tested size effects by using simulated systems containing up to 768 atoms, but we find that with only 288 atoms the size-effect errors are less than the statistical errors of *ca.* 30 meV. For the *ab-initio*/reference differences $F_{Fe/O}^{AI} - F_{Fe/O}^{ref}$ and $F_{Fe}^{AI} - F_{Fe}^{ref}$, the fluctuations of $U_{Fe/O}^{AI} - U_{Fe/O}^{ref}$ and $U_{Fe}^{AI} - U_{Fe}^{ref}$ are so small that explicit thermodynamic integration over λ is unnecessary, and we can use instead the small-λ approximation explained elsewhere (Alfè et al. submitted). We have studied the size errors for these *ab initio*/reference differences, and we find that results obtained with 36, 64 and 96 atoms are identical within statistical errors. The overall statistical error on the *ab initio* difference $F_{Fe/O}^{AI} - F_{Fe}^{AI}$ is *ca.* 90 meV. We have repeated all the above calculations at the four volumes 6.86, 6.97, 7.20 and 7.40 Å^3/atom, and from the dependence on volume we obtain the pressure change on replacing Fe by O and hence the Gibbs free energy difference $G_{Fe/O}^{AI} - G_{Fe}^{AI}$.

Our calculated Gibbs free energies ΔG for reaction (1) are displayed in Fig. 1 for the two temperatures 5000 and 7000 K. We note the very large entropic lowering of ΔG, which, at $P = 330$ GPa comes down from 4.7 to *ca.* 1.7 eV

at the temperature $T \simeq 6000$ K expected at the ICB. This is still a substantial positive value, but implies that the stability-limit concentration $c_{max} = \exp(-\Delta G/k_B T)$ is $ca.$ 3 mol %, which is far from negligible.

In assessing our c_{max} value, one should note the remaining uncertainties in our calculations. First, we have ignored anharmonicity in the pure Fe and FeO crystals. Our recent work on the effect of anharmonicity in pure Fe (Alfè et al. submitted) showed that at the melting point, anharmonicity can contribute as much as 70 meV/atom to the free energy; the same might be true of FeO. These effects could shift ΔG by perhaps 0.15 eV. Second, there is the question of strong electronic correlation in FeO, which is a prototypical Mott insulator at low pressures. Such correlation effects will be much weakened at Earth's core pressures, but could still shift ΔG by a few tenths of an eV. This means that our prediction for c_{max} at a given temperature is probably not reliable to better than a factor of 3. We are therefore cautious about the detailed numerical value of c_{max}, and claim only that it could be a few mol % at ICB pressure and temperature.

In summary, we conclude that, because substitutional oxygen atom fits so loosely into the Fe lattice and has so much freedom of movement, it undergoes a very large entropic lowering of free energy at high temperatures, this lowering being as much as 3 eV at 6000 K and 330 GPa. The consequence is that substitutional O dissolved in h.c.p. Fe may be thermodynamically stabilised at concentrations up to a few mol %. Earlier *ab initio* calculations (Sherman 1995) which ignored entropic effects should therefore not be taken at face value. Finally, we point out that a wide range of geological problems depend on an understanding of chemical potentials – for example, all problems concerned with the partitioning of elements between coexisting phases. The *ab initio* techniques for calculating chemical potentials outlined here should therefore be of wide interest.

References

Alfè, D., Gillan, M. J., and Price, G. D., 'The melting curve of iron at the pressures of the Earth's core from *ab initio* calculations', *Nature*, 401, 462–464, 1999a.

Alfè, D., Price, G. D., and Gillan, M. J., 'Oxygen in the Earth's core: A first-principles study', *Phys. Earth Planet. Inter.*, 110, 191–210, 1999b.

Alfè, D., Kresse, G., and Gillan, M. J., 'Structure and dynamics of liquid iron under Earth's core conditions', *Phys. Rev. B*, 61, 132–142, 2000a.

Alfè, D., de Wijs, G. A., Kresse, G., and Gillan, M. J., 'Recent developments in ab initio thermodynamics', *Int. J. Quant. Chem.*, 77, 871–879, 2000.

Alfè, D., Price, G. D., and Gillan, M. J., 'Thermodynamics of hexagonal-close-packed iron under Earth's core conditions', *Phys. Rev. B*, submitted.

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

Cohen, R. E., Mazin, I. I., and Isaak, D. G., 'Magnetic collapse in transition metal oxides at high pressure: Implications for the Earth', *Science*, 275, 654–657, 1997.

Dubrovskiy, V., and Pan'kov, V. L. 'On the composition of the Earth's core', *Acad. Sci. USSR, Phys. Solid Earth*, 7, 452–455, 1972.

Fang, Z., Soloviev, I. V., Sawada, H., and Terakura, K., 'First-principles study on electronic structures and phase stability of MnO and FeO under high pressure', *Phys. Rev. B*, 59, 762-774, 1999.

Fei, Y., and Mao, H.-K, '*In situ* determination of the NiAs phase of FeO at high pressure and temperature', *Science*, 266, 1678, 1994.

Frenkel, D., and Smit, B., *Understanding Molecular Simulation*, Ch. 4 (Academic, New York), 1996.

Jephcoat, A. and Olson, P. 'Is the inner core of the Earth pure iron?', *Nature* 325, 332–335 , 1987.

Kresse, G., Furthmüller, J. and Hafner, J., 'Ab-initio force-constant approach to phonon dispersion relations of diamond and graphite' *Europhys. Lett.*, 32, 729–734, 1995.

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

Perdew, J. P., Chevary, J. A., Vosko, S. H., Jackson, K. A., Pederson, M. R., Singh, D. J., and Fiolhais, C., 'Atoms, molecules, solids and surfaces: Applications of the generalized gradient approximation for exchange and correlation', *Phys. Rev. B*, 46, 6671–6687, 1992.

Poirier J.-P., 'Light elements in the Earth's outer core: A critical review', *Phys. Earth Planet. Inter.*, 85, 319–337, 1994.

Ringwood, A. E. 'Composition of the core and implications for the origin of the earth', *Geochem. J.*, 11, 111–135, 1977.

Sherman, D. M., 'Stability of possible Fe-FeS and Fe-FeO alloy phases at high pressure and the composition of the Earth's core', *Earth Planet. Sci. Lett.*, 132, 87–98, 1995.

Söderlind, P., Moriarty J. A., and Wills, J. M., 'First-principles theory of iron up to earth-core pressures: Structural, vibrational and elastic properties', *Phys. Rev. B*, 53, 14063–14072, 1996.

Stixrude, L., Wasserman, E., and Cohen, R. E. 'Composition and temperature of the Earth's inner core', *J. Geophys. Res.*, 102, 24729–24739, 1997.

Stixrude, L., Cohen, R. E., and Singh, D. J., 'Iron at high pressure: Linearized-augmented-plane-wave computations in the generalized gradient approximation', *Phys. Rev. B*, 50, 6442–6445, 1994.

Vanderbilt, D., 'Soft self-consistent pseudopotentials in a generalized eigenvalue formalism', *Phys. Rev. B*, 41, 7892–7895, 1990.

Vočadlo, L., Brodholt, J., Alfè, D., Price, G. D., and Gillan, M. J., 'The structure of iron under the conditions of the Earth's inner core', *Geophys. Res. Lett.*, 26, 1231–1234, 1999.

Vočadlo, L., Alfè, D., Brodholt, J., Price, G. D., and Gillan, M. J., 'Ab-initio free energy calculations on iron and its stability in the inner core', *Phys. Earth Planet. Inter.*, 117, 123–137, 2000.

de Wijs, G. A., Kresse, G., Vočadlo, L., Dobson, D., Alfè, D., Gillan, M. J., Price, G. D., 'The viscosity of liquid iron at the physical conditions of the Earth's core', *Nature*, 392, 805–807, 1998a.

de Wijs, G. A., Kresse, G., and Gillan, M. J., 'First-order phase transitions by first-principles free-energy calculations: The melting of Al', *Phys. Rev. B*, 57, 8223–8334, 1998b.

D. Alfè, Research School of Geological and Geophysical Sciences Birkbeck College and University College London Gower Street, London WC1E 6BT, UK. (e-mail: d.alfe@ucl.ac.uk)

G. D. Price, Research School of Geological and Geophysical Sciences Birkbeck College and University College London Gower Street, London WC1E 6BT, UK. (e-mail: d.price@ucl.ac.uk)

M. J. Gillan, Physics and Astronomy Department, University College London Gower Street, London WC1E 6BT, UK. (e-mail: m.gillan@ucl.ac.uk)