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The effect of nickel on the properties of iron at the conditions of Earth's inner core: *Ab initio* calculations of seismic wave velocities of Fe–Ni alloys

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ABSTRACT

We have performed athermal periodic plane-wave density functional calculations within the generalised gradient approximation on the bcc, fcc and hcp structures of $Fe_{1-X}Ni_X$ alloys ($X=0$, 0.0625, 0.125, 0.25, and 1) in order to obtain their relative stability and elastic properties at 360 GPa and 0 K. For the hcp structure, using *ab initio* molecular dynamics, we have also calculated the elastic properties and wave velocities for $X=0$, 0.0625, and 0.125, at 360 GPa and 5500 K, with further calculations for $X=0$, and 0.125 at 360 GPa and 2000 K. At 0 K, the hcp structure is the most stable for $X=0$, 0.0625, 0.125, and 0.25, with the fcc structure becoming the most stable above $X\sim0.45$; the bcc structure is not the most stable phase for any composition. At 0 K, compressional and shear wave velocities are structure dependent; in the case of fcc the velocities are very similar to pure Fe, but for the hcp structure the addition of Ni strongly reduces V_S. Ni also reduced velocities in fcc iron, but to a lesser extent. However, at 5500 K and 360 GPa, Ni has little effect on the wave velocities of the hcp structure, which remain similar to those of pure iron throughout the range of compositions studied and, in the case of V_S, $>30\%$ greater than that from seismological models. The effect of temperature on Fe–Ni alloys is, therefore, very significant, indicating that conclusions based on the extrapolation of results obtained at much lower temperatures must be treated with great caution. The significance of temperature is confirmed by the additional simulation at 2000 K for $X=0$, and 0.125 which reveals a remarkably linear temperature dependence of the change in V_S relative to that of pure iron. At 0 K, the maximum anisotropy in V_P is found to be only very weakly dependent on nickel content, but dependent on structure, being $\sim15\%$ for fcc and $\sim8\%$ for hcp. For the hcp structure at 2000 and 5500 K, the maximum anisotropy in V_P is also $\sim8\%$ and almost independent of the Ni content. We conclude that Ni can safely be ignored when considering its effect on the seismic properties of hcp-Fe under core pressures and temperatures and that the negligible effect of nickel on the physical properties of iron in the core arises not because of the chemical similarities between iron and nickel, but because of the high temperature of the system.

1. Introduction

The study of the Earth's inner core is challenging due to its inaccessibility (>5200 km depth) and considerable high pressures ($330<P<360$ GPa) and temperatures ($T<\sim6000$ K). The Earth's inner core is predominantly made of iron but is commonly assumed to contain 5–10% of Ni (Birch, 1952) and also light elements such as Si, C, O and S ($\sim2\%$; Birch, 1964; Poirier, 1994). Although data for seismic wave velocities through the inner core are known, seismological and mineralogical models for the inner core do not agree (Cao et al., 2005; Vočadlo, 2007). A major discrepancy between the observed data and the current mineralogical models, derived from *ab initio* calculations, is that the mineralogical models predict a shear wave velocity that is at least 10% greater than the observed values (Vočadlo, 2007). To explain this discrepancy, several arguments have been proposed, including: lateral density inhomogenities at the inner–outer core boundary (Chuikova and Maksimova, 2010), a core formed by randomly oriented aggregates and defects (Calvet and Margerin, 2008; Belonoshko et al., 2007), anelasticity at high temperature (Lin et al., 2005), melt inclusions in the inner core (Vočadlo, 2007), or even very different compositions of the inner core, such as Fe_3C, Fe_3S, and Fe–Si alloys (Gao et al., 2011; Tsuchiya and Fujibuchi, 2009; Antonangeli et al., 2010; Lin et al., 2004). However, until now, the effect of nickel on iron at core conditions has received relatively little attention, whilst, because of their supposedly larger effect, the effects of light elements have been studied extensively (*e.g.*, Gao et al., 2011; Vočadlo, 2007; Tsuchiya and Fujibuchi, 2009; Antonangeli et al., 2010; Lin et al., 2004). In the

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present paper, therefore, we have used *ab initio* calculations to study how the presence of nickel affects the crystal structure and elastic properties of iron at inner core pressures and temperatures.

The structural properties of pure iron, the main component for the Earth's core, have been studied extensively both experimentally and theoretically. Experimental studies at high pressure (from ~60 to 377 GPa) and high temperature (from room temperature up to 5700 K) show the hcp structure of iron is the most stable (Tateno et al., 2010; Kuwayama et al., 2008). This agrees with *ab initio* simulations on iron at high P and T where the hcp structure has also been found to be the most stable phase (Vočadlo et al., 1999), although the fcc structure is only marginally less stable (by ~14 meV/atom; Vočadlo et al., 2008a). These free energies are so similar that small amounts of light elements, such as Si, may stabilise the fcc structure (or even bcc) with respect to hcp (Vočadlo et al., 2003b, 2008a; Côté et al., 2010). Similarly, small amounts of Ni can also stabilise the fcc structure over a broad pressure range up to >300 GPa (Kuwayama et al., 2008; Shabashov et al., 2009). Some theoretical and experimental results suggest that at low Ni concentrations (below 10%) the stable phase remains hcp at high pressures (Vočadlo et al., 2006; Tateno et al., 2012; Sakai et al., 2011), while other studies suggest a more complex picture. For instance the theoretical calculations on Fe–Ni alloys at inner core pressure of Ekholm et al. (2011) also showed the hcp structure to be the stable phase up to 4000 K, and that nickel reduces the free energy difference between fcc and hcp structures. However, at higher temperatures (~6600 K) the picture changes with the fcc structure becoming the stable phase for pure iron, and they argue that it is the hcp structure that is then stabilised by the addition of nickel. Recent *ab initio* quasi-harmonic results of Côté et al. (2012) also show that the fcc structure becomes favoured over hcp for pure iron at very high temperatures and core pressures, but in contrast to Ekholm et al. (2011) they find that Ni further stabilises the fcc phase, such that the core could well be in the fcc phase or a two phase mixture of fcc and bcc. A further complication is added by Kádas et al. (2012), who demonstrated recently that small quantities of Mg (5% in molar fraction) stabilises the bcc structure of Fe at 7000 K.

One possible way to obtain information on the crystalline phase of the inner core and the concentration of light elements and nickel is to compare the seismic properties of these phases at various compositions with those observed in the core. The elastic properties and wave propagation velocities in pure hcp-Fe have been studied both at high P and at simultaneously high P and T. *Ab initio* molecular dynamics calculations (Vočadlo, 2007) have shown that the hcp-Fe P-wave velocity (V_P) at 5500 K and core density (11.14 km s^{-1}) agrees with values from the Preliminary Reference Earth Model (PREM; Dziewonski and Anderson 1981) of 11.03–11.26 km s^{-1} between the inner core boundary and the Earth's centre; however, the shear wave velocity (V_S) is predicted to be considerably higher (4.01 km s^{-1} compared to 3.50–3.67 km s^{-1}). This effect was also observed experimentally by Antonangeli et al. (2004) using inelastic X-ray scattering (IXS) to measure V_P and V_S for hcp-Fe at 112 GPa and room temperature; it was found that extrapolation of the results to the density of the Earth's core gave very good agreement with PREM for V_P, but overestimated V_S by 30%. Experiments (Antonangeli et al., 2004; Lin et al., 2010) and calculations (Vočadlo et al., 2009) have also shown that both the P and S wave velocities of iron show anisotropy at Earth's core conditions.

The effect of the addition of Ni on the elastic properties of iron has not been so widely studied. Experimentally, an IXS study on fcc-$Fe_{0.78}Ni_{0.22}$ between 12 and 72 GPa (Kantor et al., 2007) showed that the presence of Ni did not introduce any measurable effect on V_P and V_S, when plotted as a function of density, with respect to those of pure iron. Once again, extrapolation to Earth's core conditions leads to good agreement for V_P, but V_S is overestimated. In a theoretical paper, Asker et al. (2009) used the Coherent Potential Approximation (CPA) to take into account the random chemical structure of the alloy (from 5% to 25% of Ni). They observed that the addition of Ni slightly decreases the bulk modulus (K) of hcp and fcc structured alloys, by <2% at 360 GPa and 0 K; however the reduction of the shear modulus (G) is much larger, especially for hcp structures (11.1% at 360 GPa and 0 K). It was also found that the fcc structures showed a larger elastic anisotropy than the hcp structures.

The aim of this paper is to evaluate the extent to which the presence of Ni in the Earth's inner core affects the inner core properties. To do this we have calculated the effect of Ni (from 0% to 100% Ni) on the elastic properties and the wave propagation velocities of Fe–Ni alloys at 360 GPa. The calculations have been performed at 0 K and for the hcp structure also at 5500 K; for pure Fe one alloy composition we have performed further calculations at 2000 K. We have found that (i) for hcp-Fe, Ni has little effect on the elastic properties and seismic wave velocities at inner core P and T, and (ii) the effect of temperature (especially on V_S) is very significant, indicating that conclusions based on the extrapolation of results obtained at much lower temperatures must be treated with great caution.

2. Computational details

2.1. Electronic structure calculations

The calculations performed in this work are based on density functional theory (DFT) using the Vienna *Ab Initio* Simulation Package (VASP; Kresse and Hafner, 1993a, 1993b, 1994). The effect of the core electrons on the valence electrons is described by the projector augmented wave method (PAW; Blochl, 1994; Kresse and Joubert, 1999), and we used PAW parameters with 14 and 16 valence electrons for Fe and Ni, respectively. A tight convergence of the plane-wave expansion was obtained with a cut-off of 500 eV. The generalised gradient approximation (GGA) was used with the functional of Perdew and Wang (1992). All calculations were performed at 360 GPa.

Initially, calculations were performed in the athermal limit (effectively at 0 K). For selected structures, we then performed finite temperature *ab initio* molecular dynamics (AIMD) simulations at ~5500 K—a possible temperature of the Earth's inner core and that used in previous calculations on pure hcp-Fe (Vočadlo et al., 2009); for pure iron one alloy composition, a simulation was also performed at 2000 K in order establish the presence or otherwise of systematic trends in the seismic velocities.

For the athermal calculations, simulation cells of 16 atoms were used, since this is the minimum cell size necessary to allow a Ni molar fraction of 0.0625. We used the most symmetric simulation cell for each structure: for bcc this was a $2\times2\times2$ supercell of the basic 2-atom bcc crystallographic unit cell; for fcc this was a $2\times2\times1$ supercell of the basic 4-atom fcc crystallographic cell; for hcp this was a $2\times1\times2$ supercell of the 4-atom C-centred crystallographic cell with orthogonal axes. Different Monkhorst-pack grids of special k points were used in each case: a $6\times6\times6$ Monkhorst-pack grid for the bcc structure, a $5\times5\times10$ grid for the fcc structure, and a $6\times8\times4$ for the hcp structure. These grids were chosen after testing the convergence of the total energy with the number of k-points in the unit cell. Calculations were performed for Ni concentrations in the $Fe_{1-X}Ni_X$ alloy of $X=0$, 0.0625, 0.125, 0.25, and 1. Although for pure Fe, pure Ni and $Fe_{0.9375}Ni_{0.0625}$ only one configuration exists within a 16 atom supercell with periodic boundary conditions, for $X=0.125$ and