Configurational thermodynamics of Fe-Ni alloys at Earths core conditions

Marcus Ekholm, Arkady Mikhaylushkin, Sergey Simak, B Johansson and Igor Abrikosov

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1016/j.epsl.2011.05.035
Copyright: Elsevier
http://www.elsevier.com/

Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-70218
Abstract

By means of ab-initio calculations, we perform an analysis of the configurational thermodynamics, effects of disorder, and structural energy differences in Fe-Ni alloys at the pressure and temperature conditions of the Earth’s core. We show from ab-initio calculations that the ordering energies of fcc- and hcp-structured Fe-Ni solid solutions at these conditions depend sensitively on the alloy configuration, i.e., on the degree of chemical disorder, and are on a scale comparable with the structural energy differences. From configurational thermodynamics simulations we find that a distribution of Fe and Ni atoms in the solutions should be very close to completely disordered at these conditions. Using this model of the Fe-Ni system, we have calculated the fcc–hcp structural free energy difference in a wide pressure-temperature range of 120–360 GPa and 1000–6600 K. Our calculations show that alloying of Fe with Ni below 3000 K favours stabilisation of the fcc phase over the
hcp, in agreement with experiments. However, above 3000 K the effect is reversed, and at conditions corresponding to those of the Earth’s inner core, Ni acts as an agent to stabilise the hcp phase.

1. Introduction

Understanding the physics of the Earth’s core can give insight into the origin and behaviour of not only our own planet, but also the other terrestrial planets. In order to interpret seismic data and build geophysical models, knowing the core composition and structure is of high priority. It is generally accepted that the inner core consists of Fe with 5-15 at. % Ni content. The exact composition and crystal structure of this solid solution is still debated due to the difficulty of experimentally reproducing and performing measurements under the extreme pressure and temperature conditions prevailing in the core. At ambient conditions, Fe-Ni alloys are found in both bcc and fcc structures depending on composition — with the latter also found as an underlying lattice in ordered phases for high Ni concentration. At ultra-high pressure and temperature, an hcp phase has been reported in pure Fe up to 380 GPa and 5700 K (Tateno et al., 2010), whilst increasing temperature at moderate pressure has been shown to stabilise an fcc phase (Lin et al., 2002). The fcc phase was also found to be stabilised by increased Ni content (Mao et al., 2006; Kuwayama et al., 2008) at temperatures up to 3500 K and pressures of 200 GPa. In a combined theoretical and experimental study, a bcc phase has also been found in Fe$_{0.9}$Ni$_{0.1}$, at 225 GPa and 3400 K (Dubrovinsky et al., 2007).

Theoretical work on pure Fe has shown that the fcc-hcp-bcc structural
energy differences are very small — in the order of a few mRy/atom (Mikhaylushkin et al., 2007; Vočadlo et al., 2003; Belonoshko et al., 2003). With the inclusion of Si defects, Côté et al. (2010) showed that the energy difference spans 2 mRy/atom. As will be revealed in this Letter, the chemical configurational energy — the energy difference between different distributions of Fe and Ni atoms on the same underlying lattice — is on the same scale as the structural energy difference. This means that the alloy configuration assumed for simulations of phase stability and properties of Fe-Ni alloys cannot be arbitrarily chosen. This is a critical issue which should be addressed accordingly. However, to the best of our knowledge, no systematic study of the alloy configuration has yet been presented, and in many cases the alloys are simulated by ordered systems of the same composition (Vočadlo et al., 2008).

In this work we have investigated the degree of short-range order in Fe-Ni alloys at the conditions of the Earth’s core by ab initio calculations. Using the results as a basis, we have investigated the effect of Ni on the fcc–hcp energy relation in a wide pressure/temperature range, including Earth core conditions. We show that single phase solid solutions of Fe and Ni on underlying fcc and hcp lattices should be very close to completely disordered, and at these conditions, Ni should stabilise the hcp phase with respect to the fcc phase — opposite to what has been reported experimentally at lower temperatures.
2. Computational methodology

2.1. Alloy configuration energetics

We have performed electronic structure calculations within the framework of density functional theory (DFT) for fcc- and hcp-based Fe-Ni alloys. Since the bcc phase found by Dubrovinsky et al. (2007) is dynamically unstable at low temperature and high pressure conditions (Vočadlo et al., 2003), its electronic structure should be very different to that of ambient conditions, as shown by Asker et al. (2008) for the case of Mo. The computational scheme used in this study would therefore lead to a poor description of the electronic structure of such an alloy, and we therefore do not consider this phase at present.

In order to calculate the energies of different distributions of Fe and Ni atoms on the fcc and hcp lattices, we have used a scalar-relativistic implementation of the exact muffin-tin orbitals method (EMTO), in conjunction with the full charge density technique (Vitos, 2001, 2007). Chemically disordered alloys were modelled within the coherent potential approximation (CPA) (Vitos, 2007; Vitos et al., 2005, 2001). The basis set included $s, p, d$ and $f$ muffin-tin orbitals, and we converged absolute total energy with respect to the number of $k$-points in the irreducible Brillouin zone to within 0.1 mRy/atom, using 1785 points for fcc and 1184 points for hcp. Core states were recalculated in each iteration of the self-consistency scheme. We used the generalised gradient approximation (GGA) to the DFT exchange-correlation functional as parametrised by Perdew et al. (1996). This technique has previously been successfully used for simulating the effect of pressure on the properties of Fe-based alloys (Dubrovinsky et al., 2003, 2007; Asker et al.,
2009, 2010; Dubrovinskaia et al., 2005), and is known to yield good agree-
ment with experiment for properties of interest in this study, e.g., short-range
order and mixing enthalpy (Ruban and Abrikosov, 2008)

We have restricted ourselves to non-magnetic calculations, as the mag-
netic moments are expected to be quenched at the extreme pressure of the
Earth’s core in hcp-Fe (Steinle-Neumann et al., 2004) and fcc-FeNi alloys
(Abrikosov et al., 2007). When considering hcp-based alloys, we also found
the total energy to be rather insensitive to the choice of \(c/a\)-ratio. This
observation is in line with previous results of a weakly pressure dependent
\(c/a\)-ratio in Fe-Ni hcp alloys (Asker et al., 2009). By changing the \(c/a\)-ratio
obtained at \(T = 0\) K and \(P = 0\) GPa by an amount corresponding to the
expansion with pressure reported by Asker et al. (2009), the enthalpy change
is less than 0.1 mRy/atom. Furthermore, the \(c/a\)-ratio has been previously
been found rather insensitive to temperature (Tateno et al., 2010). In or-
der to limit the computational burden in our alloy configuration calculations
(Sections 3.1 and 3.2), we therefore used equilibrium \(c/a\)-ratios obtained at
\(T = 0\) K and \(P = 0\) GPa also at elevated temperature and pressure for our
studies of mixing enthalpy and short-range order. Table 1 accounts for the
values used. However, in studies of the hcp-fcc lattice stability (Section 3.3),
the \(c/a\)-ratio was relaxed.

To validate our EMTO-CPA calculations, we have considered the Fe\(_{0.5}\)Ni\(_{0.5}\)
system and calculated total energy differences between a disordered and
an ordered arrangement of the atoms, which is called the ordering energy,
\(\Delta E = E^{\text{ord.}} - E^{\text{disord.}}\) at high pressure. The ordered structure was mod-
elled with Fe and Ni occupying alternating layers in the (001) direction of
the fcc lattice, called L1₀-configuration in the Strukturbericht designation scheme (Crystal Lattice Structures Web page, 2004). For comparison, the ordering energy was also calculated using the projector augmented waves (PAW) (Blöchl, 1994) method, as implemented in the Vienna ab initio simulation package (VASP) (Kresse and Furthmüller, 1996a,b; Kresse and Joubert, 1999). The disordered alloy was in this case modelled using a 64-atom supercell constructed according to the special quasirandom structure (SQS) (Zunger et al., 1990) technique, while setting the basis set cut-off energy to 400 eV and including the 3p-states in the valence band. We used 1183 and 432 irreducible k-points for the ordered and disordered cells, respectively. The resulting difference in the obtained ordering energy, ΔE, from using either the EMTO-CPA or the PAW-SQS methods was below 0.1 mRy / atom.

2.1.1. Thermodynamic calculations

EMTO-CPA calculations were performed for fixed lattices, and the influence of temperature on electronic structure was included in terms of thermal electronic population effects, which can be achieved by including the Fermi-Dirac distribution function, f, when solving the Kohn-Sham equations (Mermin, 1965). Electronic entropy at temperature T for a given system can then be evaluated as:

\[
S_{el}(T) = - \int dE N(E, T) \cdot [f(E, T) \ln f(E, T) + (1 - f(E, T)) \ln(1 - f(E, T))],
\]

where \(N(E, T)\) is the electronic density of states (Ruban and Abrikosov, 2008).

For each concentration of Ni considered, \(x\), we fitted the total energy obtained from first-principles calculations to the third-order Birch-Murnaghan...
equation of state (Birch, 1947) in order to interpolate enthalpy, $H$, as a function of pressure, $P$. The volumes and compositions at which total energy was calculated are given in the Supplementary Material. The $K'$ parameter was found to be between 4.4 and 4.7 in all systems considered. We then calculated the isostructural enthalpy of mixing as:

$$\Delta H(x, P, T) = H(x, P, T) - xH_{\text{Ni}}(P, T) - (1-x)H_{\text{Fe}}(P, T),$$

where all the enthalpies were evaluated assuming the same underlying crystal structure, which is the appropriate method for the analysis of configurational thermodynamics on a fixed underlying crystal lattice. Positive sign of $\Delta H$ indicates instability of the mixture of Fe and Ni atoms with respect to segregation into pure Fe and Ni components at low $T$. We have also evaluated the electronic entropy difference between mixing and segregation as:

$$\Delta S_{\text{el}}(x, P, T) = S_{\text{el}}(x, P, T) - xS_{\text{el}}^{\text{Ni}}(P, T) - (1-x)S_{\text{el}}^{\text{Fe}}(P, T).$$

2.1.2. Estimation of ordering temperature

It has been shown (Zarkevich et al., 2007) that for phase segregating alloys where the difference in electronegativity between the constituents is small and the mixing enthalpy is symmetric with respect to the equiatomic composition, a quick estimate of the temperature of transition from segregation to mixing, $T_c$, can be found from evaluating:

$$T_c(x) = \frac{\Delta H(x)}{\Delta S_{\text{conf}}(x)},$$

where $\Delta S_{\text{conf}}(x)$ is the configurational entropy difference taken as:

$$\Delta S_{\text{conf}}(x) \propto -[x \log x + (1-x) \log(1-x)].$$
The difference in electronegativity between Fe and Ni is 0.08, which is a small
value and justifies the use of Eqs. (4) and (5) for this system.

We have investigated the alloy configuration at high temperature and
pressure by performing Monte-Carlo simulations using the effective interac-
tion parameters of the (screened) generalised perturbation method (GPM)
(Ruban et al., 2004). A review of such simulations has been presented by
Ruban and Abrikosov (2008). The concentration-dependent GPM parama-
ters can be expected to provide a good description of atomic configurations
in phase-segregating systems at temperatures far above or below the order-
disorder transition. When calculating GPM parameters we increased the
number of \( k \)-points to 3146 in the irreducible Brillouin zone. Further de-
tails of GPM effective interaction parameters in Fe-Ni are accounted for in
the supplementary materials. The size of the Monte-Carlo simulation box
was \( 20 \times 20 \times 20 \) unit cells. We tested the accuracy of our GPM parama-
ters by calculating the ordering energy, \( \Delta E \), (see previous section) for the
\( \text{Fe}_{0.75}\text{Ni}_{0.25} \) system by cluster expansion, and comparing the result with that
obtained from direct total energy calculations of \( E^{\text{ord.}} \) and \( E^{\text{disord.}} \) with the
EMTO-CPA method. For the ordered system the \( \text{L}_1^2 \) (Strukturbericht) con-
figuration (Crystal Lattice Structures Web page, 2004) was chosen, where the
corner sites of the cubic fcc conventional cell (Kittel, 1996) are occupied by
Ni and the face sites are occupied by Fe atoms. We found the difference in
the resulting value of \( \Delta E \) obtained from cluster expansion and total energy
calculations to be within 0.4 mRy.
2.1.3. Short-range ordering

To quantify the degree of order in the alloys we use the well known Warren-Cowley short-range order parameter (Cowley, 1950). For a binary alloy of $A$ and $B$ atoms, this can be defined as:

$$\alpha_i^{AB} = 1 - \frac{P_i(A|B)}{c_B},$$  \hspace{1cm} (6)

where $P_i(A|B)$ is the average conditional probability of finding a $B$-atom in the $i$:th coordination shell of an $A$-atom and $c_B$ is the concentration of $B$-atoms. In a completely disordered (random) alloy, $\alpha_i = 0$.

2.2. Vibrational effects

In order to account for vibrational effects neglected in Sec. 2.1, and their effect on the free energy at high temperature, we have performed calculations of the electronic and phononic spectra of Fe and Fe$_{1-x}$Ni$_x$, with $x = 0, 0.05, 0.10, 0.20$, using the PAW method. We used fine $k$-meshes with about 1000 irreducible $k$-points chosen according to the Monkhorst-Pack scheme for each structure. The basis set energy cut-off was set to 500 eV and we treated the $4s$, $4p$, $3d$ as well as the $3p$ semicore states of Fe and Ni as valence states. The $k$-mesh for the fcc (27 atoms) and hcp (54 atoms) structures were $8 \times 8 \times 8$ and $5 \times 5 \times 5$, respectively, which allowed us to converge the fcc–hcp free energy difference to within a few tenths of mRy/atom.

2.2.1. Free energy calculations

Phonon-frequency calculations were carried out within the framework of the supercell approach (small displacement method), as described in detail by Alfé (2009), with supercells consisting of $3 \times 3 \times 3$ unit cells. Since both the fcc
and hcp phases of Fe and Fe-Ni alloys are dynamically stable in the considered
$P-T$ range, the vibrational energy, can be treated within the quasiharmonic
approximation, an assumption further validated for these systems by the
close agreement of quasiharmonic and anharmonic calculations in pure Fe
(Mikhaylushkin et al., 2007; Vočadlo et al., 2008). The Helmholtz free energy
of the crystal, $F$, can then obtained as the sum of contribution to the static
unit cells, and the vibrational part of the free energy, $F = F_0 + F_{\text{vib}}$.

In order to model the disordered alloy configuration while investigating
the dynamical behavior of the Fe-Ni alloys with the PAW technique, we
have used the so-called virtual crystal approximation (VCA) (for details,
see Mikhaylushkin et al. (2005); Haussermann and Mikhaylushkin (2010)).
The VCA is known to work well for alloys between neighbouring elements
in the periodic table (Faulkner, 1982). In order to establish its accuracy for
our system, we have calculated the fcc-hcp enthalpy differences at $T = 0$ K
for pure Fe and the Fe$_{0.75}$Ni$_{0.25}$ alloy within the EMTO-CPA and PAW-
VCA, which are compared in Fig. 1. For pure Fe, the EMTO–PAW energy
difference is approximately 1 mRy / atom, which should be attributed to
the difference between the underlying methods for the electronic structure
calculations. As the Ni content is increased to 25%, the difference is below
0.5 mRy / atom at 350 GPa, indicating that the VCA error is about 0.5–1
mRy / atom. We thus observe quantitatively good agreement between the
CPA and VCA results for Fe-Ni system.

In these calculations, we relaxed the $c/a$-ratio of the hcp structure by
minimisation of the electronic free energy contribution, $F_0$. By fitting to-
tal energy as a function of volume to the Birch-Murnaghan (Birch, 1947)
Figure 1: Enthalpy difference between disordered fcc- and hcp-FeNi alloys at $T = 0$ K, calculated within the PAW-VCA and EMTO-CPA approximations for disordered alloys.

equation of state, we obtained the Gibb’s free energy, $G$, for the fcc and hcp phases.

3. Results and discussion

3.1. Isostructural mixing enthalpy

3.1.1. fcc

Using the EMTO-CPA method, we have studied formation energy of Fe-Ni systems with respect to the pure Fe and Ni constituents. In Fig. 2 we show mixing enthalpy of the ordered compounds $L_1^2$-Fe$_3$Ni, $L_1^0$-FeNi, and $L_1^2$-FeNi$_3$ with respect to fcc-Fe and fcc-Ni. In all cases the mixing enthalpy is positive, indicating the tendency of the Fe and Ni atoms to segregate. It should be noted that at ambient conditions, this tendency is reversed, and the system shows pronounced mixing trends (Ruban et al., 2007; Massalki et al.,
Figure 2: Mixing enthalpies of ordered $L1_2$-$Fe_3Ni$, $L1_0$-$FeNi$ and $L1_2$-$FeNi_3$.

Figure 3: Mixing enthalpy (in mRy/atom) for disordered fcc-$Fe_{1-x}Ni_x$. 
Figure 4: Mixing enthalpies of disordered hcp-FeNi at 12.5, 25, 50 and 75% Ni composition.

Figure 5: Mixing enthalpies of ordered L1_2-Fe_3Ni, L1_0-FeNi and L1_2-FeNi_3 calculated with electronic temperature of 5000 K.
Figure 6: Mixing enthalpy in (mRy/atom) for disordered fcc-Fe$_{1-x}$Ni$_x$ (in mRy) including electronic temperature of 5000 K.

Figure 7: Mixing enthalpy for disordered hcp-FeNi at 12.5, 25, 50 and 75 % Ni composition including electronic temperature of 5000 K.
1986). As previously demonstrated for Fe-based alloys, the main reason for this opposite behaviour is that the magnetic interactions are suppressed at high pressure (Abrikosov et al., 1996). This can be compared to the case of disordered fcc-Fe$_{1-x}$Ni$_x$, shown in Fig. 3, which also shows positive mixing enthalpy.

Since the mixing enthalpy of the fcc-based alloys is very symmetric with respect to composition, we may use Eq. (4) for a quick estimate of the critical temperature of phase transition from segregation to disordered mixing, which we compute to 790 K at $x = 0.125$ and $P = 350$ GPa. This is far below the temperature of the core.

We also note that the mixing enthalpy is clearly lower for the disordered alloy than for the ordered compounds throughout the entire pressure and composition range, which means that the completely disordered state is more favourable than the perfectly ordered state. In particular, at 350 GPa the disordered Fe$_{0.75}$Ni$_{0.25}$ alloy has a lower mixing enthalpy than the ordered Fe$_3$Ni compound by 3 mRy, which is a non-negligible amount compared to the reported structural energy differences (see Sec 1). This observation clearly demonstrates the inadequacy of using small ordered supercells as models of Fe-Ni alloys at the conditions of the Earth’s core; and motivates further investigation of the Fe-Ni alloy configuration at these conditions, in order to establish a more appropriate model, which we present in Sec. 3.2.

3.1.2. hcp

Fig. 4 shows mixing enthalpy of the disordered hcp-based alloy. A mean field estimation yields transition temperature 1400 K at Earth’s core conditions, although the mixing enthalpy is not as symmetric as in the case of fcc.
This indicates that mixing will occur also on the hcp lattice at the conditions of the Earth’s core.

To estimate the importance of finite temperature effects in our simulations, we have calculated the isostructural mixing enthalpy while including electronic excitations through the Fermi function, with $T = 5000$ K. We obtain the mixing enthalpy shown in Fig. 5 for the ordered fcc compounds. Fermi smearing *increases* the mixing enthalpy, a feature in common with the case of the disordered fcc- and hcp-based phases, shown in Figs. 6 and 7. Increase of the mixing enthalpy with electronic temperature can be understood from comparing its influence on the electronic structure of the alloy and on the pure Fe and Ni constituents separately. When Fe and Ni atoms are disordered on the fcc lattice, the lifetime of electronic states becomes finite due to the chemical disorder. The bands are broadened in comparison to the pure constituents, which translates into smearing of the Van-Hove singularities in the electronic density of states. Therefore, the effect of temperature smearing is not as pronounced in the alloy as in the pure constituents, which have peaks close to the Fermi level. Smearing of these peaks lowers total energy, and by Eq. (2), mixing enthalpy is therefore increased. Nevertheless, at this temperature, $T\Delta(S_{\text{conf}} + S_{\text{el}}) \sim 12.1$ and 13.1 mRy / atom at 12.5% Ni content for fcc and hcp respectively, which is much larger than $\Delta H$, indicating that in spite of the increase in $\Delta H$, mixing should still occur at Earth core conditions.

3.1.3. Impact of lattice vibrations

We have also evaluated the effect of lattice vibrations on isostructural mixing, which was absent in the above considerations, by separately performing
VCA calculations of the vibrational contribution to the mixing enthalpy in disordered fcc-based Fe-Ni alloys at the temperature of 5000 K. This contribution is negative, as shown in Fig. 8, indicating its stabilising effect on the disordered alloy as compared to the segregated state.

In light of the results presented in this section, we may therefore conclude that Fe and Ni atoms will mix at the conditions of the Earth’s core. Although this conclusion may seem intuitive, the results concerning the structural and chemical ordering energies also prove that it is essential to develop an appropriate configurational model of Fe-Ni alloys at extreme conditions. We address this issue in the following section.

3.2. Short-range order

As our results for mixing enthalpy presented in Sec. 3.1 indicate mixing for both fcc- and hcp-based alloys, and the chemical ordering energy is comparable to the structural energy difference, it is crucial to investigate what degree of clustering that will prevail at high temperature and pressure. We have therefore performed Monte-Carlo simulations for the fcc- and hcp-based solutions at 5000 K and 400 GPa, and then calculated the Warren-Cowley short-range order parameter — defined in Eq. (6) — as a function of coordination shell, \( i \).

Results are presented in Fig. 9. For both underlying crystal structures, the short-range order parameter is finite. However, the magnitude of \( \alpha \) is so small that the fcc and hcp phases can be considered close to completely disordered. These results show that a mixture of Fe and Ni atoms on the fcc and hcp lattices should be described by models of completely disordered alloys. In particular, we draw the conclusion that in dynamical simulations of
Figure 8: Vibrational contribution to the mixing enthalpy of disordered fcc-FeNi alloys at 5000 K calculated with the VCA method.
phase stability at the conditions of the Earth’s core, the Fe-Ni system should not be modelled an ordered compound, and results for the properties of such systems, obtained for ordered compounds (Vočadlo et al., 2008), should be taken with caution.

3.3. **fcc-hcp free energy differences at high temperature and pressure**

Having established the validity of the chemically disordered model of Fe-Ni alloys at the conditions of the Earth’s core, we are in a position of applying the effective methods of alloy theory developed for this particular case (Ruban and Abrikosov, 2008). In this section, we show calculated Gibbs free energy differences of hcp- and fcc-FeNi alloys, including vibrational effects with the VCA method.

In previous work on pure Fe by Mikhaylushkin et al. (2007), it was shown
that in the high pressure range, the slope of the fcc-hcp transition curve in
the $P - T$ phase diagram essentially decreases compared to the slope of the
melting curve. Since in this region, the melting temperature is increased with
pressure, the fcc phase may be stabilised at the conditions of the Earth’s core.

To analyse the influence of incorporating Ni into Fe, we computed the Gibbs
free energy differences between the fcc and hcp phases ($\Delta G$) as a function
of pressure at various temperatures. Our results are presented in Fig. 10,
where $\Delta G > 0$ indicates relative stability of hcp phase and $\Delta G < 0$ indicates
stability of the fcc phase at fixed alloy composition. We find that at 2000 K,
hcp has lower energy than fcc in the entire pressure range for both pure Fe
and Fe-Ni alloys. Compression increases $\Delta G$, i.e., it works in favour of the
hcp phase. However, we note that $\Delta G$ is lower for Fe-Ni than for pure Fe and
is further decreased as the Ni content increases in the entire pressure range,
which means that incorporation of Ni stabilises the disordered fcc alloy rel-
ative to hcp. When temperature is increased to 4000 K, we observe that
the $\Delta G$ curve is shifted down considerably, so that the fcc phase becomes
lower in energy within the pressure range below 170 GPa for pure Fe, and
below 190 GPa for Fe$_{0.8}$Ni$_{0.2}$. Upon further heating, this region expands.
Our results concerning the effect of Ni are so far in accordance with available
electric- and laser-heating high-pressure experiments (see Kuwayama et al.
(2008) and references therein). Interestingly, we may also note that as com-
pared to the low temperature (2000 K) regime, the influence of Ni on the
fcc-hcp energy difference also decreases. Remarkably, in the temperature in-
terval 3000–4000 K, the $\Delta G$ curve for the Fe$_{0.9}$Ni$_{0.1}$ alloy approaches that of
pure Fe.
To further investigate the observed effect, we raised the temperature to 6600 K. The free energy difference never exceeds 1.3 mRy / atom, and becomes very small as the pressure approaches 360 GPa. The pressure range in which the fcc structure is lower in energy increases to 360 GPa for up to 10 % Ni. Moreover, the order of the curves is reversed as compared to simulations at lower temperatures. This means that the influence of Ni incorporation in Fe at this temperature is opposite to that found in both theory and experiment at lower temperature. In the Supplementary Materials, we provide a discussion of this effect in terms of the behaviour of the electronic density of (free energy) states, which we have calculated high temperature and pressure. It should be noted that at actual conditions of the Earth’s core, ∆G is close to 0, which is similar to the situation in pure Fe (Mikhaylushkin et al., 2007) Nevertheless, we may conclude that the stabilising effect of Ni incorporation changes continuously under heating. In particular, at 6600 K, the effect of Ni incorporation has a tendency to destabilise the fcc phase in favour of the hcp phase.

Moreover, it should be mentioned that it has been shown theoretically and experimentally, that Ni has a very strong stabilising effect on the bcc phase (Dubrovinsky et al., 2007), not considered in this study. Also, at conditions close to the Earth’s core, the differences in the Gibbs energies among all the phases of Fe-Ni alloys becomes very small. Therefore, the presence of either one cannot be ruled out, and the subtle energy difference between the phases at such temperatures may lead to a co-existence of two or more phases.
Figure 10: Gibb’s free energy difference between disordered fcc- and hcp-based Fe-Ni alloys at high pressure and temperature, where $\Delta G > 0$ indicates relative stability of the hcp phase. For $T = 2000$ K and $4000$ K, Ni acts to stabilise the fcc phase, in line with experiment. At $T = 6600$ K, its effect is the opposite, stabilising the hcp phase.
4. Summary and conclusions

We have performed ab-intio calculations of the mixing enthalpy of fcc-based Fe-Ni alloys at the pressure and temperature conditions prevailing in the Earth's core. We find that the difference in mixing enthalpy between ordered and disordered fcc-based alloys, is on the same scale as the fcc-hcp structural energy difference. This means that the model used for simulations of this structural stability must be carefully constructed with respect to chemical configuration. By means of Monte-Carlo simulations, using calculated effective interaction parameters, we find that that fcc- and hcp-FeNi alloys will be very close to completely disordered at these conditions. In particular, this means that predictions of properties of Fe-Ni alloys, based on models of ordered Fe-Ni compounds, should be interpreted with caution.

Modelling Fe-Ni alloys as completely disordered, we have determined structural energy differences between the fcc and hcp phases of Fe-Ni alloys at extreme $P - T$ conditions. In the $P - T$ intervals available for the existing experimental tools ($\sim 100–250$ GPa and $\sim 1000–3000$ K) we find excellent agreement between our results and experimental data. In particular, we observe that incorporating small amounts of Ni into Fe has a stabilising effect on the fcc phase in a wide $P - T$ range. In contrast, at higher temperature ($\sim 4000–8000$ K) the effect of Ni alloying in the Fe-Ni system is profoundly changed: Ni acts as an agent to stabilise the hcp phase.

We gratefully acknowledge L. Dubrovinsky for useful discussions. This project was supported by the Swedish Research Council (VR) and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine. Calculations were performed at the facilities provided within the Swedish Na-
tional Infrastructure for Computing (SNIC).
A. Hcp unit cell shape

Table 1: Obtained equilibrium $c/a$-ratios for hcp-Fe$_{1-x}$Ni$_x$ at $T = 0$ K and $P = 0$ GPa.

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.00</th>
<th>12.5</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(c/a)_0$</td>
<td>1.59</td>
<td>1.60</td>
<td>1.60</td>
<td>1.62</td>
<td>1.63</td>
<td>1.64</td>
</tr>
</tbody>
</table>

References


Asker, C., Kargn, U., Dubrovinsky, L., Abrikosov, I., 2010. Equation of state and elastic properties of face-centered-cubic fe-mg alloy at ultrahigh


Dubrovinskaia, N., Dubrovinsky, L., Kantor, I., Crichton, W. A., Dmitriev, V., Prakapenka, V., Shen, G., Vitos, L., Ahuja, R., Johansson, B.,


Vitos, L., Abrikosov, I. A., Johansson, B., 2001. Anisotropic lattice distor-


