

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:

Marcus Ekholm, Arkady Mikhaylushkin, Sergey Simak, B Johansson and Igor Abrikosov, Configurational thermodynamics of Fe-Ni alloys at Earths core conditions, 2011, Earth and Planetary Science Letters, (308), 1-2, 90-96.

<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>

Configurational thermodynamics of Fe-Ni alloys at Earth's core conditions

M. Ekholm^{1,2}, A. S. Mikhaylushkin¹, S. I. Simak¹, B. Johansson³,
I.A. Abrikosov¹

⁽¹⁾ *Department of Physics, Chemistry and Biology (IFM)
Linköping University, SE-58183 Linköping, Sweden*

⁽²⁾ *Swedish e-Science Research Centre (SeRC)*

⁽³⁾ *Applied Materials Physics
Department of Materials and Engineering
Royal Institute of Technology (KTH)
SE-10044 Stockholm, Sweden*

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 $\text{Fe}_{0.9}\text{Ni}_{0.1}$, at 225 GPa and 3400 K (Dubrovinsky et al., 2007).

Theoretical work on pure Fe has shown that the fcc-hcp-bcc structural

22 energy differences are very small — in the order of a few mRy/atom (Mikhay-
23 lushkin et al., 2007; Vočadlo et al., 2003; Belonoshko et al., 2003). With the
24 inclusion of Si defects, Côté et al. (2010) showed that the energy difference
25 spans 2 mRy/atom. As will be revealed in this Letter, the chemical con-
26 figurational energy — the energy difference between different distributions
27 of Fe and Ni atoms on the same underlying lattice — is on the same scale
28 as the structural energy difference. This means that the alloy configuration
29 assumed for simulations of phase stability and properties of Fe-Ni alloys can-
30 not be arbitrarily chosen. This is a critical issue which should be addressed
31 accordingly. However, to the best of our knowledge, no systematic study of
32 the alloy configuration has yet been presented, and in many cases the alloys
33 are simulated by *ordered* systems of the same composition (Vočadlo et al.,
34 2008).

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

44 **2. Computational methodology**

45 *2.1. Alloy configuration energetics*

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

55 In order to calculate the energies of different distributions of Fe and Ni
56 atoms on the fcc and hcp lattices, we have used a scalar-relativistic imple-
57 mentation of the exact muffin-tin orbitals method (EMTO), in conjunction
58 with the full charge density technique (Vitos, 2001, 2007). Chemically dis-
59 ordered alloys were modelled within the coherent potential approximation
60 (CPA) (Vitos, 2007; Vitos et al., 2005, 2001). The basis set included s , p , d
61 and f muffin-tin orbitals, and we converged absolute total energy with respect
62 to the number of \mathbf{k} -points in the irreducible Brillouin zone to within 0.1 mRy
63 / atom, using 1785 points for fcc and 1184 points for hcp. Core states were
64 recalculated in each iteration of the self-consistency scheme. We used the
65 generalised gradient approximation (GGA) to the DFT exchange-correlation
66 functional as parametrised by Perdew et al. (1996). This technique has pre-
67 viously been successfully used for simulating the effect of pressure on the
68 properties of Fe-based alloys (Dubrovinsky et al., 2003, 2007; Asker et al.,

69 2009, 2010; Dubrovinskaia et al., 2005), and is known to yield good agree-
70 ment with experiment for properties of interest in this study, e.g., short-range
71 order and mixing enthalpy (Ruban and Abrikosov, 2008)

72 We have restricted ourselves to non-magnetic calculations, as the mag-
73 netic moments are expected to be quenched at the extreme pressure of the
74 Earth’s core in hcp-Fe (Steinle-Neumann et al., 2004) and fcc-FeNi alloys
75 (Abrikosov et al., 2007). When considering hcp-based alloys, we also found
76 the total energy to be rather insensitive to the choice of c/a -ratio. This
77 observation is in line with previous results of a weakly pressure dependent
78 c/a -ratio in Fe-Ni hcp alloys (Asker et al., 2009). By changing the c/a -ratio
79 obtained at $T = 0$ K and $P = 0$ GPa by an amount corresponding to the
80 expansion with pressure reported by Asker et al. (2009), the enthalpy change
81 is less than 0.1 mRy / atom. Furthermore, the c/a -ratio has been previously
82 been found rather insensitive to temperature (Tateno et al., 2010). In or-
83 der to limit the computational burden in our alloy configuration calculations
84 (Sections 3.1 and 3.2), we therefore used equilibrium c/a -ratios obtained at
85 $T = 0$ K and $P = 0$ GPa also at elevated temperature and pressure for our
86 studies of mixing enthalpy and short-range order. Table 1 accounts for the
87 values used. However, in studies of the hcp-fcc lattice stability (Section 3.3),
88 the c/a -ratio was relaxed.

89 To validate our EMTO-CPA calculations, we have considered the $\text{Fe}_{0.5}\text{Ni}_{0.5}$
90 system and calculated total energy differences between a disordered and
91 an ordered arrangement of the atoms, which is called the ordering energy,
92 $\Delta E = E^{\text{ord.}} - E^{\text{disord.}}$ at high pressure. The ordered structure was mod-
93 elled with Fe and Ni occupying alternating layers in the (001) direction of

94 the fcc lattice, called L1₀-configuration in the Strukturbericht designation
 95 scheme (Crystal Lattice Structures Web page, 2004). For comparison, the
 96 ordering energy was also calculated using the projector augmented waves
 97 (PAW) (Blöchl, 1994) method, as implemented in the Vienna ab initio sim-
 98 ulation package (VASP) (Kresse and Furthmüller, 1996a,b; Kresse and Jou-
 99 bert, 1999). The disordered alloy was in this case modelled using a 64-atom
 100 supercell constructed according to the special quasirandom structure (SQS)
 101 (Zunger et al., 1990) technique, while setting the basis set cut-off energy to
 102 400 eV and including the 3*p*-states in the valence band. We used 1183 and 432
 103 irreducible **k**-points for the ordered and disordered cells, respectively. The
 104 resulting difference in the obtained ordering energy, ΔE , from using either
 105 the EMTO-CPA or the PAW-SQS methods was below 0.1 mRy / atom.

106 *2.1.1. Thermodynamic calculations*

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

$$\begin{aligned}
 S_{\text{el}}(T) = & - \int dE N(E, T) \cdot [f(E, T) \ln f(E, T) \\
 & + (1 - f(E, T)) \ln(1 - f(E, T))], \tag{1}
 \end{aligned}$$

113 where $N(E, T)$ is the electronic density of states (Ruban and Abrikosov,
 114 2008).

115 For each concentration of Ni considered, x , we fitted the total energy ob-
 116 tained from first-principles calculations to the third-order Birch-Murnaghan

117 equation of state (Birch, 1947) in order to interpolate enthalpy, H , as a func-
 118 tion of pressure, P . The volumes and compositions at which total energy
 119 was calculated are given in the Supplementary Material. The K' parameter
 120 was found to be between 4.4 and 4.7 in all systems considered. We then
 121 calculated the isostructural enthalpy of mixing as:

$$\begin{aligned} \Delta H(x, P, T) = & H(x, P, T) \\ & - xH^{\text{Ni}}(P, T) - (1 - x)H^{\text{Fe}}(P, T), \end{aligned} \quad (2)$$

122 where all the enthalpies were evaluated assuming the same underlying crystal
 123 structure, which is the appropriate method for the analysis of configurational
 124 thermodynamics on a fixed underlying crystal lattice. Positive sign of ΔH
 125 indicates instability of the mixture of Fe and Ni atoms with respect to seg-
 126 regation into pure Fe and Ni components at low T . We have also evaluated
 127 the electronic entropy difference between mixing and segregation as:

$$\begin{aligned} \Delta S_{\text{el}}(x, P, T) = & S_{\text{el}}(x, P, T) \\ & - xS_{\text{el}}^{\text{Ni}}(P, T) - (1 - x)S_{\text{el}}^{\text{Fe}}(P, T). \end{aligned} \quad (3)$$

128 2.1.2. Estimation of ordering temperature

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

$$T_c(x) = \frac{\Delta H(x)}{\Delta S_{\text{conf}}(x)}, \quad (4)$$

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

$$\Delta S_{\text{conf}}(x) \propto -[x \log x + (1 - x) \log(1 - x)]. \quad (5)$$

135 The difference in electronegativity between Fe and Ni is 0.08, which is a small
136 value and justifies the use of Eqs. (4) and (5) for this system.

137 We have investigated the alloy configuration at high temperature and
138 pressure by performing Monte-Carlo simulations using the effective interac-
139 tion parameters of the (screened) generalised perturbation method (GPM)
140 (Ruban et al., 2004). A review of such simulations has been presented by
141 Ruban and Abrikosov (2008). The concentration-dependent GPM parame-
142 ters can be expected to provide a good description of atomic configurations
143 in phase-segregating systems at temperatures far above or below the order-
144 disorder transition. When calculating GPM parameters we increased the
145 number of \mathbf{k} -points to 3146 in the irreducible Brillouin zone. Further de-
146 tails of GPM effective interaction parameters in Fe-Ni are accounted for in
147 the supplementary materials. The size of the Monte-Carlo simulation box
148 was $20 \times 20 \times 20$ unit cells. We tested the accuracy of our GPM parame-
149 ters by calculating the ordering energy, ΔE , (see previous section) for the
150 $\text{Fe}_{0.75}\text{Ni}_{0.25}$ system by cluster expansion, and comparing the result with that
151 obtained from direct total energy calculations of $E^{\text{ord.}}$ and $E^{\text{disord.}}$ with the
152 EMTO-CPA method. For the ordered system the L1₂- (Strukturbericht) con-
153 figuration (Crystal Lattice Structures Web page, 2004) was chosen, where the
154 corner sites of the cubic fcc conventional cell (Kittel, 1996) are occupied by
155 Ni and the face sites are occupied by Fe atoms. We found the difference in
156 the resulting value of ΔE obtained from cluster expansion and total energy
157 calculations to be within 0.4 mRy.

158 *2.1.3. Short-range ordering*

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

$$\alpha_i^{AB} = 1 - \frac{P_i(A|B)}{c^B}, \quad (6)$$

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

165 *2.2. Vibrational effects*

166 In order to account for vibrational effects neglected in Sec. 2.1, and their
167 effect on the free energy at high temperature, we have performed calcu-
168 lations of the electronic and phononic spectra of Fe and $\text{Fe}_{1-x}\text{Ni}_x$, with
169 $x = 0, 0.05, 0.10, 0.20$, using the PAW method. We used fine \mathbf{k} -meshes with
170 about 1000 irreducible \mathbf{k} -points chosen according to the Monkhorst-Pack
171 scheme for each structure. The basis set energy cut-off was set to 500 eV
172 and we treated the $4s$, $4p$, $3d$ as well as the $3p$ semicore states of Fe and Ni as
173 valence states. The \mathbf{k} -mesh for the fcc (27 atoms) and hcp (54 atoms) struc-
174 tures were $8 \times 8 \times 8$ and $5 \times 5 \times 5$, respectively, which allowed us to converge
175 the fcc-hcp free energy difference to within a few tenths of mRy/atom.

176 *2.2.1. Free energy calculations*

177 Phonon-frequency calculations were carried out within the framework of
178 the supercell approach (small displacement method), as described in detail by
179 Alfé (2009), with supercells consisting of $3 \times 3 \times 3$ unit cells. Since both the fcc

180 and hcp phases of Fe and Fe-Ni alloys are dynamically stable in the considered
181 $P-T$ range, the vibrational energy, can be treated within the quasiharmonic
182 approximation, an assumption further validated for these systems by the
183 close agreement of quasiharmonic and anharmonic calculations in pure Fe
184 (Mikhaylushkin et al., 2007; Vočadlo et al., 2008). The Helmholtz free energy
185 of the crystal, F , can then be obtained as the sum of contribution to the static
186 unit cells, and the vibrational part of the free energy, $F = F_0 + F_{\text{vib}}$.

187 In order to model the disordered alloy configuration while investigating
188 the dynamical behavior of the Fe-Ni alloys with the PAW technique, we
189 have used the so-called virtual crystal approximation (VCA) (for details,
190 see Mikhaylushkin et al. (2005); Häussermann and Mikhaylushkin (2010)).
191 The VCA is known to work well for alloys between neighbouring elements
192 in the periodic table (Faulkner, 1982). In order to establish its accuracy for
193 our system, we have calculated the fcc-hcp enthalpy differences at $T = 0$ K
194 for pure Fe and the $\text{Fe}_{0.75}\text{Ni}_{0.25}$ alloy within the EMTO-CPA and PAW-
195 VCA, which are compared in Fig. 1. For pure Fe, the EMTO-PAW energy
196 difference is approximately 1 mRy / atom, which should be attributed to
197 the difference between the underlying methods for the electronic structure
198 calculations. As the Ni content is increased to 25%, the difference is below
199 0.5 mRy / atom at 350 GPa, indicating that the VCA error is about 0.5–1
200 mRy / atom. We thus observe quantitatively good agreement between the
201 CPA and VCA results for Fe-Ni system.

202 In these calculations, we relaxed the c/a -ratio of the hcp structure by
203 minimisation of the electronic free energy contribution, F_0 . By fitting to-
204 tal energy as a function of volume to the Birch-Murnaghan (Birch, 1947)

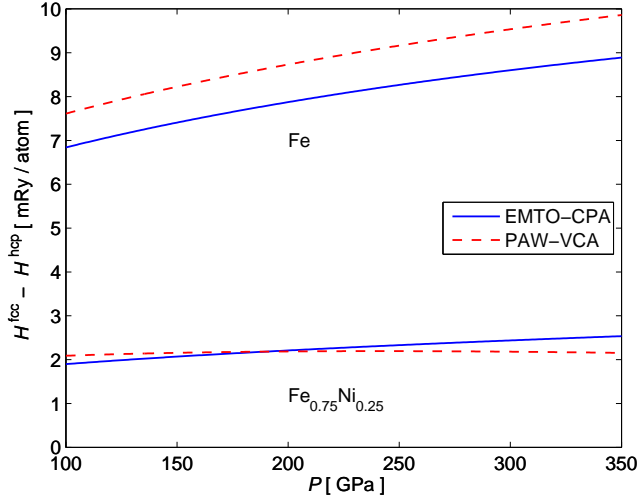


Figure 1: Enthalpy difference between disordered fcc- and hcp-FeNi alloys at $T = 0$ K, calculated within the PAW-VCA and EMTO-CPA approximations for disordered alloys.

205 equation of state, we obtained the Gibb's free energy, G , for the fcc and hcp
 206 phases.

207 3. Results and discussion

208 3.1. Isostructural mixing enthalpy

209 3.1.1. fcc

210 Using the EMTO-CPA method, we have studied formation energy of Fe-
 211 Ni systems with respect to the pure Fe and Ni constituents. In Fig. 2 we
 212 show mixing enthalpy of the ordered compounds $L1_2$ -Fe₃Ni, $L1_0$ -FeNi, and
 213 $L1_2$ -FeNi₃ with respect to fcc-Fe and fcc-Ni. In all cases the mixing enthalpy
 214 is positive, indicating the tendency of the Fe and Ni atoms to segregate. It
 215 should be noted that at ambient conditions, this tendency is reversed, and the
 216 system shows pronounced mixing trends (Ruban et al., 2007; Massalki et al.,

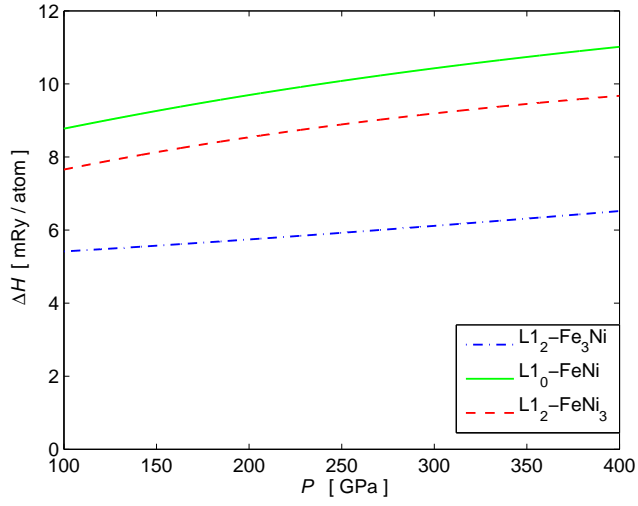


Figure 2: Mixing enthalpies of ordered L1₂-Fe₃Ni, L1₀-FeNi and L1₂-FeNi₃.

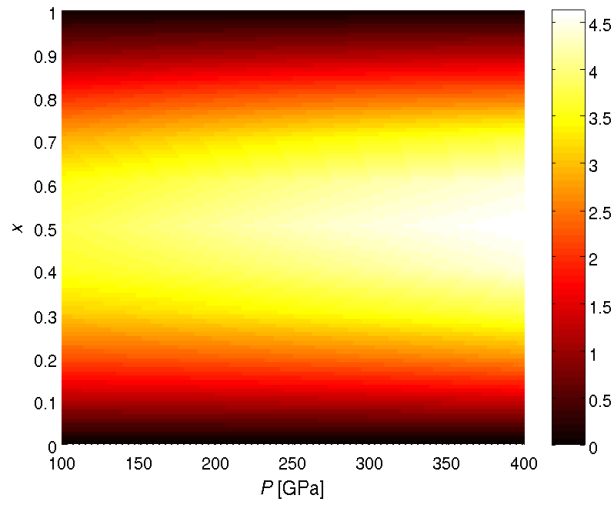


Figure 3: Mixing enthalpy (in mRy/atom) for disordered fcc-Fe_{1-x}Ni_x.

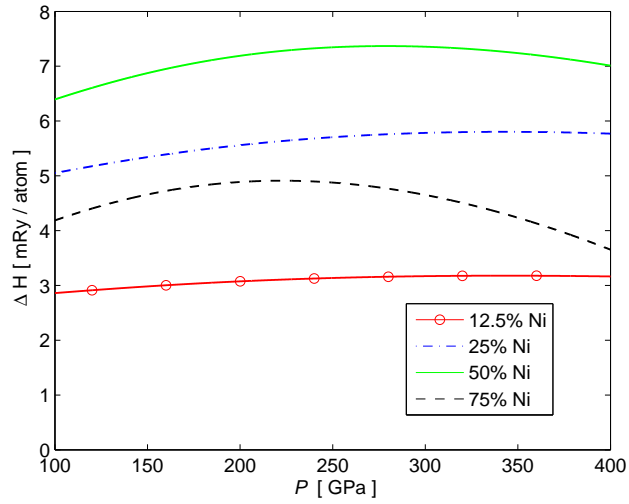


Figure 4: Mixing enthalpies of disordered hcp-FeNi at 12.5, 25, 50 and 75% Ni composition.

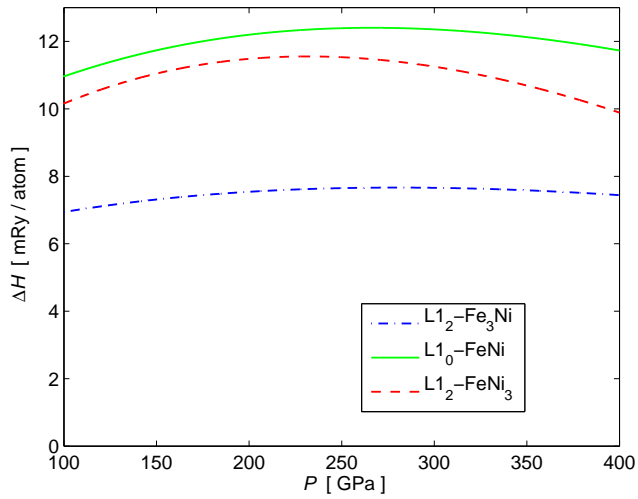


Figure 5: Mixing enthalpies of ordered L1₂-Fe₃Ni, L1₀-FeNi and L1₂-FeNi₃ calculated with electronic temperature of 5000 K.

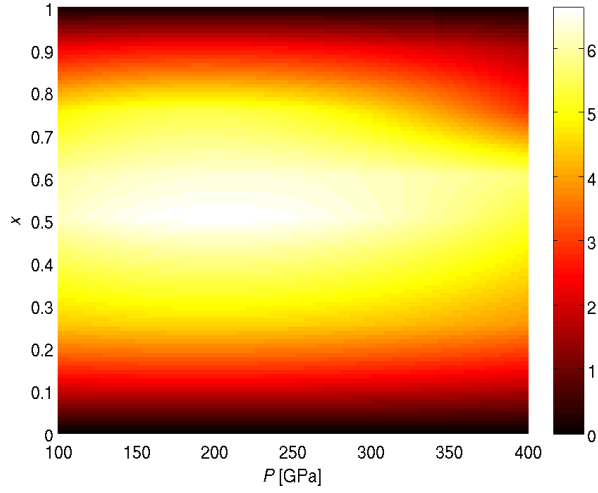


Figure 6: Mixing enthalpy in (mRy/atom) for disordered fcc-Fe_{1-x}Ni_x (in mRy) including electronic temperature of 5000 K.

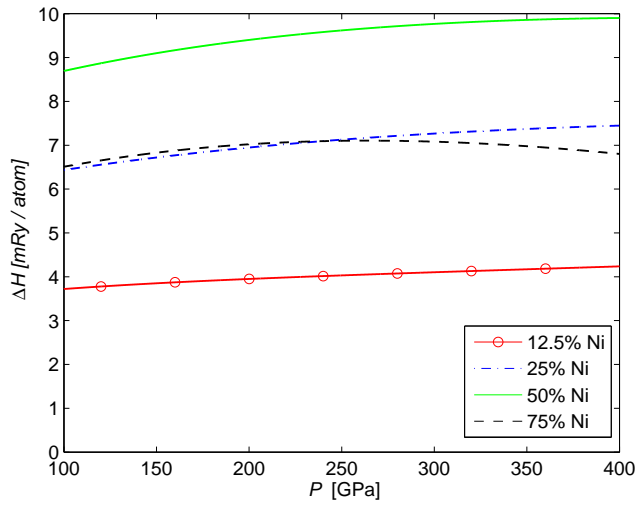


Figure 7: Mixing enthalpy for disordered hcp-FeNi at 12.5, 25, 50 and 75 % Ni composition including electronic temperature of 5000 K.

217 1986). As previously demonstrated for Fe-based alloys, the main reason for
218 this opposite behaviour is that the magnetic interactions are suppressed at
219 high pressure (Abrikosov et al., 1996). This can be compared to the case of
220 disordered fcc- $\text{Fe}_{1-x}\text{Ni}_x$, shown in Fig. 3, which also shows positive mixing
221 enthalpy.

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

227 We also note that the mixing enthalpy is clearly lower for the disordered
228 alloy than for the ordered compounds throughout the entire pressure and
229 composition range, which means that the completely disordered state is more
230 favourable than the perfectly ordered state. In particular, at 350 GPa the
231 disordered $\text{Fe}_{0.75}\text{Ni}_{0.25}$ alloy has a lower mixing enthalpy than the ordered
232 Fe_3Ni compound by 3 mRy, which is a non-negligible amount compared to the
233 reported structural energy differences (see Sec 1). This observation clearly
234 demonstrates the inadequacy of using small ordered supercells as models of
235 Fe-Ni alloys at the conditions of the Earth’s core; and motivates further
236 investigation of the Fe-Ni alloy configuration at these conditions, in order to
237 establish a more appropriate model, which we present in Sec. 3.2.

238 3.1.2. *hcp*

239 Fig. 4 shows mixing enthalpy of the disordered hcp-based alloy. A mean
240 field estimation yields transition temperature 1400 K at Earth’s core condi-
241 tions, although the mixing enthalpy is not as symmetric as in the case of fcc.

242 This indicates that mixing will occur also on the hcp lattice at the conditions
243 of the Earth’s core.

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

264 3.1.3. Impact of lattice vibrations

265 We have also evaluated the effect of lattice vibrations on isostructural mix-
266 ing, which was absent in the above considerations, by separately performing

267 VCA calculations of the vibrational contribution to the mixing enthalpy in
268 disordered fcc-based Fe-Ni alloys at the temperature of 5000 K. This contri-
269 bution is negative, as shown in Fig. 8, indicating its stabilising effect on the
270 disordered alloy as compared to the segregated state.

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

277 *3.2. Short-range order*

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

286 Results are presented in Fig. 9. For both underlying crystal structures,
287 the short-range order parameter is finite. However, the magnitude of α is
288 so small that the fcc and hcp phases can be considered close to completely
289 disordered. These results show that a mixture of Fe and Ni atoms on the
290 fcc and hcp lattices should be described by models of completely disordered
291 alloys. In particular, we draw the conclusion that in dynamical simulations of

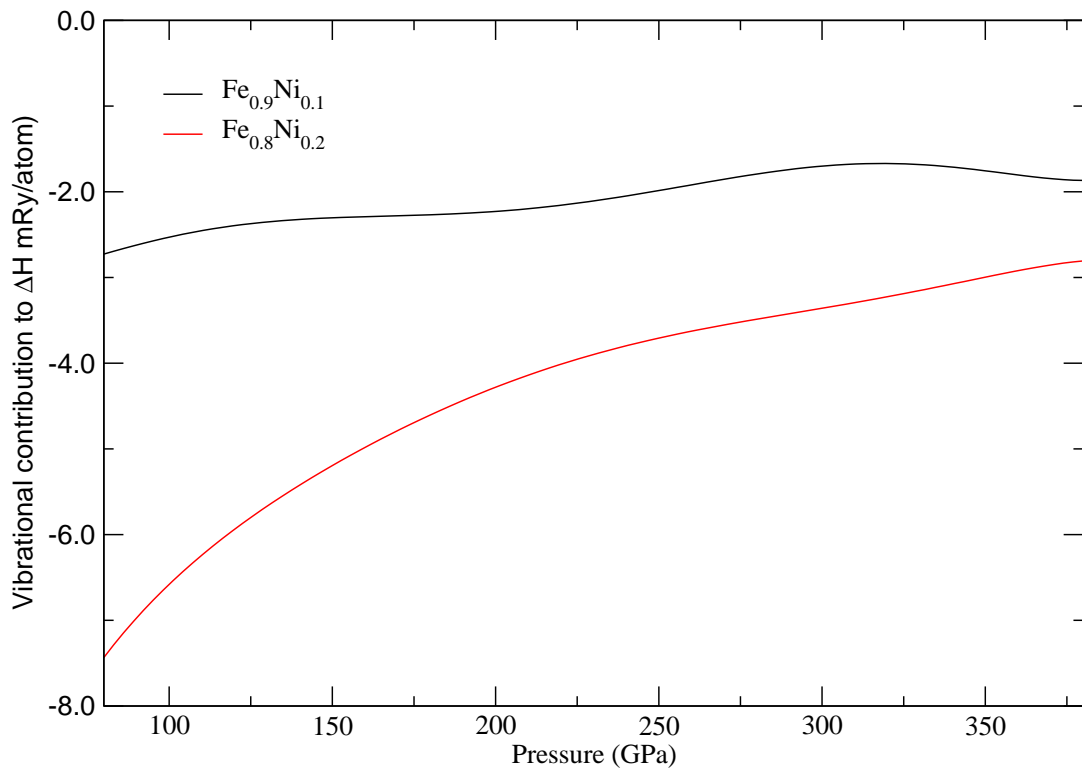


Figure 8: Vibrational contribution to the mixing enthalpy of disordered fcc-FeNi alloys at 5000 K calculated with the VCA method.

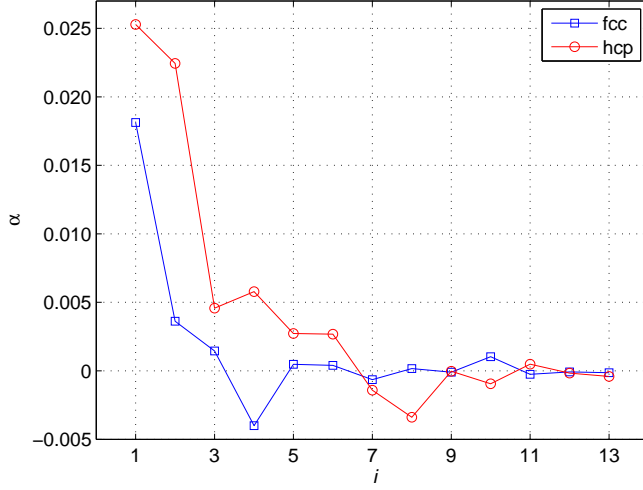


Figure 9: Short-range order parameter in fcc- and hcp- $\text{Fe}_{0.875}\text{Ni}_{0.125}$, calculated at 5000 K, as a function of coordination shell.

292 phase stability at the conditions of the Earth’s core, the Fe-Ni system should
 293 not be modelled an ordered compound, and results for the properties of such
 294 systems, obtained for ordered compounds (Vočadlo et al., 2008), should be
 295 taken with caution.

296 *3.3. fcc-hcp free energy differences at high temperature and pressure*

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

303 In previous work on pure Fe by Mikhaylushkin et al. (2007), it was shown

304 that in the high pressure range, the slope of the fcc-hcp transition curve in
305 the $P - T$ phase diagram essentially decreases compared to the slope of the
306 melting curve. Since in this region, the melting temperature is increased with
307 pressure, the fcc phase may be stabilised at the conditions of the Earth's core.
308 To analyse the influence of incorporating Ni into Fe, we computed the Gibbs
309 free energy differences between the fcc and hcp phases (ΔG) as a function
310 of pressure at various temperatures. Our results are presented in Fig. 10,
311 where $\Delta G > 0$ indicates relative stability of hcp phase and $\Delta G < 0$ indicates
312 stability of the fcc phase at fixed alloy composition. We find that at 2000 K,
313 hcp has lower energy than fcc in the entire pressure range for both pure Fe
314 and Fe-Ni alloys. Compression increases ΔG , i.e., it works in favour of the
315 hcp phase. However, we note that ΔG is lower for Fe-Ni than for pure Fe and
316 is further decreased as the Ni content increases in the entire pressure range,
317 which means that incorporation of Ni stabilises the disordered fcc alloy rel-
318 ative to hcp. When temperature is increased to 4000 K, we observe that
319 the ΔG curve is shifted down considerably, so that the fcc phase becomes
320 lower in energy within the pressure range below 170 GPa for pure Fe, and
321 below 190 GPa for $\text{Fe}_{0.8}\text{Ni}_{0.2}$. Upon further heating, this region expands.
322 Our results concerning the effect of Ni are so far in accordance with available
323 electric- and laser-heating high-pressure experiments (see Kuwayama et al.
324 (2008) and references therein). Interestingly, we may also note that as com-
325 pared to the low temperature (2000 K) regime, the influence of Ni on the
326 fcc-hcp energy difference also decreases. Remarkably, in the temperature in-
327 terval 3000–4000 K, the ΔG curve for the $\text{Fe}_{0.9}\text{Ni}_{0.1}$ alloy approaches that of
328 pure Fe.

329 To further investigate the observed effect, we raised the temperature to
330 6600 K. The free energy difference never exceeds 1.3 mRy / atom, and be-
331 comes very small as the pressure approaches 360 GPa. The pressure range in
332 which the fcc structure is lower in energy increases to 360 GPa for up to 10 %
333 Ni. Moreover, the order of the curves is reversed as compared to simulations
334 at lower temperatures. This means that the influence of Ni incorporation in
335 Fe at this temperature is opposite to that found in both theory and exper-
336 iment at lower temperature. In the Supplementary Materials, we provide a
337 discussion of this effect in terms of the behaviour of the electronic density of
338 (free energy) states, which we have calculated high temperature and pressure.
339 It should be noted that at actual conditions of the Earth's core, ΔG is close
340 to 0, which is similar to the situation in pure Fe (Mikhaylushkin et al., 2007)
341 Nevertheless, we may conclude that the stabilising effect of Ni incorporation
342 changes continuously under heating. In particular, at 6600 K, the effect of
343 Ni incorporation has a tendency to destabilise the fcc phase in favour of the
344 hcp phase.

345 Moreover, it should be mentioned that it has been shown theoretically and
346 experimentally, that Ni has a very strong stabilising effect on the bcc phase
347 (Dubrovinsky et al., 2007), not considered in this study. Also, at conditions
348 close to the Earth's core, the differences in the Gibbs energies among all the
349 phases of Fe-Ni alloys becomes very small. Therefore, the presence of either
350 one cannot be ruled out, and the subtle energy difference between the phases
351 at such temperatures may lead to a co-existence of two or more phases.

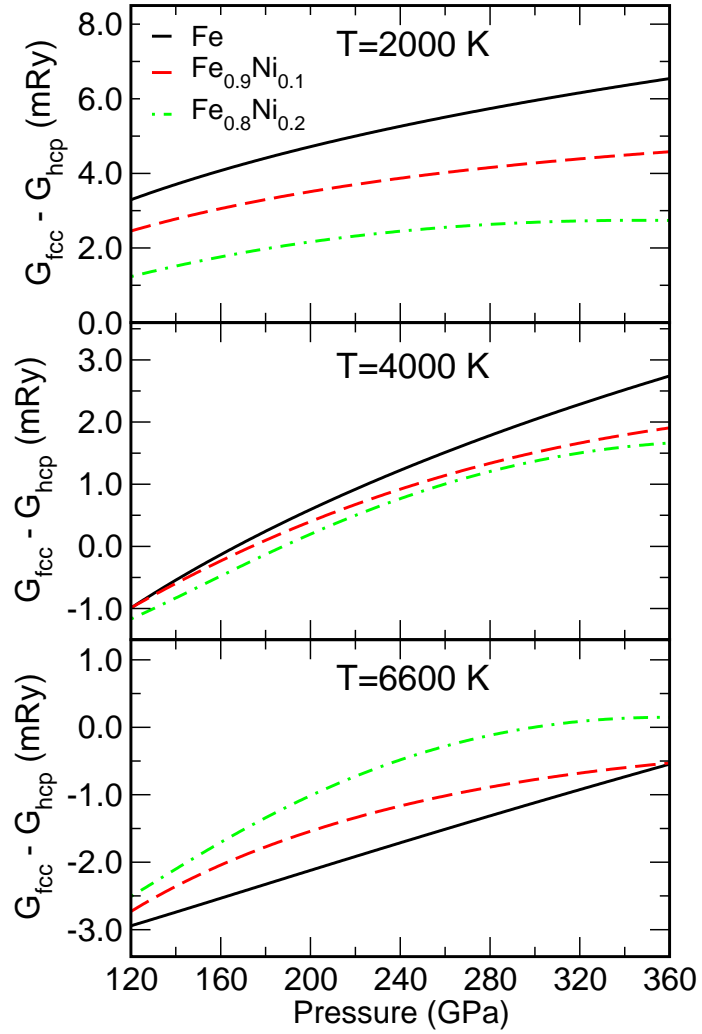


Figure 10: Gibb's free energy difference between disordered fcc- and hcp-based Fe-Ni alloys at high pressure and temperature, where $\Delta G > 0$ indicates relative stability of the hcp phase. For $T = 2000\text{ K}$ and 4000 K , Ni acts to stabilise the fcc phase, in line with experiment. At $T = 6600\text{ K}$, its effect is the opposite, stabilising the hcp phase.

352 4. Summary and conclusions

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

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

373 We gratefully acknowledge L. Dubrovinsky for useful discussions. This
374 project was supported by the Swedish Research Council (VR) and the Göran
375 Gustafsson Foundation for Research in Natural Sciences and Medicine. Cal-
376 culations were performed at the facilities provided within the Swedish Na-

377 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.

x	0.00	12.5	0.25	0.50	0.75	1.00
$(c/a)_0$	1.59	1.60	1.60	1.62	1.63	1.64

References

- Abrikosov, I. A., James, P., Eriksson, O., Söderlind, P., Ruban, A. V., Skriver, H. L., Johansson, B., 1996. Magnetically induced crystal structure and phase stability in fe_{1-c}co_c. *Phys. Rev. B* 54, 3380–3384.
- Abrikosov, I. A., Kissavos, A. E., Liot, F., Alling, B., Simak, S. I., Peil, O., Ruban, A. V., 2007. Competition between magnetic structures in the Fe rich fcc FeNi alloys. *Physical Review B (Condensed Matter and Materials Physics)* 76 (1), 014434.
- Alfé, D., 2009. Phon: A program to calculate phonons using the small displacement method. *Computer Physics Communications* 180 (12), 2622 – 2633, 40 YEARS OF CPC: A celebratory issue focused on quality software for high performance, grid and novel computing architectures.
- Asker, C., Belonoshko, A. B., Mikhaylushkin, A. S., Abrikosov, I. A., 2008. First-principles solution to the problem of Mo lattice stability. *Physical Review B (Condensed Matter and Materials Physics)* 77 (22), 220102.
- Asker, C., Kargn, U., Dubrovinsky, L., Abrikosov, I., 2010. Equation of state and elastic properties of face-centered-cubic fe-mg alloy at ultrahigh

- pressures from first-principles. *Earth and Planetary Science Letters* 293, 130 – 134.
- Asker, C., Vitos, L., Abrikosov, I. A., 2009. Elastic constants and anisotropy in FeNi alloys at high pressures from first-principles calculations. *Physical Review B (Condensed Matter and Materials Physics)* 79 (21), 214112.
- Belonoshko, A. B., Ahuja, R., Johansson, B., 2003. Stability of the body-centred-cubic phase of iron in the Earth's inner core. *Nature* 424, 1032.
- Birch, F., Jun 1947. Finite elastic strain of cubic crystals. *Phys. Rev.* 71 (11), 809–824.
- Blöchl, P. E., Dec 1994. Projector augmented-wave method. *Phys. Rev. B* 50 (24), 17953–17979.
- Côté, A. S., Vočadlo, L., Dobson, D. P., Alfé, D., Brodholt, J. P., 2010. Ab initio lattice dynamics calculations on the combined effect of temperature and silicon on the stability of different iron phases in the Earth's inner core. *Physics of the Earth and Planetary Interiors* 178, 2–7.
- Cowley, W., 1950. An approximate theory of order in alloys. *Physical Review* 77, 669–675.
- Crystal Lattice Structures Web page, 2004. Center for computational materials science of the united states naval research laboratory. <http://cst-www.nrl.navy.mil/lattice/>, last accessed May 2, 2011.
- Dubrovinskaia, N., Dubrovinsky, L., Kantor, I., Crichton, W. A., Dmitriev, V., Prakapenka, V., Shen, G., Vitos, L., Ahuja, R., Johansson, B.,

- Abrikosov, I. A., 2005. Beating the miscibility barrier between iron group elements and magnesium by high-pressure alloying. *Phys. Rev. Lett.* 95 (24), 245502.
- Dubrovinsky, L., Dubrovinskaia, N., Langenhorst, F., Dobson, D., Rubie, D., Geszmann, C., Abrikosov, I. A., Johansson, B., Baykov, V. I., Vitos, L., Bihan, T. L., Crichton, W. A., Dmitriev, V., Weber, H.-P., 2003. *Nature* 422, 58–61.
- Dubrovinsky, L., Dubrovinskaia, N., Narygina, O., Kantor, I., Kuznetsov, A., Prakapenka, V. B., Vitos, L., Johansson, B., Mikhaylushkin, A. S., Simak, S. I., Abrikosov, I. A., 2007. Body-centered cubic iron-nickel alloy in Earth's core. *Science* 316 (5833), 1880–1883.
- Faulkner, J. S., 1982. The modern theory of alloys. *Prog. Mater. Sci.* 27, 1–187.
- Häussermann, U., Mikhaylushkin, A. S., 2010. Electron-poor antimonides: complex framework structures with narrow band gaps and low thermal conductivity. *Dalton Trans.* 39.
- Kittel, C., 1996. *Introduction to Solid State Physics*. John Wiley & Sons Inc.
- Kresse, G., Furthmüller, J., 1996a. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* 6 (1), 15–50.
- Kresse, G., Furthmüller, J., 1996b. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169–11186.

- Kresse, G., Joubert, D., 1999. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 59, 1758–1775.
- Kuwayama, Y., Hirose, K., Sata, N., Ohishi, Y., 2008. Phase relations of iron and iron-nickel alloys up to 300 GPa: Implications for composition and structure of the Earth’s inner core. *Earth and Planetary Science Letters* 273, 379 – 385.
- Lin, J.-F., Heinz, D. L., Campbell, A. J., Devine, J. M., Mao, W. L., Shen, G., 2002. Iron-nickel alloy in the Earth’s core. *Geophys. Res. Lett.* 29, 109.
- Mao, W. L., Campbell, A. J., Heinz, D. L., Shen, G., 2006. Phase relations of FeNi alloys at high pressure and temperature. *Physics of the Earth and Planetary Interiors* 155, 146–151.
- Massalki, T. B., Murray, J. L., Bennet, L. H., Baker, H. (Eds.), 1986. *Binary Alloy Phase Diagrams: Vol. 1*. American Society for Metals.
- Mermin, N. D., Mar 1965. Thermal properties of the inhomogeneous electron gas. *Phys. Rev.* 137 (5A), A1441–A1443.
- Mikhaylushkin, A. S., Simak, S. I., Dubrovinsky, L., Dubrovinskaia, N., Johansson, B., Abrikosov, I. A., Oct 2007. Pure iron compressed and heated to extreme conditions. *Phys. Rev. Lett.* 99 (16), 165505.
- Mikhaylushkin, A. S., Simak, S. I., Johansson, B., Häussermann, U., Oct 2005. Electron-concentration and pressure-induced structural changes in the alloys $\text{In}_{1-x}\text{X}_x$ ($X=\text{Cd},\text{Sn}$). *Phys. Rev. B* 72 (13), 134202.

- Perdew, J. P., Burke, K., Ernzerhof, M., Oct 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77 (18), 3865–3868.
- Ruban, A. V., Abrikosov, I. A., 2008. Configurational thermodynamics of alloys from first principles: effective cluster interactions. *Rep. Prog. Phys.* 71, 046501.
- Ruban, A. V., Khmelevskiy, S., Mohn, P., Johansson, B., 2007. Magnetic state, magnetovolume effects, and atomic order in $\text{Fe}_{65}\text{Ni}_{35}$ invar alloy: A first principles study. *Phys. Rev. B* 76 (1).
- Ruban, A. V., Shallcross, S., Simak, S. I., Skriver, H. L., Sep 2004. Atomic and magnetic configurational energetics by the generalized perturbation method. *Phys. Rev. B* 70 (12), 125115.
- Steinle-Neumann, G., Cohen, R. E., Stixrude, L., 2004. Magnetism in iron as a function of pressure. *Journal of Physics: Condensed Matter* 16 (14), S1109–S1119.
- Tateno, S., Hirose, K., Ohishi, Y., Tatsumi, Y., 2010. The structure of iron in earths inner core. *Science* 330, 359.
- Vitos, L., 2001. Total-energy method based on the exact muffin-tin orbitals theory. *Physical Review B* 64, 014107.
- Vitos, L., 2007. *Computational Quantum Mechanics for Materials Engineers: the EMTO Method and Applications*. Springer-Verlag, London.
- Vitos, L., Abrikosov, I. A., Johansson, B., 2001. Anisotropic lattice distor-

- tions in random alloys from first-principles theory. *Phys. Rev. Lett.* 87, 156401.
- Vitos, L., Abrikosov, I. A., Johansson, B., 2005. Coherent potential approximation within the exact muffin-tin orbitals theory. In: Turchi, P. E. A., Gonis, A., Rajan, K., Meike, A. (Eds.), *Complex Inorganic Solids*. Springer.
- Vočadlo, L., Alfé, D., Gillian, M. J., Wood, I. G., Bodholt, J. P., Price, G. D., 2003. Possible thermal and chemical stabilization of body-centred-cubic iron in the Earth's core. *Nature* 424, 536.
- Vočadlo, L., Wood, I. G., Alfé, D., Price, G., 2008. Ab initio calculations on the free energy and high p-t elasticity of face-centred-cubic iron. *Earth and Planetary Science Letters* 268 (3-4), 444 – 449.
- Zarkevich, N. A., Tan, T. L., Johnson, D. D., 2007. First-principles prediction of phase-segregating alloy phase diagrams and a rapid design estimate of their transition temperatures. *Phys. Rev. B* 75, 104203.
- Zunger, A., Wei, S. H., Ferreira, L. G., Bernard, J. E., 1990. Special quasirandom structures. *Physical Review Letters* 65 (3), 353–356.