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Influence of Ni on the lattice stability of Fe-Ni alloys at multimegabar pressures

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The lattice stability trends of the primary candidate for Earth's core material, the Fe-Ni alloy, were examined from first principles. We employed the exact muffin-tin orbital method (EMTO) combined with the coherent potential approximation (CPA) for the treatment of alloying effects. It was revealed that high pressure reverses the trend in the relative stabilities of the body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) phases observed at ambient conditions. In the low pressure region the increase of Ni concentration in the Fe-Ni alloy enhances the bcc phase destabilization relative to the more close-packed fcc and hcp phases. However, at 300 GPa (Earth's core pressure), the effect of Ni addition is opposite. The reverse of the trend is associated with the suppression of the ferromagnetism of Fe when going from ambient pressures to pressure conditions corresponding to those of Earth's core. The first-principles results are explained in the framework of the canonical band model.

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I. INTRODUCTION

Iron is one of the most abundant metals on Earth. Due to its unique properties, it is widely used in numerous technological applications. Since the discovery of the Earth's core about a century ago, the idea that Fe is its dominant component has gained strong support from geochemical observations, seismic data, etc. Presently, it is generally presumed that Earth's inner core consists of iron alloyed with a substantial amount of nickel (5 to 15 at.%) and a few percent of light elements such as sulfur and silicon.[1–5] The pressure and temperature conditions in this region are estimated to be in the range of 300–400 GPa and 4000–6000 K, respectively. Until recently, the hexagonal close-packed (hcp) phase of iron was considered the only candidate for Earth's inner core. However, lately it was predicted theoretically that the body-centered cubic (bcc) and face-centered cubic (fcc) phases of iron at Earth's core conditions may be as stable as the hcp structure.[6–8] Moreover, it is well established that at ambient pressure even relatively small amount of impurities can influence the phase equilibria and thermodynamic properties of Fe alloys,[9,10] and one should expect that a similar situation may also occur at Earth's core conditions. To address the problem of phase stability of iron and its alloys at ultrahigh pressure is important to both physics and geophysics.[11–17]

There is no unambiguous experimental data indicating the stable iron phase, though experiments have started to approach these extreme conditions.[15,18] A number of reliable experiments on Fe-based alloys were carried out at slightly lower pressures and temperatures.[12,16] An important contribution here is due to Dubrovinsky *et al.*[15] who have reported stabilization of the bcc phase of iron alloyed with 10 at.% of Ni. At first it may seem surprising because from the ambient pressure phase diagram of the Fe-Ni alloy[19] it follows that the addition of Ni stabilizes the closed-packed (fcc) phase and destabilizes the bcc phase. Furthermore, *ab initio* calculations by Vocadlo *et al.*[20] show that at relatively low pressures (up to ∼20 GPa) Ni destabilizes the bcc phase of Fe-Ni in favor of the hcp phase as it does at ambient conditions.

So, is it possible that with a further increase of pressure the effect is reversed? In this paper, we demonstrate it can be the case. We study the effect of Ni on the lattice stability of the bcc, fcc, and hcp phases of Fe. We show from first-principles calculations that the stabilization effect of Ni strongly depends on the magnetic state of the Fe-Ni system, which is, in turn, controlled by pressure. Therefore the effect of Ni on the structural energy differences between the competing phases of Fe-Ni alloy turns out to be opposite at ambient conditions and at pressure conditions corresponding to Earth's inner core. We support our calculations by an explanation in terms of the canonical band theory, which successfully describes crystal structure trends for transition metals[21–23] and their alloys.[24]

The paper is organized as follows: Section II introduces the concept of lattice stability. Section III contains the description of the method of calculations and the obtained results. Section IV presents the results of first-principles calculations, which are discussed and explained in the framework of the canonical band model. Section V summarizes the results.

II. CONCEPT OF LATTICE STABILITY

A concept of lattice stability was introduced by Kaufman.[25,26] It referred to the differences in the Gibbs free energies among different crystal structures of pure elements. Originally, the lattice stability was determined by means of the semiempirical thermochemical approach, which is based on the assessment of experimental data. In particular, it includes extrapolations from the liquidus-solidus lines in phase diagrams of alloy systems relevant for corresponding pure elements. Further, the method may involve extrapolations of enthalpies of mixing as a function of composition, as well as extrapolations of high-temperature data to zero temperature. The *zero-temperature* lattice stabilities constitute the cornerstone of the powerful calculation of phase diagrams Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) approach to calculating phase equilibria at *finite* *temperatures*. This is explained and discussed in detail by Saunders and Miodownik in Ref. 27.

First-principles calculations of lattice stabilities were pioneered by Pettifor[23] and Skriver,[21] who demonstrated that the first-principles theory is capable of reproducing correctly the crystal structures of transition metals and related the observed hcp–bcc–hcp–fcc sequence, which takes place across the transition metal series, to the change in the occupation of the *d* electron states. Despite the problem with comparing absolute values of *ab initio* structural energy differences with thermochemical lattice stabilities for some elements,[28,29] the trends, which govern the stabilization of different crystal structures upon the increase of valence electron concentration, are very similar in theory and experiment.[27] Thus, the study of lattice stability variation upon adding Ni into Fe is essential for understanding of stabilization effect of Ni on the crystal structure of Fe-Ni alloys. As a matter of fact, understanding the energetic effect of the Ni substitution into different crystal structures of Fe in terms of lattice stability is conceptually very close to the methodology suggested in Ref. 30 for the estimation of the stabilization energy of the bcc phase of Fe with respect to the hcp phase due to alloying with Si. The advantage of the former concept is that it can be related to a change of the *d* occupation by means of the canonical band theory,[21,31,32] as will be discussed in Sec. IV.

III. FIRST-PRINCIPLES CALCULATIONS OF LATTICE STABILITY

A. Methodology

The calculations were performed within the density functional theory (DFT). The generalized gradient approximation (GGA)[33,34] was used for the exchange-correlation potential and energy, and the Kohn–Sham equations were solved in the framework of the exact muffin-tin orbital (EMTO) method.[35,36] The effect of alloying was taken into account within the coherent potential approximation (CPA).[37–39] The CPA is known as the successful method for electronic structure calculations of disordered metallic alloys, providing accurate description of the electronic structure for alloys with common, as well as split-band behavior, and for the total energies.[40] A comparison of this method and the supercell approach for the Fe-Ni random alloys at ambient conditions was carried out in Ref. 41, where its high accuracy was proven. The disordered local moment (DLM) model was used to describe the paramagnetic (PM) state.[42] The ambient conditions were modeled as $T = 0$ K and $P = 0$ GPa.

All the calculations were well converged with respect to the number of k points used for the integration over the Brillouin zone and other parameters of the method. It is known that the GGA provides better agreement between calculated and experimental equilibrium volumes, and accordingly pressure-volume relations, but leads to an overestimation of the magnetic moment of bcc Fe. Therefore the self-consistent electron densities were obtained within the local density approximation (LDA),[43] and then the total energies were calculated in the GGA using the full charge-density formalism. As pointed out in Ref. 44, this scheme gives a very accurate description of both magnetic and thermodynamic properties of transition metal alloys. The energy integration has been carried out in the complex plane using a semielliptic contour comprising 24 energy points. The calculations were performed for a basis set including valence s, p, d, and f orbitals. The core states were recalculated at each iteration of the self-consistency loop. In our CPA calculation, we included the screening contribution to the electrostatic potential and energy to take into account the effect of charge transfer between the alloy components.[45] For the explanation of the theoretical results, the canonical band model was used. The methodology of the canonical band calculations is given in Ref. 24.

B. Results

In order to examine the influence of Ni on the stability of iron phases, first-principles calculations of the formation enthalpies were carried out. The pressure-temperature phase diagram of iron discloses three solid Fe phases at low pressures, namely ferromagnetic (FM) bcc (α), PM fcc (γ), and PM bcc (δ) (see Refs. 6 and 15). In the low temperature interval up to 1200 K, the FM bcc α phase of iron is thermodynamically stable relative to the δ and γ phases. The three aforementioned phases were examined together with the hcp iron phase, which is known to be stable at higher pressures. For this reason, the PM hcp ε phase was modeled within the DLM approximation. The results of the enthalpy calculations are summarized in Figs. 1 and 2.

In Fig. 1 the results obtained at zero pressure are presented. In order to provide a clear representation of the lattice stability influenced by Ni addition, the enthalpies of FM bcc, nonmagnetic (NM) bcc, and FM fcc Fe-Ni alloys were plotted in comparison with the PM hcp one, which was taken as the reference (see Fig. 1). Here we would like to point out that the ground state of Fe-rich FeNi fcc alloys is believed to

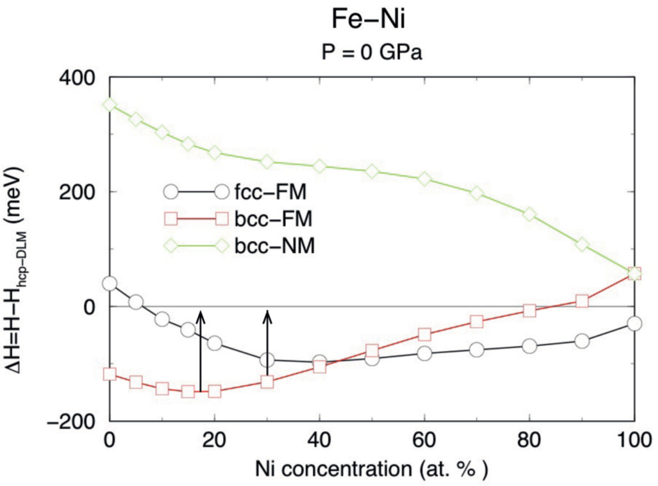

FIG. 1. (Color online) Formation enthalpies calculated for the FM bcc (red line, squares), NM bcc (green line, diamonds), and FM fcc (black line, circles) phases of Fe-Ni alloy as a function of Ni content. The simulations were carried out at zero pressure and temperature. Enthalpies of the considered phases are given in comparison with the enthalpy of the PM hcp phase calculated within the DLM approximation. The DLM hcp enthalpy is taken as the zero level line. The arrows are a guide for the eye to illustrate the decreasing relative stability of the bcc phase with increasing Ni concentration.

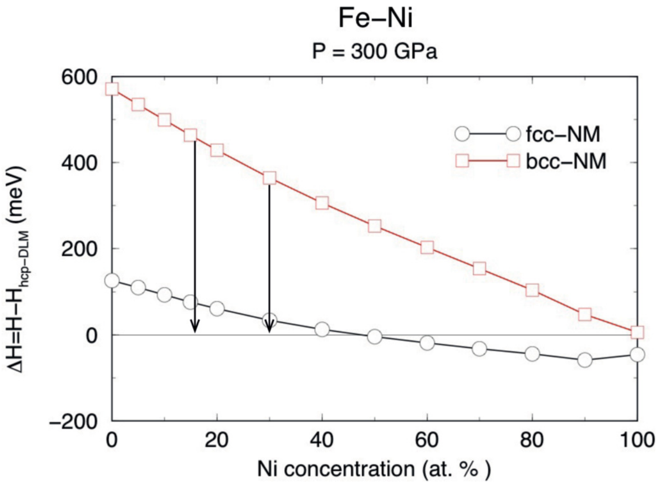

FIG. 2. (Color online) Formation enthalpies calculated for the NM bcc (red line, squares) and fcc (black line, circles) phases of Fe-Ni alloy as a function of Ni content. The simulations were carried out at pressure 300 GPa and zero temperature. Enthalpies of the considered phases are given in comparison with the enthalpy of the PM DLM hcp phase. The DLM hcp enthalpy is taken as the zero level line. The arrows are a guide for the eye to illustrate the decreasing relative instability of the bcc phase at zero temperature with increasing Ni concentration.

be complex antiferromagnetic (AFM). However, the energy difference between these and the FM state is very small, of the order of few millielectron volts,[46] so it is not essential for the present discussion. Similarly, hcp Fe is predicted to be AFM in calculations.[47–51] However, the predicted magnetic ordering temperature is rather low, ∼69 K,[51] and, moreover, hcp $Fe_{0.9}Ni_{0.1}$ alloy does not show any experimental evidence of the AFM order down to 11 K at $P = 21$ GPa.[49] This justifies our choice of approximations for the description of magnetic structure of close-packed fcc and hcp alloys.

The calculations were carried out for Ni concentrations from 0 at.% up to 100 at.%, that is from pure Fe to pure Ni, respectively. From Fig. 1 it is seen that at zero pressure the enthalpy of the FM bcc Fe-Ni alloy with Ni content up to 45 at.% is the lowest one, indicating the thermodynamic stability of this phase relative to the other considered phases. The hcp phase is more stable than the FM fcc phase up to ∼7 at.% of Ni. However, at concentrations higher than 7 at.% of Ni the FM fcc phase becomes energetically more stable than the PM hcp one. The NM bcc state at $P = 0$ GPa is so much higher in energy that it does not compete with the hcp and fcc phases in the whole concentration interval. With an increase of Ni concentration (up to ∼45 at.%), the enthalpy difference between the FM bcc and the FM fcc phases decreases, and finally at concentrations higher than ∼45 at.% of Ni the FM fcc phase becomes energetically favorable relative to the FM bcc one. Thus, at ambient pressures the Ni addition tends to stabilize the fcc phase of Fe and therefore destabilizes the FM bcc phase. This result is in qualitative agreement with the experimental phase diagram.[19]

However, at high pressures corresponding to Earth's core conditions (∼300 GPa) the effect of Ni on the behavior of lattice stability turns out to be completely opposite to the one at ambient conditions. In Fig. 2 the results for the lattice stability of the bcc, fcc, and hcp Fe-Ni alloys obtained at 300 GPa are presented. Here again the hcp iron phase is taken as a reference. As magnetism in Fe in DFT calculations disappears with increasing pressure, the bcc and fcc phases were considered as NM for the high pressure calculations. We also notice that in the DLM calculations at 300 GPa the magnetic moment disappears in the PM hcp phase of Fe-Ni alloys except at concentrations very close to pure Ni. From Fig. 2, one may see that at low Ni concentrations the hcp PM phase has the lowest enthalpy. However, with the increase of Ni content up to ∼50 at.%, the NM fcc phase becomes more stable with respect to the hcp one. Furthermore, the decrease of the gap between the bcc and hcp curves with increasing Ni concentration can be clearly seen. The same trend is observed for the gap between the bcc and fcc phase enthalpy curves. Thus, we stress that at high pressures the Ni addition tends to make the bcc phase less unstable, while at zero pressures the opposite effect takes place. This is in agreement with the experimental results indicating stabilization of the high-pressure bcc phase of Fe alloyed with Ni.[15]

IV. DISCUSSION

The opposite trends in the lattice stability behavior at zero and 300 GPa pressures can be explained in terms of the canonical band model.[21,22,31,32] The canonical energy is of particular interest since it gives an element-independent description of the relative crystal structure stability. According to the canonical band model, the canonical energy difference among different structures can be determined from a sum of all band energies up to the Fermi energy. The Fermi energy is defined by the number of electrons with all azimuthal quantum numbers l. Hence, the crystal structure stability can be written as a function of the occupation of the l states. In transition metals one may, to good approximation, neglect all but the d bands ($l = 2$). Therefore one can derive the atomic number independent estimation of the band contribution to the cohesive energy in terms of the first-order moment canonical state density.[21,22,52] The canonical band theory is a classic way to analyze and explain trends of the lattice stability upon the change of the band filling, which is one of the main effects of alloying Fe with Ni. Because it is derived from the fundamental principles of quantum mechanics, its conclusions do not depend on methodological details, and they are unaffected by numerical inaccuracies inherent in first-principles calculations. Certainly, the model cannot be used for quantitative prediction of a specific crystal structure at particular pressures and temperatures. In particular, it neglects the pressure-induced sp to d charge transfer, which may influence the quantitative energy balance.[53,54] Nevertheless it is a powerful theoretical tool to understand, explain, and predict stability trends across transition metal series.

In Fig. 3 we show the structural trend as a function of band occupation, obtained from the canonical d band model[21,31] generalized for spin-polarized systems.[24] To compare lattice stability trends in FM and NM systems, one assumes that the former are completely saturated ferromagnets, and their spin-up d band is full. This is a reasonable assumption for Fe and Ni at ambient pressure. Because the spin-up band

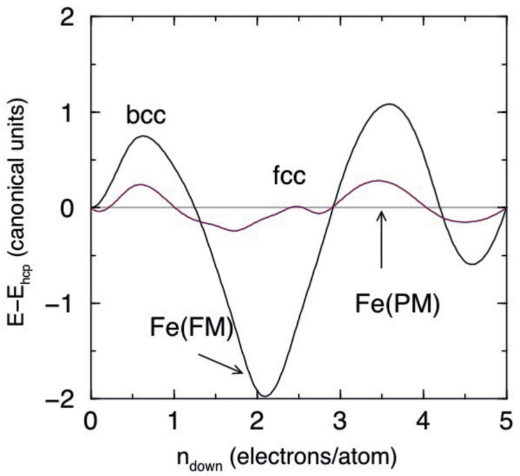

FIG. 3. (Color online) Results of the canonical band model calculations for the lattice stability of transition metals. The canonical *d* band energies are given for the fcc and bcc crystal structures relative to the hcp structure as a function of the *d* occupation of the spin-down band.[60] In the case of FM order the spin-up band is assumed to be fully saturated. For the NM case occupations of both spin-up and spin-down bands are equal.

is full, it does not contribute to the bonding, and the lattice stability in this case is determined by the fractional filling of the spin-down *d* band, which contains ∼1.9 electrons for Fe. On the contrary, if the magnetic moment is quenched, e.g., by ultrahigh pressure, the structural energy differences are functions of the total *d* occupation number, and the electrons are distributed equally between spin-up and spin-down bands, contributing ∼3.5 electrons to the spin-down band of Fe. Söderlind *et al.* pointed out in Ref. 55 that the observed crystal structure sequence for FM 3*d* metals subject to increasing *d* occupation, i.e., bcc → fcc → hcp, stems from the same band-filling arguments as for the well-known PM 4*d* and 5*d* transition metal sequence hcp → bcc → fcc → hcp.

Now we can use Fig. 3 to understand the stabilization effect of Ni on the different iron phases in the FM ambient pressure and NM high-pressure states. One can see that occupation of the *d* band of the FM bcc iron phase corresponds to a position near the energy difference minimum, while it is located near the maximum in the NM state. Adding 10–15 at.% of Ni into the FM iron phase changes the number of spin-down electrons per atom and shifts the band occupation away from the minimum, making the bcc structure less stable with respect to the fcc and hcp phases. Thus alloying of Fe with Ni destabilizes the bcc phase at ambient pressure, in agreement with experiment and *ab initio* calculations. On the contrary, the Ni addition to the NM Fe shifts the *d* band occupation off the maximum and therefore tends to decrease the instability of the bcc phase with respect to the more close-packed hcp and fcc phases. In summary, the canonical band model correctly shows that at ambient conditions the alloying with Ni should lead to the stabilization of more closed-packed crystal structures of Fe, as is known from experiments and reported in previous publications.[9,10] However, at Earth's core conditions, when high pressure suppresses the FM order,[56–58] the addition of Ni contributes to stabilization of the more open bcc structure.

It is important to point out that the first-principles calculations presented in Sec. III, as well as the canonical band model, give lattice stability trends at $T = 0$ K. It is rather obvious that this approximation may significantly overestimate the amplitude of the structural energy differences.[28] However, the trend of the lattice stability as a function of the *d* band occupation (or concentration of element with higher number of valence electrons) is still correct.[27] In this respect, the approach adopted by us is similar to that used by Vocadlo *et al.* in Ref. 30 to discuss the stabilization effect of Si on the bcc crystal structure of Fe and by Dubrovinsky *et al.* in Ref. 15 to estimate this effect for Ni. Certainly, though the calculated enthalpies of the bcc alloy phases approach those of the close-packed phases, the difference between them is still rather large. However, as demonstrated in Ref. 30 by means of *ab initio* molecular dynamics simulations, the anharmonic contribution to lattice vibrations, which is much more pronounced in the bcc phase than in close-packed structures, compensates to a very large degree for the zero-temperature energy difference. For example, it reduces the free energy difference between the bcc and hcp phases by an order of magnitude, down to 35–50 meV at $T = 5000$–6000 K.[30] As one can see in Fig. 2, the energetic effect of alloying with 10–15 at.% of Ni on the stabilization of the bcc phase is comparable to these numbers. This may explain the fact that the bcc phase has not been observed in pure Fe at ultrahigh pressure and temperature,[18] but it is observed in the Fe-Ni alloy.[15] We notice that a more precise quantitative analysis of possible thermodynamic stabilization of the bcc phase at high pressures requires full consideration of lattice dynamics, including anharmonic vibrations.[8,30] This is, however, out of scope of the present paper.

We also emphasize that the model adopted by us approximates high-pressure bcc and fcc phases as NM, and electron correlations are assumed to be weak. Recent dynamical mean field theory calculations demonstrated that fcc and hcp phases of Fe are indeed Pauli paramagnets at Earth's core conditions.[59] Their potential energies should therefore be adequately described by NM calculations at the level of accuracy needed for the present study. On the contrary, the magnetic susceptibility of the bcc phase shows linear dependence on temperature,[59] indicating that local magnetic moments may survive at Earth's core conditions. However, it was found that this effect did not influence energy difference between the hcp and bcc phases.[59] Thus, a more accurate treatment of the PM state should not affect our main conclusion: Ni in Fe acts as a bcc phase stabilizer at ultrahigh pressure.

V. SUMMARY

We have shown from first-principles calculations that application of ultrahigh pressure reversed the trend among the relative stabilities of the bcc, fcc, and hcp phases of Fe-Ni alloys. In the low pressure region the increase of Ni concentration in Fe-Ni alloy leads to the bcc phase destabilization relative to the fcc and hcp phases, in agreement with the experiment. However, at Earth's core pressures, Ni addition reduces the instability of the bcc phase relative to the closer packed phases. This diverse behavior is associated with the suppression of ferromagnetism of Fe when going from the ambient conditions to the conditions of Earth's core.

The results of first-principles calculations are explained in the framework of the canonical band model.

We notice that our finding, though obtained at zero temperature, is expected to have implications for the case of Earth's inner core pressure and temperature conditions. In particular, we conclude that experiments carried out for pure Fe and for Fe-Ni alloy should not be compared directly. Even though experiments could not confirm the stability of the bcc phase of pure Fe at high pressures,[18] the presence of Ni may drastically change this picture and promote the bcc phase stabilization. This possibility together with the tendency of the bcc phase to be stabilized at high temperatures makes the bcc Fe-Ni alloy a strong candidate to be present in Earth's inner core.

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