



Ab initio phase stability of some cubic phases of ordered Ni-Fe alloys at high temperatures and pressures



Zhen-Wei Niu^{a,b,*}, Ling-Cang Cai^b

^aLaboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology, 621010 Mianyang, Sichuan, China

^bNational Key Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, Chinese Academy of Engineering Physics, Mianyang 621900, China

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ABSTRACT

To address the temperature-induced stabilization of different phases, we studied some special structures of ordered Ni-Fe alloys by applying the recently developed self-consistent ab initio lattice dynamics approach. A simple but efficient scheme was also used to calculate the free energy and entropy. We found that the ordered structures with high nickel content are easier to stabilize at high temperature. Especially, the anharmonic part of free energy plays an important role in stabilizing the fcc-Ni₃Fe structure at high temperatures and pressures. Finally, the dynamically stable regions of Ni₃Fe compound are predicted in the phase diagram, and bcc-Ni₃Fe phase is expected to be stable at high temperature and pressure.

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1. Introduction

The Ni-Fe system is important for understanding the inner core and iron meteorites and the crystal structure of iron alloy is necessary for understanding the core dynamics. In Ni-Fe alloys, the body-centred cubic (bcc) phase is stable with small Ni concentration of about 7% at 720 K, while the face-centred cubic (fcc) phase is stable in the whole range of concentrations when the temperature is above 1185 K [1]. Hence, it is found that temperature plays an important role in stabilizing the Fe-Ni alloys. In particular, an ordered L1₂ structure with Ni₃Fe composition, the most stable structure at high temperature, has an important feature in the phase diagram [2]. The first-principles calculations [3] also showed that the fcc-Ni₃Fe structure has the most negative formation energy out of all other compounds. So far, a number of theoretical researches mainly focused on the effect of magnetic spin configurations [4–10] and little attention has been given to thermal vibration effect. Only Mohri et al. [11,12] explored the importance of the thermal vibration on L1₀-disorder phase equilibria by Debye Grüneisen theory within quasi harmonic approximation. However, it has not been explained why the face-centred cubic phase is more stable than body-centred cubic phase at high temperature. Thus, in order to solve this problem, it is necessary to understand the effect of temperature on different structures of ordered Ni-Fe alloys.

Especially, the possible occurrence of ordered NiFe and NiFe₃ compounds, which were found in meteorites for the first time [13–15], are worth exploring deeply.

In principle, combining with the phonon dispersion relations, ab initio techniques have been widely used to describe the gibbs free energy of material at high pressure and temperature. As is known, the quasiharmonic approximation (QHA) is usually utilized to predict the vibrational part of gibbs free energy [16] and can yield reliable results in some situations due to the small anharmonic effect. However, considering the phonon spectrum only relate to the corresponding volume, it fails to reproduce the free energy of solids at elevated temperatures where the intrinsic anharmonic effect is significant. The reason is that at high temperature anharmonic contributions like electron excitation and phonon interactions play indispensable roles. Because of the obvious drawbacks of QHA, a method developed from self-consistent ab initio lattice dynamics (SCAILD) [17,18] is adopted in our calculations, and the detail description can be found in Section 2: The theoretical methods.

In present report we are addressing the temperature-induced stabilization of ordered Ni-Fe alloys with special structures. For this purpose, we perform a recently developed scheme to take the anharmonic effect into account at elevated temperatures within the self-consistent ab initio lattice dynamics (SCAILD) method. Heretofore, SCAILD method has been successfully applied to measure the temperature-induced stabilization of Ti-V and V-Cr alloys by Söderlind et al. [19,20]. But the effect of thermal expansion is not considered in their calculations. Because the volume

* Corresponding author at: Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology, 621010 Mianyang, Sichuan, China.
E-mail address: z.w.niu@foxmail.com (Z.-W. Niu).

change due to alloying is far greater than that of the thermal expansion, their approximation is justified to a certain degree. However, thermal expansion actually usually increases with rising temperature at a given pressure. As a result, it may be unreasonable to ignore the influence of thermal expansion completely at high temperature. In our calculation the thermal expansion is fully considered although plenty of additional computations are required. Section 2 deals with computational parameters and methods for free energy. The results and detailed discussions are presented in Section 3. Section 4 is a summary of the results and a general conclusion.

2. Theoretical methods

The general idea of SCAILD is to account for thermal vibrations of the atoms and their interactions. This method has been detailed in reference 17 and not included here. In addition, a convergence free energy is necessary in SCAILD method. The self-consistent cycle was terminated when the difference in the approximate free energy of the lattices between two consecutive iterations was less than 1 meV in our calculations.

In our calculations, the equilibrium free energy is achieved by minimizing free energy with respect to the remaining internal coordinates and volumes at a given pressure and temperature:

$$F(P, T) = \min_{x, V} F^*(x, V; P, T), \quad (1)$$

where lowest free energy is obtained by the variation of internal coordinates. Since it is different to calculate the whole potential energy surface of the free energy, the restricted internal variables are used here to obtain a minimization of the static energy:

$$x_{opt}(V, T) \leftrightarrow F_{sta}(V, T) = \min_x F_{sta}(x, V, T). \quad (2)$$

During numerical modeling, the static free energy as a function of temperature and volume is divided into the following parts:

$$F_{sta}(x_{opt}, V, T) = E_0(x_{opt}, V) + F_e(x_{opt}, V, T) + F_{phon}(x_{opt}, V, T), \quad (3)$$

where $E_0(x_{opt}, V)$ is the static energy with the fixed ionic positions, $F_e(x_{opt}, V, T)$ is the thermal free energy from the electronic excitations, and $F_{phon}(x_{opt}, V, T)$ is the vibrational free energy of the ions. The temperature is introduced by SCAILD scheme [17]. The static energy $E_0(x_{opt}, V)$ at the applied pressure is obtained by fitting our E - V data to the third-order Birch-Murnaghan equation of state (EOS) [21]

$$\begin{aligned} \Delta E(V) &= E - E_0 \\ &= \frac{9V_0 B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}. \end{aligned} \quad (4)$$

where V_0 is the equilibrium cell volume at 0 GPa and 0 K, and V is the cell volume corresponding to the applied pressure P at 0 K, B_0 and B'_0 are the bulk modulus and its pressure derivative. The temperature dependent parts of the free energy can be found as

$$\begin{aligned} F_{ph}(x_{opt}, V, T) + F_e(x_{opt}, V, T) &= \frac{1}{N_I} \sum_{\{E_R\}} \Delta F^*(\{E_R\}, V, T) \\ &\quad + \frac{3}{2} k_B T - TS_{ph}(V, T). \end{aligned} \quad (5)$$

Here ΔF^* is the relative free energy to the ground-state energy E_0 induced by the atomic displacements and thermal excitations of the electronic states. The effects of electrons at finite temperature are introduced by Fermi-Dirac function and the Mermin theorem [29]. N_I is the number of atomic configurations. The phonon kinetic

energy is given by $\frac{3}{2} k_B T$ per atom which means that atomic motion is considered as classical; typically, the phase transformations induced from temperatures are higher than the Debye temperature. Thus, this approximation is well justified. E_R is the displacements of atoms. $\{E_R\}$ is generated throughout the SCAILD self-consistent run. Since ΔF^* are calculated at atomic configurations accommodating the different frozen phonon superposition of E_R , ΔF^* not only contains the finite-temperature contribution to the electronic free energy for a given atomic configuration, but also, the potential energy provided by the frozen lattice waves, i.e. the potential energy of the phonons at a particular phonon superposition [22]. Here R represent the N Bravais lattice sites of the supercell. TS_{ph} is the contribution of vibrational entropy. However, it is an important problem how to calculate the exact phonon entropy. Since the same state phonons is the noninteracting bosons, it can be assumed that the entropy depends on the phonon occupation numbers n_{qs} . In other words, the entropy can be expressed from the phonon density of states $g(\omega)$,

$$S_{ph}(V, T) = \frac{1}{T} \int_0^\infty d\omega g(\omega, V, T) \hbar \omega \left[n \left(\frac{\hbar \omega}{k_B T} \right) - \frac{k_B T}{\hbar \omega} \ln \left(1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right] \quad (6)$$

Here the phonon frequencies used to calculate the phonon density of states $g(\omega)$, are the normal mode configurational mean values

$$\langle \hbar \omega \rangle = \frac{1}{N_I} \sum_{\{E_R\}} \frac{\delta E_{tot}(\{E_R\}, V, T)}{\delta n_{qs}}. \quad (7)$$

It is stressed that both the accuracy of the phonon potential energy and the phonon entropy should be maximized in the partitioning of the free energy through Eqs. (3) and (5). More details can be found in Ref. 22.

For the lattice dynamic calculations, the highly accurate frozen core all-electron projector augmented wave (PAW) methods were adopted with the Vienna ab initio simulation package (VASP) [23,24]. The exchange and correlation potentials were treated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [25]. The calculations were performed with cut-off energy of 400 eV. For the static structural calculations, the $17 \times 17 \times 17$ Γ -centred k meshes were used. The self-consistent convergence of the total energy is 1.0×10^{-6} eV/atom, and the maximum ionic Hellmann-Feynman force is set to 0.02 eV/Å. Supercells of 32, 108, and 256 atoms are used in our calculations with Monkhorst-Pack $3 \times 3 \times 3$ k -point grid. All necessary convergence tests were performed. In addition, we focus on the effect of thermal vibration on the phase stability of ordered Ni-Fe alloys at high pressures and temperatures, where their total magnetic moments are weak. Thus, only nonmagnetic cases were treated in our calculations.

3. The results and detailed discussions

The convergence of the free energy of fcc-Ni₃Fe is presented in Fig. 1. In all of our calculations, the termination condition of the loop is that the difference of free energy of the lattice between two consecutive iterations was less than 1 meV in the approximation. The present precision is sufficient enough to produce reliable results on the phase stability induced from temperature, since crystallographic energy difference is of the level of a few meV. In Fig. 1, it can be found that after 100 iterations the free energy difference reaches the required convergence and numerical accuracy. However, as a comparison, the relative free energy does not reach the minimum energy after the hundredth step. This will affect the calculation of the final vibrational free energy and should be treated carefully. Furthermore, to obtain effective free energy, twelve

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