



Ab initio based study of finite-temperature structural, elastic and thermodynamic properties of FeTi

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ABSTRACT

We employ density functional theory (DFT) to calculate pressure dependences of selected thermodynamic, structural and elastic properties as well as electronic structure characteristics of equiatomic B2 FeTi. We predict ground-state single-crystalline Young's modulus and its two-dimensional counterpart, the area modulus, together with homogenized polycrystalline elastic parameters. Regarding the electronic structure of FeTi, we analyze the band structure and electronic density of states. Employing (i) an analytical dynamical matrix parametrized in terms of elastic constants and lattice parameters in combination with (ii) the quasiharmonic approximation we then obtained free energies, the thermal expansion coefficient, heat capacities at constant pressure and volume, as well as isothermal bulk moduli at finite temperatures. Experimental measurements of thermal expansion coefficient complement our theoretical investigation and confirm our theoretical predictions. It is worth mentioning that, as often detected in other intermetallics, some materials properties of FeTi strongly differ from the average of the corresponding values found in elemental Fe and Ti. These findings can have important implications for future materials design of new intermetallic materials.

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1. Introduction

Ti-based alloys represent a class of materials with a great potential in automotive, aerospace and biomechanical applications because of their low density ($\sim 4.5 \text{ kg/m}^3$), sufficient corrosion resistance, high strength ($\sim 1000 \text{ MPa}$), and good ductility with a plastic elongation to failure of 10–15% [1–3]. Specially the ultrafine eutectic Ti–Fe alloys, containing FeTi in the B2 (CsCl) phase and a β -Ti(Fe) solid solution, have been shown to simultaneously possess both high strength and good ductility in recent experiments [4–6]. In order to identify and understand the mechanisms governing the mechanical behavior of eutectic Ti–Fe alloys, a first but critical step is to describe separately each of the two phases, FeTi and β -Ti(Fe).

Focusing specifically on FeTi, this equiatomic intermetallic compound has attracted a large number of experimental and

theoretical studies recently, partly due to the fact that it is one of the important materials for hydrogen storage [7]. Regarding experimental studies, the bulk band structure of FeTi has been studied by photo-electron spectroscopy with synchrotron radiation [8]; the elastic constants of FeTi at room temperature have been determined by ultrasonic method [9] and inelastic neutron scattering [10], respectively; the optical properties of FeTi were measured by spectroscopic ellipsometry and the measured data were partially compared to the calculated band structures and optical conductivity spectra [11].

As far as theoretical studies are concerned, zero temperature properties for FeTi, such as electronic structures (density of states) for bulk, surfaces and interfaces [12–16] and elastic properties (elastic constants and bulk modulus) [17–19], have been studied based on first-principles density-functional calculations. However, a theoretical prediction of finite-temperature thermodynamic properties of FeTi is still missing despite of experimental data [9,10] available in literature.

The reason for lacking theoretical data may be related to the fact that density-functional calculations [20–22] are mostly used for calculating $T = 0 \text{ K}$ properties. Fully *ab initio* based approaches to finite temperatures do exist but are computationally expensive and

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thus still rather rare (see e.g. Ref. [23]). A simplified method for thermal expansion calculations, Debye–Grüneisen based model [24], is the one which has already been applied to various materials [25–27]. In our study, we followed the same method [24] but replaced the empirical Debye treatment by a fully consistent first-principles approach to compute the temperature dependence of the free energy [28] (see Computational methods). The vibrational free energy we obtain using the quasiharmonic approximation (QHA). In this approximation, anharmonic effects are included through the explicit volume dependence of the vibrational frequencies. Our choice was motivated by previous theoretical studies of thermal expansion of cubic metals that were based on the quasiharmonic approximation [29–32] and that accurately predicted thermal properties.

Our paper is structured as follows. We first introduce our computational methods and then apply *ab initio* calculations to predict $T = 0$ K structural, elastic and electronic properties of FeTi. Then we extend our study to finite temperatures and predict thermal expansion coefficients, heat capacities at constant pressure and at constant volume, as well as the isothermal bulk moduli.

2. Computational methods

For our density-functional-theory calculations, we employed the projector augmented wave (PAW) method [33] and the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) parametrization [34] as implemented in the Vienna Ab initio Simulation Package (VASP) [35–37]. The convergence of the total energies was checked with respect to the plane-waves basis-set size and the number of k -points. The plane-wave energy cutoff of 350 eV was used to guarantee a numerical accuracy of the results of about 1 meV per atom. The 7d and 1s electrons for Fe and the 3p6 3d3 4s1 electrons for Ti were treated as valence. The Brillouin zones of the unit cell was sampled by an $18 \times 18 \times 18$ Monkhorst-Pack k -point mesh for the 2-atomic cubic cell of FeTi.

In order to predict finite-temperature properties, we have employed the quasiharmonic approximation (QHA) within which we determined phonon frequencies for different volumes. Phonon spectra were for each volume derived approximatively (i) in the long-wave-length limit, i.e. from the single-crystalline elastic constants, and (ii) the FeTi B2 crystal was modeled as an effective single-component bcc lattice (see details in Appendix). The thermal properties of solids at constant volume can be calculated from their phonon density of states as a function of frequencies.

The heat capacity C_V and the entropy S at constant volume (see details e.g. in Ref. [38]) read

$$C_V = \sum_{\mathbf{q},\nu} k_B \left(\frac{\hbar\omega_{\mathbf{q},\nu}}{k_B T} \right)^2 \frac{\exp(\hbar\omega_{\mathbf{q},\nu}/k_B T)}{[\exp(\hbar\omega_{\mathbf{q},\nu}/k_B T) - 1]^2}, \quad (1)$$

and

$$S = -k_B \sum_{\mathbf{q},\nu} \ln[1 - \exp(-\hbar\omega_{\mathbf{q},\nu}/k_B T)] - \frac{1}{T} \sum_{\mathbf{q},\nu} \frac{\hbar\omega_{\mathbf{q},\nu}}{\exp - \hbar\omega_{\mathbf{q},\nu}/k_B T - 1}, \quad (2)$$

where $\mathbf{q}$ and ν are the wave vector and band index, respectively, $\omega_{\mathbf{q},\nu}$ is the phonon frequency at $\mathbf{q}$ and ν , and T is the temperature. Further, k_B and $\hbar$ are the Boltzmann constant and the reduced Planck constant. In many practical thermodynamical studies related to solids, the thermal properties are necessary to be known at constant pressure. They can be calculated from the previous

quantities through thermodynamic relationships. The Gibbs free energy G is given by

$$G(T, p) = \min_V [U(V) + F_{\text{vib}}(T; V) + pV], \quad (3)$$

where V and p are the volume and pressure, and $U(V)$ is the total energy of electronic structure (here computed by *ab initio* means) at constant volume. Regarding the right-hand side of Eq. (3), the function inside the square brackets is minimized with respect to the volume for each couple of T and p variables. Subsequently, the heat capacity at constant pressure is derived from $G(T, p)$ by

$$C_p(T, p) = -T \frac{\partial^2 G(T, p)}{\partial T^2} = T \frac{\partial V(T, p)}{\partial T} \frac{\partial S(T; V)}{\partial V} \Big|_{V=V(T, p)} + C_V[T, V(T, p)], \quad (4)$$

where $V_{T,p}$ is the equilibrium volume at T and p .

Both total energies $U(V)$ and free energies $F_{\text{vib}}(T; V)$ were calculated for 10 different volumes V . The thermodynamic functions of Eq. (3) were fitted to the integral form of the Murnaghan equation of state (EOS) [44] at $p = 0$. Gibbs free energies at finite temperatures were obtained as the minimum values of the thermodynamic functions, and the corresponding equilibrium volumes and isothermal bulk modulus were obtained simultaneously from the equation of states. The thermal expansion is observed as an increase in the equilibrium volume.

3. Experimental measurements

Cylindrical specimens of FeTi B2 measuring 26 mm in length and 8 mm in diameter, were cast in a cold crucible device. The casting conditions ensure homogeneity of the chemical composition and defect free (non-porous) samples. Detailed investigation of the microstructural properties of Fe–Ti alloy reported in earlier studies [6]. Thermal expansion of FeTi was measured with Netzsch dilatometer DIL 402C in the range of -120 °C to 480 °C (170 K– 750 K) in argon atmosphere with heating and cooling ratios of 2 K/min. The dilatometer is equipped with an inductive displacement transducer to measure the thermal elongation of the specimens automatically. The calibration of the dilatometer and treatment of the results were made according to the standard procedure using Proteus Analysis Software (Netzsch).

4. $T = 0$ K thermodynamic, structural, elastic, and electronic properties

FeTi has a particularly stable CsCl structure (B2 phase, as shown in Fig. 1(a)) with a melting point of almost 1600 K (for details see e.g. the PhD thesis of Jorge Alberto Muñoz Jr [39]). Our theoretical calculations predict the formation energy to be -0.421 eV/atom (see our previous paper [19]) in a reasonable agreement with other theoretical calculations, such as all-electron calculations by Kellou et al. [13], who reported -0.476 eV/atom, and those by Gonzales-Ormeño and Schön [40], who predicted -0.457 eV/atom, or -0.422 eV/atom reported by J. A. Muñoz Jr. [39] who employed the same computational code (VASP). The only exception is recent CASTEP calculations by Nong et al. [41] who report -0.67 eV/atom. It should be noted that, as a long-standing issue (see e.g. a discussion in Ref. [40]), theoretical calculations for yet unknown reasons overestimate the stability of the B2 FeTi intermetallics and predict the formation energies about a factor of two different when compared with experimental data such as -0.207 eV/atom

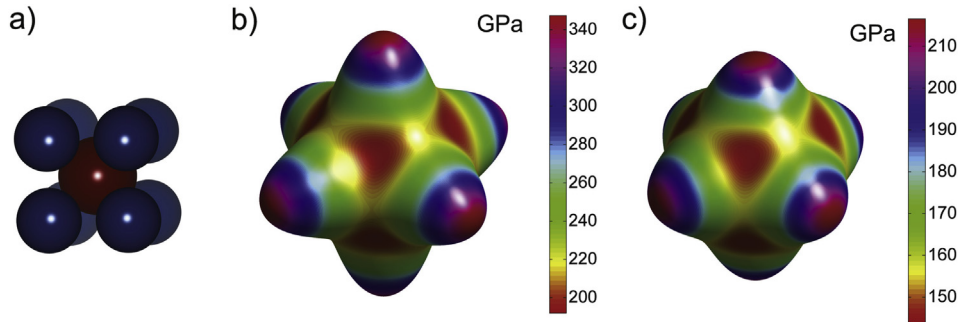


Fig. 1. The B2 (CsCl prototype) structure of FeTi (a) with the smaller blue ball representing a Ti atom and the bigger reddish ball a Fe atom, and the orientation dependences of (b) the single-crystalline Young's modulus and (c) area modulus A of FeTi. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reported by Kubaschewski and Dench [42] or recently (-0.233 eV/atom) by Gasior and Debski [43].

The equilibrium lattice constant is predicted to be 2.95 Å, which agrees well with our own experimental value 2.98 Å [6]. The calculated bulk modulus B (192 GPa) was derived from the Murnaghan equation of states [44]. The single crystalline elastic constants C_{11} , C_{12} and C_{44} were obtained by following the approach described in Ref. [45]. These C_{ij} were then used to determine a directional dependence of single-crystalline Young's modulus (see Fig. 1b). We found that FeTi has strongly anisotropic elastic properties and shows the largest Young's modulus about 340 GPa along the [001] direction.

As far as the elastic response of FeTi to biaxial strains is concerned, we have also analyzed the directional dependence of the area modulus $A(\mathbf{r})$ as recently introduced e.g. in Refs. [46,47]. The area modulus is a 2-dimensional counterpart of the Young's modulus. In a similar manner as the Young's modulus describes uniaxial loadings along a vector $\mathbf{r}$, the area modulus describes the change of the area within a plane with the plane normal vector $\mathbf{r}$. Specifically for cubic systems it was derived [47] that the following relation between the single-crystalline Young's modulus $Y(\mathbf{r})$ (describing an uniaxial loading along the direction $\mathbf{r}$) and the bulk modulus B holds

$$\frac{1}{A(\mathbf{r})} = \frac{1}{Y(\mathbf{r})} + \frac{1}{3B}. \quad (5)$$

The area modulus is a useful visualization of the amount of elastic energy that is necessary in order to e.g. epitaxially deposit a studied material on a substrate in a fully coherent manner. Fig. 1(c) can be thus interpreted such that the elastic energy will be lowest when growing FeTi on cubic {111}-terminated substrates and the energy will be highest for {100}-terminated substrates.

In order to predict polycrystalline properties, we employed Hershey's homogenization approach (see e.g. [48,49]) and calculated the polycrystalline shear modulus G_H . Once the homogenized values G_H is known, it is combined with the bulk modulus B in order to predict the polycrystalline Young's modulus Y using the formula

$$Y = \frac{9BG_H}{3B + G_H}. \quad (6)$$

The Poisson's ratio ν could be calculated from

$$\nu = \frac{1}{2} \left(1 - \frac{Y}{3B} \right). \quad (7)$$

The lattice constant, single crystalline elastic constants, polycrystalline moduli from our first-principles calculations and the

corresponding experimental results for FeTi are summarized in Table 1. In addition, the mechanical properties of pure Fe [50,51] and pure Ti [52,53] are also given for comparison together with the mass densities of FeTi [7], pure Fe and pure Ti. Our zero temperature results for FeTi from first-principles calculations as described above agree well with the existing experimental and theoretical data (see Table 1).

After analyzing elastic properties of FeTi we have also studied its electronic properties, such as density of states (DOS) and band structures, that are shown in Fig. 2 (a and b), respectively. There is a deep minimum near the Fermi level in the DOS, which separates the higher-energy bands predominantly occupied by Ti d states and the lower energy bands predominantly occupied by Fe d states. The contributions from s, p states of Ti and Fe are quite small in the whole energy range. The stability of FeTi can be thus ascribed to the lower and flatter electron-states distribution at the Fermi level [11–13,17,18]. Our band structures and DOS obtained from GGA neatly agree with those from previous local density approximation (LDA) calculations [11] (that have been partially compared to the measured data [11]).

To analyze influence of different lattice parameters, band structures at different volumes/pressures were computed and are shown in Fig. 3. The electronic states at the Fermi level for the lattice parameter $a = 3.00$ Å and 2.80 Å show very small shifting compared to that of the equilibrium structure with lattice constant $a = 2.95$ Å. That means the electronic structures of B2 FeTi exhibits a stability with respect to the application of external hydrostatic pressures (or equivalently reduced volumes – see Table 2).

Table 1

Selected $T = 0$ K properties of FeTi. Specifically, the lattice constant a (Å), bulk modulus B (GPa), single crystalline elastic constants C_{11} , C_{12} and C_{44} (GPa), polycrystalline shear modulus G_H and Young's modulus Y (GPa), Poisson's ratio ν and ratio $R = G_H/B$ for FeTi intermetallics. The room temperature experimental results [9,10] for FeTi, pure Fe [50,51] and pure Ti [52,53], and the mass densities ρ (g/cm³) for them at room temperature were also given, respectively.

FeTi	a	B	C_{11}	C_{12}	C_{44}
Theory	2.95	192	385	95	72
Theory [13]	2.96	186	—	—	—
Theory [40]	2.97	—	—	—	—
Exp. [9]	—	160.8 ± 2	310 ± 2	86.2 ± 4	74.9 ± 1
Exp. [10]	—	189	325 ± 10	121 ± 10	69 ± 1
Fe [50,51]	—	174	—	—	—
Ti [52,53]	—	112	—	—	—
FeTi	G_H	Y	ν	G_H/B	ρ
Theory	95	245	0.287	0.496	6.5[54]
Exp. [9]	88	223	0.269	0.547	—
Exp. [10]	81	213	0.313	0.429	—
Fe [50,51]	82	—	0.289	—	7.86
Ti [52,53]	41	—	0.339	—	4.5

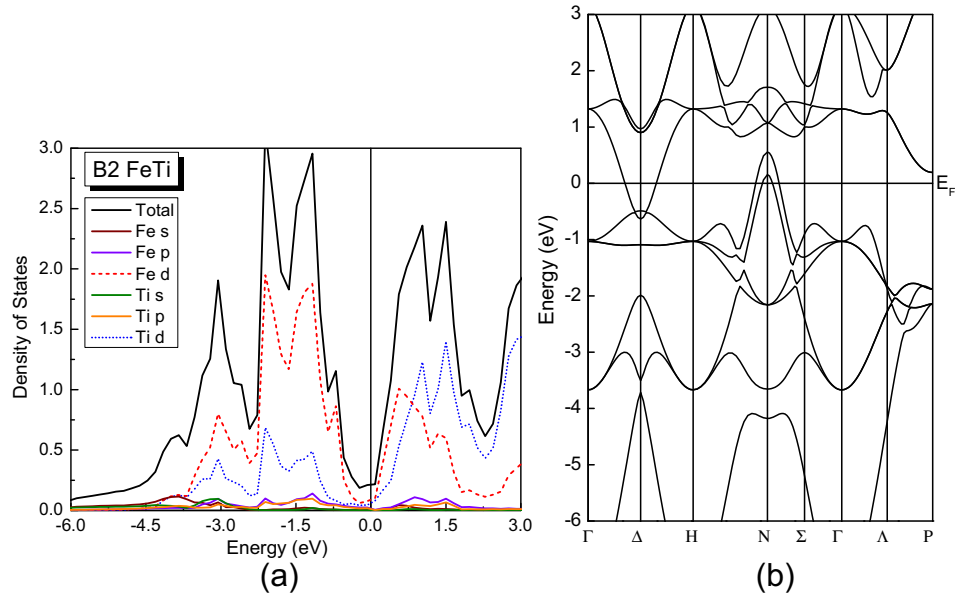


Fig. 2. Electronic structures of FeTi (a) density of states (in states/eV per formula unit), (b) band structures. In (a) the black solid line denotes the total DOS of FeTi and the partial DOS for s, p, d states of Fe and Ti were also given.

5. Thermal properties at finite temperatures

In this section we combined the first-principles calculations with the quasiharmonic approximation to obtain the thermal properties of a FeTi at finite temperatures. In order to calculate phonon spectra of FeTi crystal at different lattice parameters we use an analytical form of the dynamical matrix (see details in Appendix). We employ the virtual crystal approximation, i.e., FeTi is approximated as a bcc lattice occupied by species-averaged atoms with the atomic weight equal to the average of the atomic weights of Fe and Ti.

In order to compute finite-temperature thermodynamic properties within the quasi-harmonic approximation, the relative energy ΔE (in meV/atom) with respect to the ground-state energy, the volume per atom (in $\text{\AA}^3/\text{atom}$), the isothermal bulk modulus B (in GPa), the single crystalline elastic constants C_{11} , C_{12} , and C_{44} (in GPa) under pressure from -5.7 GPa to 3.7 GPa were calculated and are listed in Table 2. As seen, the bulk modulus B and elastic constants C_{11} , C_{12} , and C_{44} slightly increase with increasing hydrostatic pressure.

The thus computed temperature dependence of the free energies F is plotted in Fig. 4(a). The thermal expansion coefficients between $0 \sim 1200$ K, $\frac{1}{V} \frac{\partial V}{\partial T}$, of FeTi are shown in Fig. 4(b). With

increasing temperature, the thermal expansion coefficient grows rapidly up to ~ 200 K, for higher temperatures the slope becomes less steep and the trend flattens when approaching 800 K. Another pronounced increase is then for yet higher temperature, between 800 and 1200 K. As may be seen, our theoretically predicted thermal expansion coefficient (full black line in Fig. 4(b)) agrees very well with our experimental data (red data points in Fig. 4(b)) between 180 and 700 K [6].

Specifically for the room temperature, the experimental thermal expansion coefficients $9.5 \times 10^{-6} \text{ K}^{-1}$ [6] (at 300 K) and $9.8 \times 10^{-6} \text{ K}^{-1}$ [9] (at 293 K) are both slightly higher than our theoretical result $8.2 \times 10^{-6} \text{ K}^{-1}$. The experimental thermal expansion coefficients for pure bcc Fe [55] between 90 K and 960 K are also given for comparison in Fig. 4(b) and found larger (by an almost constant off-set) compared with FeTi for temperatures up to 920 K.

Fig. 4(c) visualizes calculated temperature dependences of the heat capacity C_p (experimental data were published also by Wang et al. [56]) at constant pressure (black solid line) and that at constant volume C_v (black dashed line). Our results are compared with (i) theoretical C_v which were calculated based on the experimental elastic constants [10] (blue solid line) as well as (ii) experimental data of C_v [10] (red circles). As far as the heat capacity as constant

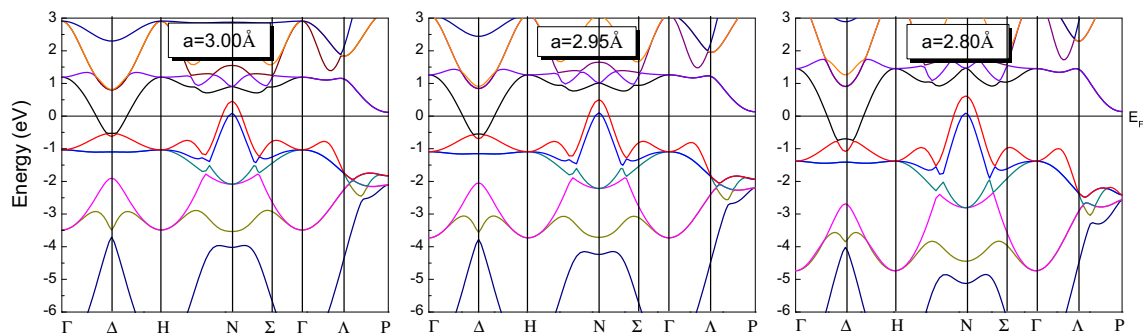


Fig. 3. Band structures of FeTi at different lattice constants.

Table 2

Pressure dependence (between -5.7 and ~ 3.7 GPa) of the relative energy ΔE (meV/atom) compared to the total energy of the equilibrium structure, volume per atom ($\text{\AA}^3/\text{atom}$), bulk modulus B (GPa), single crystalline elastic constants C_{11} (GPa), C_{12} (GPa), and C_{44} (GPa) for FeTi intermetallics.

P	ΔE	V	B	C_{11}	C_{12}	C_{44}
3.7	2.81	12.64	206.7	405.2	107.4	77.9
2.7	1.52	12.71	202.1	397.9	104.2	76.3
1.6	0.63	12.77	198.1	391.4	101.4	74.7
0.1	0.01	12.88	191.4	378.0	98.2	72.2
-1.3	0.37	12.97	185.9	371.9	92.9	70.0
-2.2	1.08	13.03	181.9	365.9	89.9	68.5
-3.1	2.20	13.10	178.1	362.4	85.9	67.0
-4.0	3.67	13.17	174.1	353.3	84.5	65.5
-4.9	5.51	13.23	170.5	347.4	82.1	64.1
-5.7	7.73	13.30	167.1	341.6	79.8	62.6

volume C_V is concerned, our results excellently agree with existing theoretical and experimental results at temperatures $200 < T < 500$ K. The heat capacities for pure Fe ($25.065 \text{ J mol}^{-1} \text{ K}^{-1}$) [57] and pure Ti ($25.095 \text{ J mol}^{-1} \text{ K}^{-1}$) [58] at 300 K are also shown in Fig. 4(c).

We also see that the experimental heat capacities of elemental Fe and Ti at room temperature are clearly higher than that of their equiatomic combination, i.e. FeTi intermetallics. It should be nevertheless noted that Ti crystallizes at room temperature in a hexagonal closed packed (hcp) structure (for which the heat capacity was measured) but the CsCl-type B2 structure of FeTi is essentially like a body-centered cubic (bcc) one.

Isothermal bulk modulus as a function of temperature is shown in Fig. 4(d). It decreases with increasing temperature. The experimental bulk moduli at room temperature [9,10], especially that from Ref. [10] (189 GPa), are quite close to our first-principles result (184 GPa). The bulk moduli of pure Fe [50,51] between 0 and 1200 K and those of pure Ti [52,53] between 293 and 1073 K are also given

in Fig. 4(d). Similarly as in case of heat capacities discussed above, it is worth to mention that, at room temperature for which experimental data exist, the bulk modulus of B2 FeTi is not any simple average of values found in both constituents, elemental Fe and Ti. Instead it is close to that of pure Fe and much higher than that in pure Ti. This particular conclusion is also true in case that the bulk modulus of body-centered cubic Ti would be considered. Despite of the fact that the bulk modulus bcc Ti may not be experimentally measured at low temperatures under ambient pressure conditions, our quantum-mechanical calculations can be used to predict it. The thus determined bulk modulus of bcc Ti at $T = 0$ K is even lower (around 90 GPa) than that in hcp Ti. The fact, that some materials characteristics of intermetallics are not related in any simple manner to their values in elemental constituents, is important for any theory-based materials design of intermetallics in general.

Above room temperature, with increasing temperature the bulk modulus of FeTi decreases significantly more than those of pure Fe and pure Ti. Below room temperature the decrease for both FeTi and pure Fe is small and the trend is almost constant.

6. Conclusion

Using density functional theory we have studied $T = 0$ K thermodynamic, structural, elastic and electronic properties of B2 FeTi intermetallics including single-crystalline Young's modulus and the area modulus, homogenized polycrystalline elastic parameters, as well as densities of states and band structures at different volumes. Our results are in good agreement with existing experimental and theoretical data and show a particularly strong stability of the electronic structure of FeTi with respect to hydrostatic pressures. Combining first-principles method with (i) an analytical dynamical matrix parameterized in terms of elastic constants and lattice parameters and (ii) the quasiharmonic approximation, we have also investigated finite-temperature thermodynamic properties of FeTi.

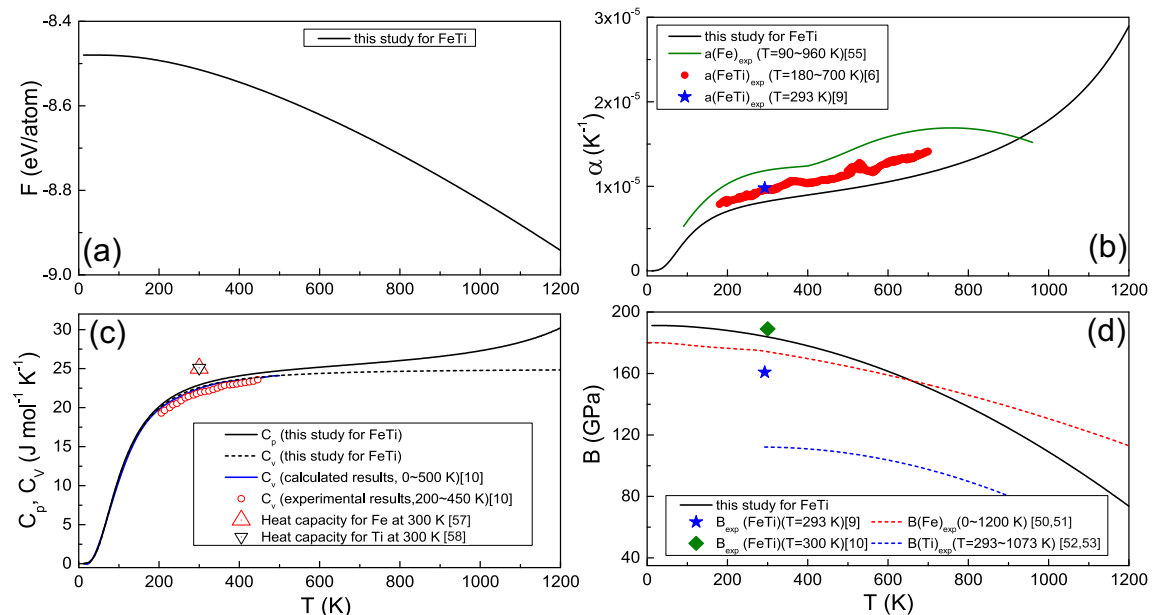


Fig. 4. Temperature dependence of (a) the free energies F (eV/atom), (b) the thermal expansion coefficients α (K^{-1}), (c) the heat capacities C_p and C_v ($\text{J mol}^{-1} \text{ K}^{-1}$), and (d) the bulk moduli B (GPa). In the four graphs, the black solid lines indicate our first-principles based results, the red dots the experimental results from Ref. [10], the blue star the experimental results from Ref. [9] and the green rhombus the experimental results from Ref. [10]. In (c), the black dashed line indicates our theoretical results for C_v and the blue solid line corresponds to C_v calculated from the experimental elastic constants [10] and the red circle the experimental results [10] of C_v . In addition, the green solid line in (b) denotes the experimental thermal expansion coefficient of pure Fe [55], the red up-triangle and black down-triangle in (c) respectively indicate the experimental heat capacities at room temperature of pure Fe [57] and pure Ti [58], the red short-dash line and the blue short-dash line in (d), respectively, indicate the temperature dependences of the bulk moduli of pure Fe [50,51] and pure Ti [52,53]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The free energies, the thermal expansion coefficients, the heat capacities at constant pressure and volume, as well as the isothermal bulk moduli at finite temperatures of B2 FeTi have been computed. Theoretical results neatly match both (i) our own experimental measurements in case of the thermal expansion coefficient as well as (ii) data available in literature. It is worth mentioning that, as often detected in other intermetallics, some materials characteristics of FeTi clearly different from the average of corresponding values known for elemental Fe and Ti. These findings can have important implications for future theory-guided materials design of advanced intermetallics.

Acknowledgment

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Appendix

Free energy is the key quantity, which defines at elevated temperatures all material thermodynamic properties, and within adiabatic approximation for nonmagnetic crystal reads

$$F(V, T) = F_{el}(V, T) + F_{vib}(V, T) \quad (8)$$

where F_{el} and F_{vib} are electronic excitations and ionic vibrations, respectively. The vibrational contribution F_{vib} to the free energy per single atom unit cell within the harmonic approximation is given by

$$F_{vib} = \frac{1}{N} \sum_i^{3N} \left\{ \frac{1}{2} h\omega_i + k_B T \ln \left[1 - \exp\left(\frac{-h\omega_i}{k_B T}\right) \right] \right\} \quad (9)$$

where h is the Planck constant, k_B is the Boltzmann constant, ω_i are phonon frequencies. Summation is carried over the complete set of $3N$ phonon states for N atoms in the crystal cell. The phonon frequencies ω_i are the values of the dynamical matrix $\mathbf{D}$.

The electronic free energy F_{el} depends on the volume and electronic temperature, by that directly influences the volume dependence of the phonon frequencies and vibrational free energy Eq. (9). However, in the following we apply quasiharmonic approximation [30–32] by replacing F_{el} with $F_{el}(T = 0 \text{ K})$ and thus omit the explicit temperature dependence in the phonon frequencies: $\omega_i = \omega_i(V)$. In contrast to previous studies (see, e.g. Ref. [28]), we employ here an analytical form of the dynamical matrix [59] in reciprocal space. The matrix is parameterized in terms of the elastic constants C_{ij} and the lattice parameter a with the latter obtained using density-functional-theory calculations as described above. In the simplest form, when only interactions between the nearest-neighbor atoms are considered [59], the analytical expression for the lattice Green's function $\mathbf{G}(\mathbf{k}) = \mathbf{D}^{-1}(\mathbf{k})$ ($\mathbf{k} \neq 0$) can be represented in terms of lattice parameters a_{bcc} and elastic constants C_{ij} . The individual components are then given

$$\begin{aligned} \mathbf{D}^{xx}(\mathbf{k}) &= 4a_{bcc}C_{44}(1 - \cos\pi a_{bcc}k_x - \cos\pi a_{bcc}k_y \cos\pi a_{bcc}k_z) \\ &\quad + a_{bcc}(C_{11} - C_{44})\cos 2\pi k_x \end{aligned} \quad (10)$$

$$\mathbf{D}^{xy}(\mathbf{k}) = 2a_{bcc}(C_{12} + C_{44})\sin\pi a_{bcc}k_x \sin\pi a_{bcc}k_y \sin\pi a_{bcc}k_z \quad (11)$$

The other components of the Green's tensor can be obtained from Eqs. (10) and (11) by cyclic permutations of the indices x, y, z .

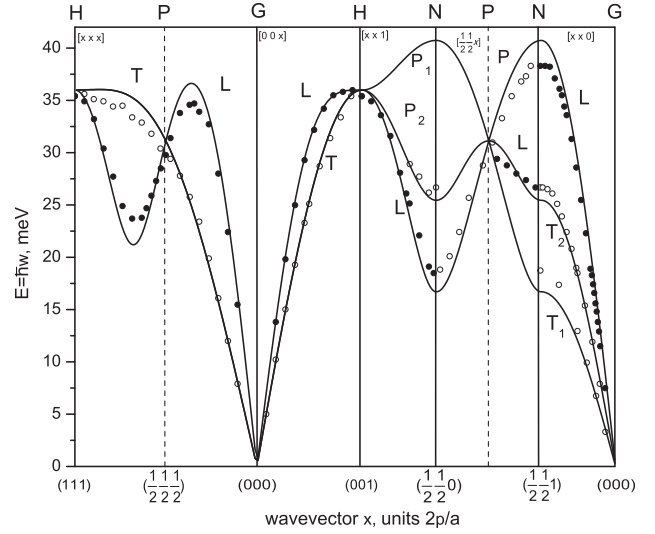


Fig. 5. Computed phonon spectra of α -Fe crystal (full lines) compared with experimental data [61].

For the calculation of the thermodynamic potential $F(V, T)$ we used $F_{el}(T = 0 \text{ K})$ obtained *ab initio* for 10 atomic volumes.

The performance of the method is demonstrated for α -Fe in Fig. 5 where computed phonon spectrum is shown by full lines and compared with experimental data [61].

It is worth mentioning that the above described analytical form of the dynamical matrix can be used as an effective tool to calculate vibrational properties of disordered systems containing atoms with not too different atomic weights after calculating their elastic properties (see e.g. our previous paper [60]).

Having the phonon spectra for FeTi (see Fig. 6), the total energy $F_{el}(T = 0 \text{ K}) + F_{vib}$ has been parameterized by a least-squares fit to the Murnaghan equation of state [44].

The results obtained from the fits for the temperature dependent lattice constant a , were used for the calculation of the linear thermal expansion η and its coefficient α

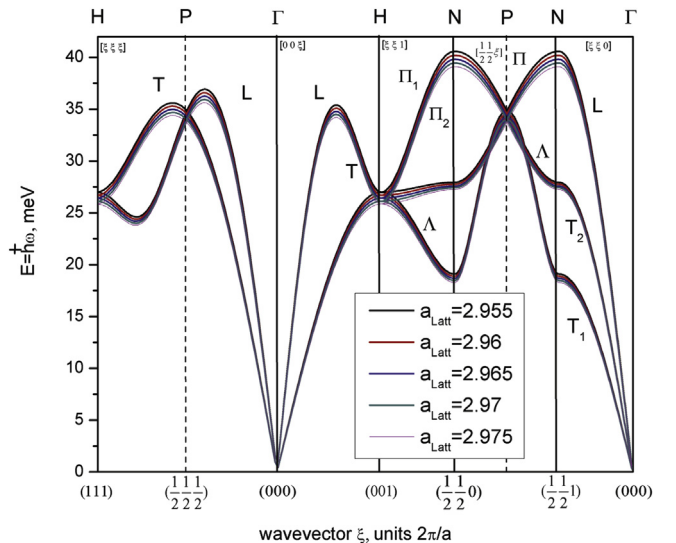


Fig. 6. Computed phonon spectra of FeTi crystal for a series of lattice parameters.

$$\eta(T) = \frac{a(T) - a(T_{\text{ref}})}{a(T_{\text{ref}})}, \quad \alpha(T) = \frac{1}{\alpha(T)} \frac{d\alpha(T)}{dT}. \quad (12)$$

with a the equilibrium lattice constant, reference temperature is $T_{\text{ref}} = 0$ K.

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