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Pressure effects on thermo-mechanical properties of intermetallic B2-type FeAl alloy

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Abstract. The pressure effects on thermo-mechanical properties of B2-type FeAl compound have been investigated based on the moment method in statistical mechanics. We derive analytical expressions of equation-of-state, isothermal bulk modulus and specific heats at constant volume and constant pressure of B2-type iron aluminide intermetallic compound. Numerical calculations for lattice parameter, isothermal bulk modulus, Young's modulus, shear modulus and specific heat at constant pressure of B2-type Fe-40 at.% Al have been performed up to pressure of 10 GPa. Our research shows that the elastic moduli are linear proportional to pressure and the specific heat at constant pressure diminishes strongly at temperature below 300 K. The present statistical moment method results are compared with available experimental data as well as ab initio calculations when possible to verify the developed theory. This research proposes the potential of the moment method in the investigation of thermo-mechanical properties of materials under pressure.

1 Introduction

The iron aluminide (FeAl) intermetallic binary compounds have attracted a lot of attention of researchers because these compounds exhibit many desired physical properties such as high melting temperature, high-temperature oxidation, relatively high strength, stiffness, and good corrosion resistance behavior at high temperatures [1,2]. These properties of iron aluminide compounds make them become potential candidates for industrial applications, especially at high temperature conditions, such as protective coating for materials, gas turbines and/or automobile engine components, substitution of ferritic stainless steels at high temperatures. Besides many interesting properties, the FeAl intermetallic systems show several structural phases at various temperatures and compositions in which B2-type and DO3-type structures remain stable over a wide range of aluminum contents [3]. While the B2-FeAl intermetallic compound, having the CsCl structure exists in aluminum composition range 35–50 at.%, the ordered DO3 cubic structure is stable in the interval of 23–36 at.% Al. The DO3 phase will transform towards the crystalline B2 phase when the Al composition increases to attain the FeAl stoichiometry.

Previously many investigations for FeAl systems have been performed to deeply understand phase stabilities [4], thermodynamic properties [5], formation energies [6], vacancy effects [7] and phonon spectra [8,9]. Numerous efforts have been devoted with a focus on the mechanical properties of B2-type FeAl intermetallic with an aim to increase strength and corrosion resistance. For example, when considering the impact of quenched-in thermal vacancies on mechanical properties of B2-FeAl, Zamanzade et al. showed that bi-vacancies increase the hardness values of alloy much more significantly in comparison to the mono-vacancies [7]. Although extensive experimental and theoretical studies of Fe-Al system have been done, the investigation of thermodynamic and mechanical properties of B2-type FeAl intermetallic alloy under pressure is still very limited. To our best knowledge, most of previous works just considered thermo-mechanical properties of B2-FeAl alloy at ambient pressure, no measurements and calculations have ever been implemented for pressure-dependent elastic moduli and specific heats of

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$$\psi^{\mathrm{Fe}} = U_0^{\mathrm{Fe}} + \psi_0^{\mathrm{Fe}} + 3N_1\left\{ \frac{\theta^2}{(k^{\mathrm{Fe}})^2}\left[\gamma_2^{\mathrm{Fe}}(X^{\mathrm{Fe}})^2 - \frac{2\gamma_1^{\mathrm{Fe}}}{3}\left(1+\frac{X^{\mathrm{Fe}}}{2}\right)\right]\right.$$
$$\left. + \frac{2\theta^3}{(k^{\mathrm{Fe}})^4}\left[\frac{4}{3}(\gamma_2^{\mathrm{Fe}})^2 X^{\mathrm{Fe}} - 2\left((\gamma_1^{\mathrm{Fe}})^2 + 2\gamma_1^{\mathrm{Fe}}\gamma_2^{\mathrm{Fe}}\right)\left(1+X^{\mathrm{Fe}}\right)\right]\left(1+\frac{X^{\mathrm{Fe}}}{2}\right)\right\} \quad (2)$$

$$\psi^{\mathrm{Al}} = U_0^{\mathrm{Al}} + \psi_0^{\mathrm{Al}} + 3N_2\left\{ \frac{\theta^2}{(k^{\mathrm{Al}})^2}\left[\gamma_2^{\mathrm{Al}}(X^{\mathrm{Al}})^2 - \frac{2\gamma_1^{\mathrm{Al}}}{3}\left(1+\frac{X^{\mathrm{Al}}}{2}\right)\right]\right.$$
$$\left. + \frac{2\theta^3}{(k^{\mathrm{Al}})^4}\left[\frac{4}{3}(\gamma_2^{\mathrm{Al}})^2 X^{\mathrm{Al}} - 2\left((\gamma_1^{\mathrm{Al}})^2 + 2\gamma_1^{\mathrm{Al}}\gamma_2^{\mathrm{Al}}\right)\left(1+X^{\mathrm{Al}}\right)\right]\left(1+\frac{X^{\mathrm{Al}}}{2}\right)\right\} \quad (3)$$

B2-type FeAl compound. As far as we known, compression plays a significant effect on the structural and thermo-mechanical properties of material due to the limitation of atomic vibrations. These physical properties can be modified by turning the environmental pressure which may have a potential in engineering applications. Therefore, it is important to determine thermo-mechanical properties of B2-type FeAl intermetallic alloy at high pressure.

In present work, with the aim of contributing to the knowledge about thermo-mechanical properties of the B2-type FeAl intermetallic under pressure, we apply the statistical moment method (SMM) in quantum statistical mechanics [10–12] for B2-type Fe-40 at.% Al alloy to investigate the pressure effects on its lattice parameter, elastic moduli (bulk modulus, Young's modulus and shear modulus), and specific heats at constant volume and pressure. Numerical calculations are performed up to pressure of 10 GPa and compared with those of available data to verify theory.

This paper is organized as follows, in Section 2, we present principle of calculations to study thermo-mechanical properties of intermetallic B2-type FeAl alloy which will be solved numerically. In Section 3, we discuss numerical results in detail followed by Section 4 in which we make the conclusions of the paper.

2 Principle of calculations

2.1 Statistical moment method

In the first part of this section, we present the SMM approach for intermetallic alloys. Let us consider the B2-type iron aluminide system with N atoms in which N_1 and N_2 are, respectively, the number of Fe and Al atoms. Then concentrations of Fe and Al atoms are $C_{\mathrm{Fe}} = N_1/N$ and $C_{\mathrm{Al}} = N_2/N$. Using the Boltzmann relation, the Helmholtz free energy of the FeAl system ψ can be written by taking into account the configuration entropy of the system S_c as [13]

$$\psi = C_{\mathrm{Fe}}\psi^{\mathrm{Fe}} + C_{\mathrm{Al}}\psi^{\mathrm{Al}} - TS_c. \quad (1)$$

In this above equation, ψ^{Fe} and ψ^{Al} are, correspondingly, the Helmholtz free energies of Fe and Al particles which have been given in term of SMM parameters (see Appendix A) as [11]

See equations (2) and (3) above,

here U_0^{Fe} and U_0^{Al} denote the sum of effective pair interaction energies of Fe and Al ions; harmonic parameters k^{Fe} and k^{Al}, anharmonic expansion coefficients γ_1^{Fe}, γ_2^{Fe}, γ_1^{Al}, and γ_2^{Al} are defined as follows [10–12]

See equation (4) next page,

with $\alpha \neq \beta = x, y$ or z, eq indicates the thermal averaging over the equilibrium ensemble, $\varphi(r)$ is the function of interaction potential between atoms, $\theta = k_B T$ (k_B is the Boltzmann constant), and ψ_0^{Fe} and ψ_0^{Al} are, respectively, the harmonicity contributions to the free energies ψ^{Fe} and ψ^{Al} which have the forms as [11,12]

$$\psi_0^{\mathrm{Fe}} = 3N_1\theta\left[x^{\mathrm{Fe}} + \ln\left(1 - e^{-2x^{\mathrm{Fe}}}\right)\right],$$
$$\psi_0^{\mathrm{Al}} = 3N_2\theta\left[x^{\mathrm{Al}} + \ln\left(1 - e^{-2x^{\mathrm{Al}}}\right)\right], \quad (5)$$

where

$$x^{\mathrm{Fe}} = \frac{\hbar\omega^{\mathrm{Fe}}}{2\theta} = \frac{\hbar}{2\theta}\sqrt{\frac{k^{\mathrm{Fe}}}{m^{\mathrm{Fe}}}}, \quad X^{\mathrm{Fe}} = x^{\mathrm{Fe}}\coth\left(x^{\mathrm{Fe}}\right),$$
$$x^{\mathrm{Al}} = \frac{\hbar\omega^{\mathrm{Al}}}{2\theta} = \frac{\hbar}{2\theta}\sqrt{\frac{k^{\mathrm{Al}}}{m^{\mathrm{Al}}}}, \quad X^{\mathrm{Al}} = x^{\mathrm{Al}}\coth\left(x^{\mathrm{Al}}\right). \quad (6)$$

The Helmholtz free energy ψ is going to be used to calculate various thermo-mechanical quantities (such as the equation-of-state, elastic moduli and specific heats at constant volume and pressure which are closely related to the anharmonicity of thermal lattice vibrations) of B2-FeAl intermetallic compound.

2.2 The SMM equation-of-state

According to thermodynamic considerations, the pressure P can be calculated through the free energy ψ of the crystal as

$$P = -\left(\frac{\partial\psi}{\partial V}\right) = -\frac{r_1}{3V}\left(\frac{\partial\psi}{\partial r}\right). \quad (7)$$

$$\begin{aligned}
k^{\mathrm{Fe}} &= \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{i0}^{\mathrm{Fe}}}{\partial u_{i\alpha}^2}\right)_{eq}, \quad \gamma_1^{\mathrm{Fe}} = \frac{1}{24}\sum_i \left(\frac{\partial^4 \varphi_{i0}^{\mathrm{Fe}}}{\partial u_{i\alpha}^4}\right)_{eq}, \quad \gamma_2^{\mathrm{Fe}} = \frac{6}{24}\sum_i \left(\frac{\partial^4 \varphi_{i0}^{\mathrm{Fe}}}{\partial u_{i\alpha}^2 \partial u_{i\beta}^2}\right)_{eq}\\
k^{\mathrm{Al}} &= \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{i0}^{\mathrm{Al}}}{\partial u_{i\alpha}^2}\right)_{eq}, \quad \gamma_1^{\mathrm{Al}} = \frac{1}{24}\sum_i \left(\frac{\partial^4 \varphi_{i0}^{\mathrm{Al}}}{\partial u_{i\alpha}^4}\right)_{eq}, \quad \gamma_2^{\mathrm{Al}} = \frac{6}{24}\sum_i \left(\frac{\partial^4 \varphi_{i0}^{\mathrm{Al}}}{\partial u_{i\alpha}^2 \partial u_{i\beta}^2}\right)_{eq} \qquad (4)
\end{aligned}$$

By substituting the Helmholtz free energy ψ from equation (1) into equation (7), we derive the SMM equation-of-state (EOS) describing the pressure versus volume relation of the system as follows

$$\begin{aligned}
Pv = -r_1\bigg\{ & C_{\mathrm{Fe}}\left[\frac{1}{6}\frac{\partial U_0^{\mathrm{Fe}}}{\partial r} + \frac{\theta X^{\mathrm{Fe}}}{2k^{\mathrm{Fe}}}\frac{\partial k^{\mathrm{Fe}}}{\partial r}\right]\\
& + C_{\mathrm{Al}}\left[\frac{1}{6}\frac{\partial U_0^{\mathrm{Al}}}{\partial r} + \frac{\theta X^{\mathrm{Al}}}{2k^{\mathrm{Al}}}\frac{\partial k^{\mathrm{Al}}}{\partial r}\right]\bigg\}, \qquad (8)
\end{aligned}$$

where v is the atomic volume $v = V/N$. The solution of the SMM EOS (8) gives us the value of nearest-neighbor distance (NND) $r_1(P,T)$ between two intermediate atoms at pressure P and temperature T. And the lattice parameter $a_h(P,T)$ of BCC or CsCl structure is calculated as $a_h(P,T) = 2/\sqrt{3}r_1(P,T)$.

2.3 The isothermal bulk modulus

Let us now consider the isothermal bulk modulus of the solid B2 phase of FeAl. According to the definition of the isothermal bulk modulus K_T, it is given in terms of the volume V and pressure P as [14]

$$K_T = -V_0\left(\frac{\partial P}{\partial V}\right)_T = V_0\left(\frac{\partial^2 \psi}{\partial V^2}\right)_T, \qquad (9)$$

where V_0 is the crystal volume at zero pressure.

Substituting equation (1) into equation (9), we derive the final expression of isothermal bulk modulus K_T of B2-type FeAl alloy as the following

$$K_T = C_{\mathrm{Fe}}K_T^{\mathrm{Fe}} + C_{\mathrm{Al}}K_T^{\mathrm{Al}}, \qquad (10)$$

where the partial bulk moduli components K_T^{Fe} and K_T^{Al} are given by

$$K_T^{\mathrm{Fe}} = -\frac{k_B}{3\alpha_T^{\mathrm{Fe}}}\left(\frac{\partial^2 \psi^{\mathrm{Fe}}}{\partial V \partial \theta}\right), \quad K_T^{\mathrm{Al}} = -\frac{k_B}{3\alpha_T^{\mathrm{Al}}}\left(\frac{\partial^2 \psi^{\mathrm{Al}}}{\partial V \partial \theta}\right), \qquad (11)$$

$$\alpha_T^{\mathrm{Fe}} = \frac{k_B}{r_1}\frac{\partial y_0^{\mathrm{Fe}}}{\partial \theta}, \quad \alpha_T^{\mathrm{Al}} = \frac{k_B}{r_1}\frac{\partial y_0^{\mathrm{Al}}}{\partial \theta}, \qquad (12)$$

here α_T^{Fe} and α_T^{Al} are the partial linear thermal expansion coefficients; y_0^{Fe} and y_0^{Al} are, respectively, the atomic displacements of Fe and Al atoms from the equilibrium positions in the B2-FeAl system [10–12].

2.4 Specific heats at constant volume and constant pressure

The Gibbs-Helmholtz relation gives us the energy E of FeAl system as

$$E = \psi - \theta\left(\frac{\partial \psi}{\partial \theta}\right) = C_{\mathrm{Fe}}E^{\mathrm{Fe}} + C_{\mathrm{Al}}E^{\mathrm{Al}}, \qquad (13)$$

where energies E^{Fe} and E^{Al} have the forms as [11–13]

$$\begin{aligned}
E^{\mathrm{Fe}} = U_0^{\mathrm{Fe}} + 3N_1\theta X^{\mathrm{Fe}} + \frac{3N_1\theta^2}{(k^{\mathrm{Fe}})^2}\bigg[& \gamma_2^{\mathrm{Fe}}(X^{\mathrm{Fe}})^2\\
& + \frac{\gamma_1^{\mathrm{Fe}}}{3}\left(2 + Y^{\mathrm{Fe}}\right) - 2\gamma_2^{\mathrm{Fe}}X^{\mathrm{Fe}}Y^{\mathrm{Fe}}\bigg], \qquad (14)
\end{aligned}$$

$$\begin{aligned}
E^{\mathrm{Al}} = U_0^{\mathrm{Al}} + 3N_2\theta X^{\mathrm{Al}} + \frac{3N_2\theta^2}{(k^{\mathrm{Al}})^2}\bigg[& \gamma_2^{\mathrm{Al}}(X^{\mathrm{Al}})^2\\
& + \frac{\gamma_1^{\mathrm{Al}}}{3}\left(2 + Y^{\mathrm{Al}}\right) - 2\gamma_2^{\mathrm{Al}}X^{\mathrm{Al}}Y^{\mathrm{Al}}\bigg], \qquad (15)
\end{aligned}$$

with

$$Y^{\mathrm{Fe}} = \frac{(x^{\mathrm{Fe}})^2}{\sinh^2 x^{\mathrm{Fe}}}, \quad Y^{\mathrm{Al}} = \frac{(x^{\mathrm{Al}})^2}{\sinh^2 x^{\mathrm{Al}}}. \qquad (16)$$

The specific heats at constant volume C_V and constant pressure C_P are then derived, respectively, as follows [15]

$$C_V = \frac{\partial E}{\partial T} = C_{\mathrm{Fe}}C_V^{\mathrm{Fe}} + C_{\mathrm{Al}}C_V^{\mathrm{Al}}, \qquad (17)$$

and

$$C_P = C_V + 9TVK_T\alpha_T^2, \qquad (18)$$

where $\alpha_T = C_{\mathrm{Fe}}\alpha_T^{\mathrm{Fe}} + C_{\mathrm{Al}}\alpha_T^{\mathrm{Al}}$ is the thermal expansion coefficient of the FeAl system; and the partial specific heats C_V^{Fe} and C_V^{Al}, respectively, are

See equations (19) and (20) next page.

2.5 Interatomic potential

In this paper, the thermo-mechanical properties of B2-type FeAl compound under pressure are numerically calculated by using the interatomic potential derived from ab initio electronic structure calculations within the Möbius lattice inversion scheme [16–20]. Based on the Möbius

$$\begin{aligned} C_V^{\mathrm{Fe}} = \frac{\partial E^{\mathrm{Fe}}}{\partial T} &= 3N_1 k_B Y^{\mathrm{Fe}} \left\{ 1 + \frac{2\theta}{(k^{\mathrm{Fe}})^2} \left[\left(2\gamma_2^{\mathrm{Fe}} + \frac{\gamma_1^{\mathrm{Fe}}}{3} \right) X^{\mathrm{Fe}} \right] \right\} \\ &\quad + 3N_1 k_B Y^{\mathrm{Fe}} \left\{ \frac{2\theta}{(k^{\mathrm{Fe}})^2} \left[\frac{\gamma_1^{\mathrm{Fe}}}{3} \Big(1/Y^{\mathrm{Fe}} + 1 \Big) - \gamma_2^{\mathrm{Fe}} \Big(Y^{\mathrm{Fe}} + 2(X^{\mathrm{Fe}})^2 \Big) \right] \Big] \right\} \end{aligned} \tag{19}$$

$$\begin{aligned} C_V^{\mathrm{Al}} = \frac{\partial E^{\mathrm{Al}}}{\partial T} &= 3N_1 k_B Y^{\mathrm{Al}} \left\{ 1 + \frac{2\theta}{(k^{\mathrm{Al}})^2} \left[\left(2\gamma_2^{\mathrm{Al}} + \frac{\gamma_1^{\mathrm{Al}}}{3} \right) X^{\mathrm{Al}} \right] \right\} \\ &\quad + 3N_1 k_B Y^{\mathrm{Al}} \left\{ \frac{2\theta}{(k^{\mathrm{Al}})^2} \left[\frac{\gamma_1^{\mathrm{Al}}}{3} \Big(1/Y^{\mathrm{Al}} + 1 \Big) - \gamma_2^{\mathrm{Al}} \Big(Y^{\mathrm{Al}} + 2(X^{\mathrm{Al}})^2 \Big) \right] \Big] \right\} \end{aligned} \tag{20}$$

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inversion in the number theory, Chen et al. proposed the lattice inversion method to obtain interatomic pair potentials from the cohesive energy curves. In this approach, the cohesive energy per atom of a crystal $E_c(r)$ can be expressed in terms of the sum of the interatomic potentials $\varphi(r)$ as [21,22]

$$E_c(r) = \frac{1}{2} \sum_{i \neq j} \varphi(r_{ij}) = \frac{1}{2} \sum_{k=1}^{\infty} z_k \varphi(\nu(k) r_1), \tag{21}$$

where r_1 is the atomic nearest neighbor distance, $\nu(k) = \nu_k$ denotes the ratio of the kth neighbor distance (r_k) to the first-neighbor distance r_1 (then $\nu_k r_1 = r_k$), and z_k is the coordination number of kth neighbor atoms which denotes the number of atoms in kth coordination sphere. With BCC or CsCl-structure, we have $\nu_1 = 1$ and $z_1 = 8$, $\nu_2 = \sqrt{4/3}$ and $z_2 = 6$, $\nu_3 = \sqrt{8/3}$ and $z_3 = 12$, $\nu_4 = \sqrt{11/3}$ and $z_4 = 24$, $\nu_5 = 2$ and $z_5 = 24$, etc.

The pair interatomic potential $\varphi(r)$ is given with an inverse operation as

$$\varphi(r) = 2 \sum_{k=1}^{\infty} I(k) E_c\Big(\nu(k) r_1 \Big), \tag{22}$$

where $I(n)$ denotes the Möbius inversion function depending on structure type.

For numerically, the pair potential $\varphi(r)$ between two intermediate atoms is assumed to be the universal binding-energy relation potential derived from the ab initio tight-binding linear muffin-tin orbital method as [23]

$$\varphi^{\alpha\beta}(r) = -p_0^{\alpha\beta} \left[1 + q_0^{\alpha\beta}(r - r_0) \right] \exp\{-q_0^{\alpha\beta}(r - r_0)\}, \tag{23}$$

where superscripts α and β indicate the α and β atoms in the binary FeAl alloy, respectively; $p_0^{\alpha\beta}$, $q_0^{\alpha\beta}$, and r_0 are potential parameters fitted within the Möbius lattice inversion scheme.

3 Numerical calculations and discussion

The above analytical formulae allow us to investigate the thermo-mechanical properties of the B2-type FeAl system under pressure. In this section, thermo-mechanical quantities including the lattice constant, elastic moduli (isothermal bulk modulus, Young's modulus and shear modulus) and specific heats of B2-type FeAl alloy are calculated self-consistently with the lattice spacing of the given system. Numerical calculations have been performed for B2-type FeAl with 40 at.% Al. The universal binding-energy relation potential parameters of B2-FeAl are given in Table 1 [22]. And the coordination sphere method is applied to calculate the interaction energies U_0^{Fe} and U_0^{Al}.

Table 1. The fitted parameters of universal binding-energy relation potential expressed for B2-type FeAl [22].

$\alpha - \beta$	r_0 (Å)	$p_0^{\alpha\beta}$ (eV)	$q_0^{\alpha\beta}$ (Å^{-1})
Fe–Fe	2.803	0.482	2.020
Al–Al	3.252	0.343	1.162
Fe–Al	2.880	0.379	1.896

Firstly, we consider the lattice parameter of B2-FeAl alloy. At ambient pressure, the lattice parameter calculated by SMM is 2.8821 Å. This result is consistent with experiment (2.908 Å) [24] and other calculations [21,25–27]. The difference between present theory and previous works is about 1%. When considering the effects of pressure, by solving SMM EOS (8), we derive the lattice parameter of B2-FeAl alloy up to 10 GPa. Here it is worth mentioning that, in this work, we assume the binary alloy B2-type FeAl remains its CsCl structure up to pressure of 10 GPa. The pressure-dependent lattice parameters calculated in SMM scheme up to 10 GPa at various temperatures are shown in Figure 1. As it can be seen from Figure 1, the lattice parameter is a decreasing function of the pressure and it increases slightly with temperature. These effects can be explained by the reduction of atomic vibrations when pressure increases, and the increasing of atomic fluctuations (or anharmonicity contributions) at high temperature. When pressure increases from ambient conditions to 10 GPa, the lattice parameter is reduced about 4.2% and the slopes of these curves (in Fig. 1) are about $|da_h/dP| \simeq 0.012 - 0.016$ Å/GPa. Meanwhile when temperature increases from 100 K to 900 K, the lattice parameter expands approximately 0.5%.

With the aid of the Helmholtz free energy ψ, using equations (1), (2) and (3) we could determine the isothermal bulk modulus K_T of B2-type FeAl alloy. At room temperature and ambient pressure conditions, while

Table 2. The lattice constant a_h, isothermal bulk modulus K_T, Young's modulus E_Y, shear modulus G and specific heats C_V and C_P at room temperature and at ambient pressure.

	a_h (Å)	K_T (GPa)	E_Y (GPa)	G (GPa)	C_P (J/mol.K)
Present study	2.8821	166.84	167.17	62.71	24.37
Experiments	2.908[a]	152.0[b]	–	–	24.62[g]
Calculations	2.893[b]	148.2[b]	148.9[b]	55.9[b]	–
	2.919[c]	172.0[f]	–	–	–
	2.873[d]	174.8[d]	–	–	–
	2.880[e]	177.0[e]	–	–	–

[a]XRD measurements [24]; [b]Embedded-atom method [21]; [c]Modified embedded-atom method [25]; Ab initio calculations: [d]Reference [26]; [e]Reference [27]; [f]Reference [28]; [g]DSC measurement [29].

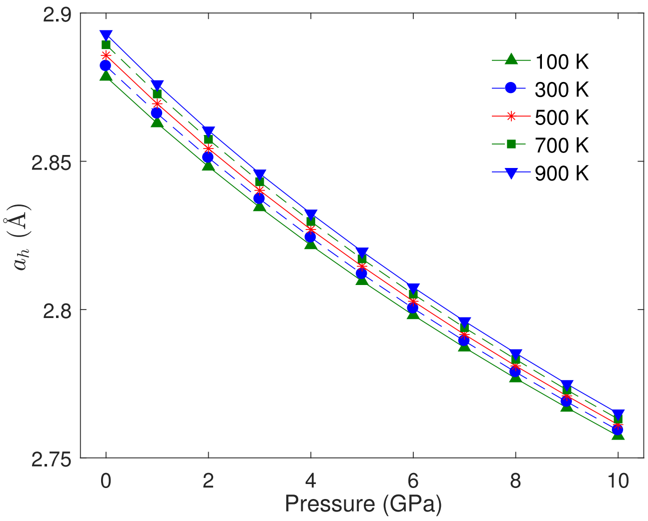

Fig. 1. Pressure-dependent lattice parameter of B2-type FeAl.

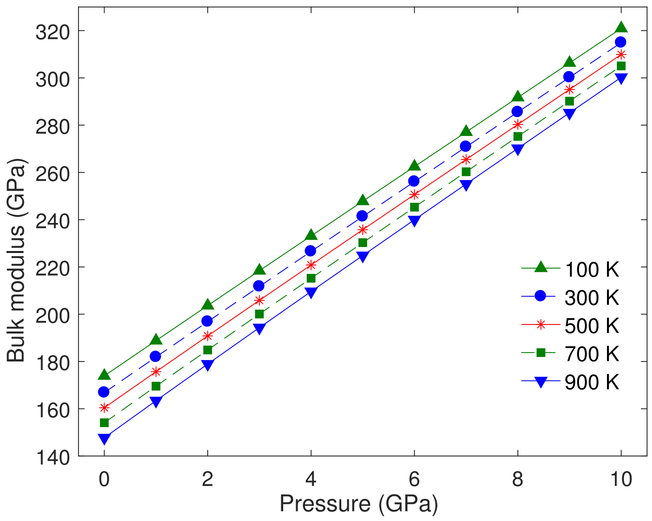

Fig. 2. Pressure dependence of the isothermal bulk modulus K_T at various temperatures calculated within the SMM scheme.

many previous theoretical determinations (172.0 GPa [28], 174.8 GPa [26] and 177.0 GPa [27]) significantly overestimate the experimental bulk modulus of B2-type FeAl, the SMM calculations give the value $K_T(300\text{ K}, 0\text{ GPa}) = 166.84$ GPa which reasonably agrees with the experimental X-ray diffraction measurement [21]. The isothermal bulk moduli K_T at various temperatures ($T = 0$ K, 300 K, 500 K, 700 K and 900 K) as functions of pressure are presented in Figure 2. From this figure, we can conclude that, at each given temperature the isothermal bulk modulus K_T increases forcibly with the increasing of pressure. The variation of K_T with pressure can be described by a linear function. The slopes of K_T lines (in Fig. 2) are about $dK_T/dP \simeq 14.7{-}15.2$. When the temperature increases, the value of K_T reduces gradually. This behavior of isothermal bulk modulus is because of the vigorous thermal fluctuations of particles at high temperatures.

Additionally, if we know the Poisson's ratio ν of material, we would obtain the Young's modulus E_Y and shear modulus G, correspondingly, from the following relations [30]

$$E_Y \approx 3\,(1-2\nu)\,K_T, \tag{24}$$

and

$$G = \frac{E_Y}{2(1+\nu)}. \tag{25}$$

Values of isothermal bulk modulus K_T, Young's modulus E_Y and shear modulus G at room temperature and zero pressure are listed in Table 2. From this table we can see that the prediction of Young's modulus E_Y and shear modulus G of B2-type FeAl alloy has been insufficient and in disagreement between two different theoretical methods. Additional theoretical as well as experimental efforts are needed to verify these evaluations. In Figure 3, we show the pressure dependence of Young's modulus E_Y and shear modulus G at different temperatures $T = 100$ K, 500 K and 900 K. Here it should be noted that, the Poisson's ratio of B2-type FeAl alloy has been assumed to remain constant and follow the Vegard's law as $\nu = C_{\text{Fe}}\nu_{\text{Fe}} + C_{\text{Al}}\nu_{\text{Al}}$, where experimental Poisson's ratio of Fe and Al metals are $\nu_{\text{Fe}} = 0.29$ and $\nu_{\text{Al}} = 0.35$, respectively. As we can see, the Young's and shear moduli are linearly proportional to pressure with slopes $dE_Y/dP \simeq 14.7{-}15.3$ and $dG/dP \simeq 5.5{-}5.7$, respectively.

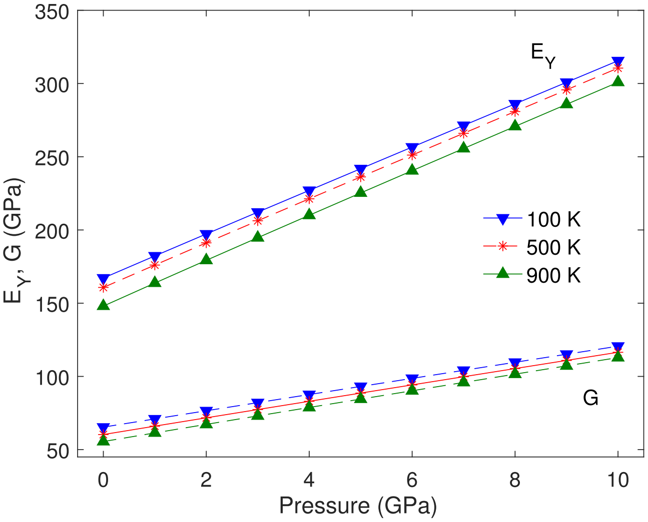

Fig. 3. Pressure dependence of the Young's modulus E_Y and shear modulus G at various temperatures calculated within the SMM scheme.

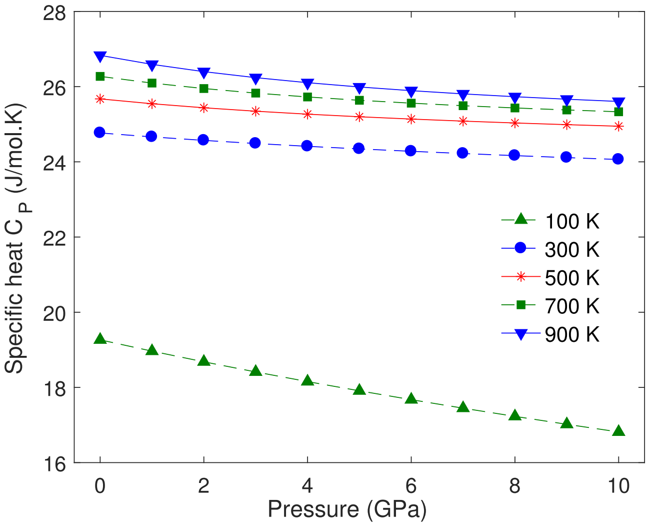

Fig. 4. Pressure dependence of the specific heat C_P at room temperatures calculated within the SMM scheme.

There are several approaches to estimate heat capacities of alloys and one of them is the well-known Neumann-Kopp approach [31]. This approach assumes a simple relation for estimation of the heat capacity of alloy by summing the heat capacities of the constituent elements. While this technique surprisingly predicts well the value of heat capacity of alloy at room temperature, it works poorly at abnormal conditions, especially at high temperatures and high pressure. The intimate reason of this effect could be caused from particular anharmonic contributions of different constituents at high temperature and pressure. In this work, the specific heat at constant pressure C_P of intermetallic FeAl alloy is determined based on the SMM approach. At ambient conditions, SMM calculations give the result $C_P = 24.37$ J/mol.K that is in very good agreement with recent experimental DSC measurements (24.62 J/mol.K) [29]. In Figure 4, we present the specific heats C_P of B2-type FeAl at various temperatures ($T = 0$ K, 300 K, 500 K, 700 K and 900 K) as functions of pressure. From this figure we can see that, at constant pressure and low temperature, especially below 300 K, the specific heat C_P increases energetically. When temperature increases from 300 K to 900 K, the C_P enhances progressively. Regarding to the pressure effects on the specific heat C_P, it diminishes slowly gradually as the compression increases. In particularly, the specific heat C_P alters strongly on pressure at low temperature. For example, the slope of the specific heat $|dC_P/dP|$ at 100 K and 900 K are, respectively, 0.25 J/mol.K.GPa and 0.12 J/mol.K.GPa.

Before making the conclusion of this research, it should be noted that, to the best of our knowledge there are seemly no calculations or measurements which have been performed to investigate the pressure effects on thermodynamic and mechanical properties of B2-type FeAl alloy. Then the comparison between our SMM calculations and other results has been ignored. Notwithstanding, this work gives us the prediction of pressure-dependent lattice parameter, elastic moduli and specific heats. On the opposite side, the current SMM approach has a limitation due to the derivation from a model potential. Numerical calculations of thermo-mechanical properties might be affected by the choosen force potential. Then the data derived from this research can be seen as useful references for future work. We hope that the aforementioned theoretical findings of these thermo-mechanical quantities will be verified experimentally in near future.

4 Conclusions

In this work, the pressure-dependent thermo-mechanical quantities of B2-type FeAl alloy have been investigated by using the statistical moment method in quantum statistical mechanics. Our development in this paper is the derivation of the Helmholtz free energy, SMM equation-of-state and solving this SMM EOS to get the pressure dependence of the lattice bond length. Furthermore, using the derived Helmholtz free energy, we establish the analytical expressions of bulk modulus and specific heats at constant volume and pressure of intermetallic B2-FeAl alloy. Numerical calculations have been performed for Fe-40 at.%Al with CsCl structure up to pressure of 10 GPa. Our research shows that the elastic moduli are linear proportional to pressure and the specific heat at constant pressure diminishes strongly at temperature below 300 K. The good and reasonable agreement between our calculated results with experimental measurements and with those of the other theoretical calculations denotes the efficiency of SMM in the investigation of the pressure effects on thermodynamic and mechanical quantities of materials. The advantage of this approach comparing to other theoretical methods is that it has taken into account the higher-order anharmonic terms in the atomic displacements and the quantum-mechanical zero-point vibrations. This method has itself included the anharmonicity contributions due to atomic fluctuations at a wide pressure and temperature ranges. Therefore, it has a great potential to be developed to study the temperature and pressure effects on thermo-mechanical properties of other intermetallic alloys with various structural phases.

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Author contribution statement

All authors contributed equally to the paper.

Appendix A: Helmholtz free energy in SMM formalism

Considering a system with Hamiltonian as

$$\widehat{H} = \widehat{H}_0 - \alpha \widehat{V}, \tag{A.1}$$

where $\widehat{H}_0$ is the lattice Hamiltonian in the harmonic approximation and the second term is due to the anharmonicity of thermal lattice vibrations. As reported by Tang and Hung [10], the Helmholtz free energy of this system at temperature T is given by

$$\psi = \psi_0 - \int_0^\alpha \langle \widehat{V} \rangle_\alpha d\alpha \,, \tag{A.2}$$

where ψ_0 is free energy of the system corresponding to the Hamiltonian $\widehat{H}_0$, and $\langle \widehat{V} \rangle_\alpha = -\partial\psi/\partial\alpha$.

If Hamiltonian $\widehat{H}$ of the system has a complex form, we should divide it into simpler parts as

$$\widehat{H} = \widehat{H}_0 - \sum_i \alpha_i \widehat{V}_i. \tag{A.3}$$

With the same procedure, we should firstly find the free energy ψ_1 of the system corresponding to the Hamiltonian $\widehat{H}_1 = \widehat{H}_0 - \alpha_1 \widehat{V}_1$. Afterwards we find the free energy ψ_2 of the system corresponding to $\widehat{H}_2 = \widehat{H}_1 - \alpha_2 \widehat{V}_2$, and so on. In this way we can derive the free energy ψ of the system with Hamiltonian $\widehat{H}$.

Assuming the potential energy of the system composed of N atoms can be written as

$$U = \frac{N}{2} \sum_i \varphi_{i0} \left(|r_i + u_i| \right) \tag{A.4}$$

where r_i is the equilibrium position of the ith atom, u_i is its displacement, and φ_{i0} is the effective interaction energy between *zero*th and ith atoms. By expanding the potential energy $\varphi_{i0} \left(|r_i + u_i| \right)$ up to the fourth-order terms of atomic displacements, we derive

$$\begin{aligned} U = \sum_i \Bigg\{ & \varphi_{i0}(|r_i|) + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta}} \right)_{eq} u_{i\alpha} u_{i\beta} \\ & + \frac{1}{6} \sum_{\alpha,\beta,\gamma} \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma}} \right)_{eq} u_{i\alpha} u_{i\beta} u_{i\gamma} \\ & + \frac{1}{24} \sum_{i,\alpha,\gamma,\eta} \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma} \partial u_{i\eta}} \right)_{eq} u_{i\alpha} u_{i\beta} u_{i\gamma} u_{i\eta} + \ldots \Bigg\}. \end{aligned} \tag{A.5}$$

Using equation (A.5), the thermal average of potential energy of the system is given in terms of the power moment $\langle u^n \rangle$, harmonic parameter k, anharmonic coefficients γ_1 and γ_2 as [11]

$$\langle U \rangle = U_0 + 3N \left[\frac{k}{2} \langle u^2 \rangle + \gamma_1 \langle u^4 \rangle + \gamma_2 \langle u^2 \rangle^2 + \ldots \right], \tag{A.6}$$

where

$$k = \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{i\alpha}^2} \right)_{eq} \tag{A.7}$$

$$\gamma_1 = \frac{1}{24} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha}^4} \right)_{eq}, \quad \gamma_2 = \frac{6}{24} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha}^2 \partial u_{i\beta}^2} \right)_{eq}, \tag{A.8}$$

with $\alpha \neq \beta = x, y$ or z, eq indicates the thermal averaging over the equilibrium ensemble and $U_0 = \sum_i \varphi_{i0} \left(r_i \right)$ denotes the total pair interaction energy $\varphi \left(r_{0i} \right)$ on the 0th atom.

In order to derive the expression of the Helmholtz free energy, we need to evaluate analytically the following integrals

$$I_1 = \int_0^{\gamma_1} \langle u_i^4 \rangle d\gamma_1, \qquad I_2 = \int_0^{\gamma_2} \langle u_i^2 \rangle_{\gamma_1 = 0}^2 d\gamma_2. \tag{A.9}$$

Then the final Helmholtz free energy of the system with N atoms is given by [11]

$$\begin{aligned} \psi = {} & U_0 + 3N\theta \left[x + \ln \left(1 - e^{-2x} \right) \right] \\ & + \frac{3N\theta^2}{k^2} \Bigg\{ \left[\gamma_2 X^2 - \frac{2\gamma_1}{3} \left(1 + \frac{X}{2} \right) \right] \\ & + \frac{2\theta}{k^2} \left[\frac{4}{3} \gamma_2^2 X - 2 \left(\gamma_1^2 + 2\gamma_1\gamma_2 \right) (1 + X) \right] \left(1 + \frac{X}{2} \right) \Bigg\}, \end{aligned} \tag{A.10}$$

where $x = \hbar\omega/2\theta$, $X = x \coth x$, $\theta = k_B T$ (k_B is the Boltzmann constant), and $\omega = \sqrt{k/m}$.

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