First-principles investigation on the structural and elastic properties of *cubic*-Fe_2TiAl under high pressures*

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The structural, elastic, and thermodynamic properties of *cubic*-Fe_2TiAl under high temperatures and pressures are investigated by performing *ab initio* calculation and using the quasi-harmonic Debye model. Some ground state properties such as lattice constant, bulk modulus, pressure derivative of the bulk modulus, and elastic constants are in good agreement with the available experimental results and theoretical data. The thermodynamic properties of Fe_2TiAl such as thermal expansion coefficient, Debye temperature, and heat capacity in ranges of 0 K–1200 K and 0 GPa–250 GPa are also obtained. The calculation results indicate that the heat capacities at different pressures all increase with temperature increasing and are close to the Dulong–Petit limit at higher temperatures, Debye temperature decreases with temperature increasing, and increases with pressure rising. The *cubic*-Fe_2TiAl is stable mechanically under 250 GPa. Moreover, under lower pressure, thermal expansion coefficient rises rapidly with temperature increasing, and the increasing rate becomes slow at higher pressure.

Keywords: Fe_2TiAl, first principles, elastic constants, thermodynamics properties

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1. Introduction

As is well known, TiAl-based alloys have aroused the great interest in the development of high-temperature materials used in aerospace and automobile industries due to their unique features, such as low densities, high specific strengths, excellent creep resistances, and other attractive elevated-temperature properties.[1,2] Recently, the TiAl–based alloys were studied by many researchers,[3–6] but most of them were concerned about the influences of alloying elements on the mechanical properties of TiAl, and the remaining studies dealt with the elastic and thermodynamic properties of Ti–Al alloys. The Fe_2TiAl is one of the TiAl-based alloys, which is a very important structural and functional material under high temperature and high pressure condition in the area of aeronautics and astronautics. The main reason is that Fe_2TiAl has high melting temperature, low density, good environmental resistance, high thermal conductivity, attractive modulus, etc.[7–10] Because of the technological interest, the extraordinary mechanical and thermal properties of TiAl basic alloys have been studied at an atomistic level modeling or simulation. Especially, some researchers have investigated the properties of Fe_2TiAl such as its electronic, phonon spectrum, mechanical stability, the thermodynamic and elastic properties, etc. But the abovementioned studies could only play a significant role from the standpoint of predicting the performances of the material under extreme conditions like high pressure and temperature.

Unfortunately, up to now, measuring the thermodynamic properties of Fe_2TiAl under high temperatures and high pressures is very difficult. To our knowledge, the data of detailed thermodynamic properties for Fe_2TiAl at different temperatures and pressures are not available experimentally. Therefore, we have to use the theoretical method to acquire these data. In our work, the structure, elastic properties, heat capacity, thermal expansion coefficient, etc. of Fe_2TiAl Fm-$3m$ structure are investigated under high temperatures and pressure by first-principles calculations in detail. As is well known, the density functional theory (DFT) has been successfully applied to the first-principles calculation of ground state properties of various materials. The elastic properties of a cubic structure of Fe_2TiAl are investigated for the first time, from which the mechanical stability are also determined. The thermodynamic properties, such as the heat capacity, thermal expansion, Debye temperature are also obtained by the quasi-harmonic Debye model. Through the abovementioned methods, the elastic and thermodynamic properties of some materials have been successfully investigated.[11–18]

This paper is organized as follows. In Section 1, we introduce the research progress briefly. The first-principles computational details are described in Section 2. The calculated results and discussions are presented in Section 3. Finally, some conclusions are drawn from the present study in Section 4.

2. Computational details

In our *ab initio* calculation, the electronic wave functions are expanded in a plane wave basis set with energy cut-off

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370 eV.[19,20] Pseudo atomic calculations are performed for Ti $3s^2 3p^6 3d^2 4s^2$, Al $3s^2 3p^1$, and Fe $3d^6 4s2$. For the Brillouin-zone sampling, we use the $6\times6\times6$ Monkhorst–Pack mesh for k-space integration, where the self-consistent convergence of the total energy is set to be 1.0×10^{-6} eV/atom. The non-local ultrasoft pseudopotential (USPP) is employed to describe the ion–electron interactions together with the Perdew–Burke–Ernzerhof (PBE) version of generalized gradient approximation (GGA).[21] The calculations of total energy electronic structure and properties are all implemented through the CASTEP code.[22] This technique has become widely recognized as the method of computationally investigating solid structural properties.[23,24] Some ground state properties such as $E(V)$, lattice parameter (a), bulk modulus (B), elastic constants (C_{ij}), etc. are obtained. The energy–volume (E–V) curve can be obtained by fitting the calculated E–V results to the Birch–Murnaghan equation of state (EOS).[25]

3. Results and discussion

3.1. Structure properties

To obtain the elastic and thermodynamic properties, we need to determine the equilibrium structure of Fe_2TiAl. The Fe_2TiAl is of cubic structure (space group Fm-$3m$) with Al occupying the position (0, 0, 0) Wyckoff site, and Fe the position (0.25, 0.25, 0.25), and Ti the position (0.5, 0.5, 0.5), obtained from inorganic crystal structure database.[26] All structure information can be described by crystal constant a and position of atom of crystal Fe_2TiAl. To investigate the ground state structure of Fe_2TiAl, we set a series of different values of lattice constant a of primitive cell to calculate the total energy E and the values of corresponding primitive cell volume V, then we can obtain the energy–volume (E–V) curve of Fe_2TiAl (see Fig. 1). Here, we fit the above E–V point to Birch–Murnaghan EOS, all the equilibrium structure information such as lattice constant a, the bulk modulus B, and the pressure derivative of bulk modulus B' for Fe_2TiAl at zero pressure are shown in Table 1, from which we can find the lattice constant a to be 4.11 Å, which is in good agreement with experimental result.[26] And the errors of lattice constant a are 1.1% and 3.5% obtained in the local density approximation (LDA) and GGA, respectively. Its means that the calculated results obtained in the GGA seems to be better than in the LDA. So, we use GGA to calculate the other properties of Fe_2TiAl in the following calculations. Figure 2 shows the variations of relative volume $(V-V_0)/V_0$ with pressure P at different values of temperature T, where V_0 is the cell volume at $P=0$ and $T=0$. It can be easily seen that the relative volume $(V-V_0)/V_0$ decreases with pressure P increasing at a given temperature for Fe_2TiAl. Its means that when $(V-V_0)/V_0>0$, cell volume of Fe_2TiAl expands, when $(V-V_0)/V_0<0$ its volume compresses, and the variation of relative volume is more sensitive to pressure, for instance when $T=1200$ K, just 6.29 GPa of pressure can restrain the volume expansion caused by temperature, which means that the cell volume keeps at V_0.

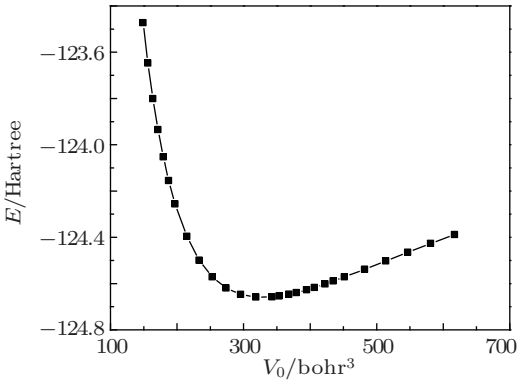


Fig. 1. Energy as a function of primitive unit cell volume of Fe_2TiAl. 1 Hartree = 27.2114 eV.

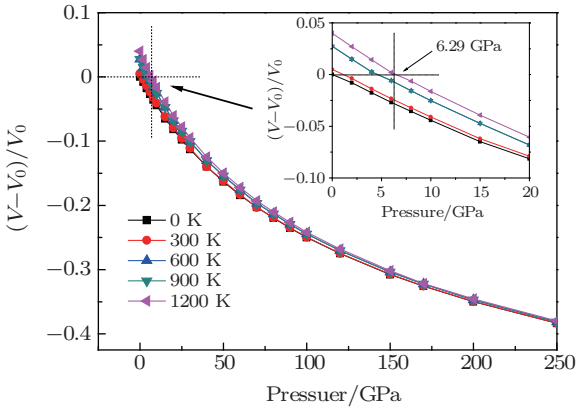


Fig. 2. (color online) Variations of $(V-V_0)/V_0$ with pressure P at different values of temperature T, where V_0 is the cell volume at $P=0$ and $T=0$.

Table 1. Calculated values of lattice constant a, bulk modules B_0, and elastic constants C_{ij} at zero temperature and zero pressure.

Methods	a/Å	B_0/GPa	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
GGA (PBE)	4.11	207.73	290.51	119.05	114.26
LDA (CA-PZ)	4.01	218.90	358.85	148.92	125.46
Experiment[a]	4.157	–	–	–	–

[a]Ref. [26].

3.2. Elastic properties

The elastic constant is an important parameter of solid-state matter. It is closely related to various fundamental physical properties of material, such as specific heat, melting point, Debye temperature, thermal expansion coefficient, etc. Elastic constants can provide a link between the mechanical and dynamic properties, and also present important information about the nature of the forces action in a solid. Especially, elastic constants provide information about the stability and stiffness of materials. In Table 1 listed are the elastic constants of Fe_2TiAl at $T=0$ K and $P=0$ GPa. Unfortunately, to the best of our knowledge, up to now there has been neither measured elastic constants for comparison, nor calculated

ones based on the *ab initio* calculations for Fe_2TiAl. Hence our work and calculated results are first prediction for elastic properties of Fe_2TiAl under high pressure and high temperature.

Figure 3 shows the curves of the crystal constant a and elastic parameters C_{11}, C_{12}, and C_{44} for Fe_2TiAl each as a function of pressure (a) or temperature (b). It is shown from Fig. 3 that as pressure P increases, crystal constant a decreases and three independent elastic constants increase at $T = 0$ K. In Fig. 3(a), it is noticed that C_{11} is more sensitive to the change of pressure than C_{12} and C_{44}. The calculated bulk modulus B increases monotonically gradually as pressure increases, which means that Fe_2TiAl becomes more and more difficult to be compressed with pressure increasing. From Fig. 3(b) we can also find that the variations of the elastic constant and bulk modulus are smaller, it is found that the effect of temperature on elastic parameter of Fe_2TiAl is not significant compared with the effect of pressure.

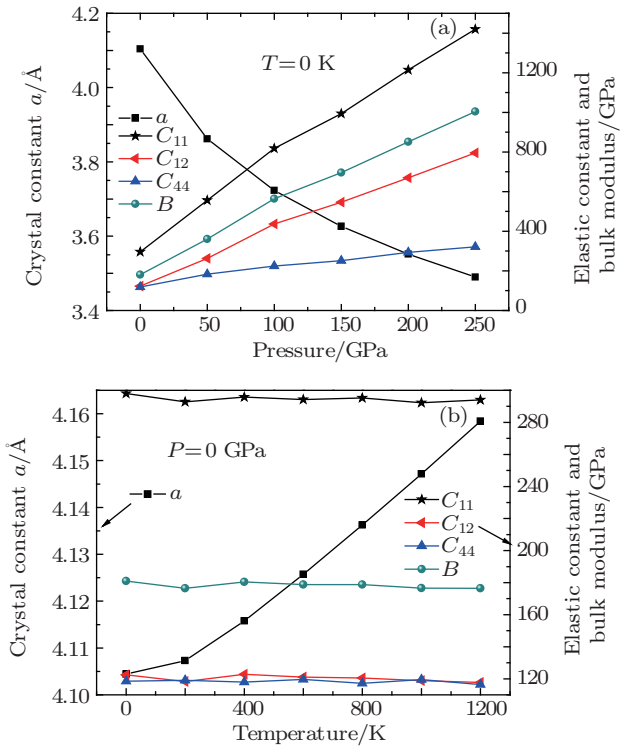


Fig. 3. (color online) Pressure and temperature dependencies of crystal constant a, elastic constants C_{ij}, and bulk modulus B at temperature 0 K (a) and pressure 0 GPa (b).

For cubic crystal, the traditional mechanical stability conditions under isotropic pressure can be expressed in terms of elastic constants as $\tilde{C}_{44} > 0$, $\tilde{C}_{11} - |\tilde{C}_{12}| > 0$, and $\tilde{C}_{11} + 2\tilde{C}_{12} > 0$ where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($a = 1, 4$), and $\tilde{C}_{12} = C_{12} + P$. In Table 1, it is clear that our calculated elastic constants C_{ij} satisfy the Born stability criteria. It is suggested that the cubic phase of Fe_2TiAl is mechanically stable under 250 GPa and 1200 K.

3.3. Thermodynamic properties

In order to obtain the thermodynamic properties of Fe_2TiAl, we use the quasi-harmonic Debye model,[27] in which the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm vib}[\Theta(V);T], \tag{1}$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and $A_{\rm vib}$ is the vibrational term which can be written using the Debye model of the phonon density of states as[28,29]

$$A_{\rm vib}(\Theta;T) = nkT\left[\frac{9\Theta}{8T} + 3\ln(1 - {\rm e}^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right)\right], \tag{2}$$

where n is the number of atoms per formula unit, $D(\Theta/T)$ is the Debye integral, and for an isotropic solid, Θ is expressed as[29]

$$\Theta = \frac{\hbar}{k}[6\pi^2 V^{1/2} n]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm s}}{M}}, \tag{3}$$

with M being the molecular mass per unit cell (here, atomic mass of Fe is 55.845, atomic mass of Ti is 47.867, atomic mass of Al is 26.981539), $B_{\rm s}$ is the adiabatic bulk modulus that can be approximated and given by the static compressibility[28]

$$B_{\rm s} \cong B(V) = V\frac{{\rm d}^2E(V)}{{\rm d}V^2}. \tag{4}$$

Here, $f(\sigma)$ is given by the following equation:[29]

$$f(\sigma) = \left\{3\left[2\left(\frac{2/3(1+\sigma)}{1-2\sigma}\right)^{3/2} + \left(\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3}. \tag{5}$$

The Poisson σ is taken to be 0.25.[30] Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of V, P, and T can be minimized with respect to volume V:

$$\left[\frac{\partial G^*(V;P,T)}{\partial V}\right]_{P,T} = 0. \tag{6}$$

The thermal EOS $V(P,T)$ is obtained by solving Eq. (6). The isothermal bulk modulus B_T, the heat capacity C_v, the thermal expansion coefficient α, and entropy S are respectively taken as[31]

$$B_T(P,T) = V\left[\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\right]_{P,T} = 0, \tag{7}$$

$$C_v = 3nk\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{{\rm e}^{\Theta/T} - 1}\right], \tag{8}$$

$$S = nk[4D(\Theta/T) - 3\ln(1 - {\rm e}^{-\Theta/T})], \tag{9}$$

$$\alpha = \frac{\gamma C_v}{B_T V}, \tag{10}$$

where γ is Grüneisen parameter and expressed as

$$\gamma = -\frac{{\rm d}\ln\Theta(V)}{{\rm d}\ln V}. \tag{11}$$

Through the above quasi-harmonic Debye model, one can calculate the thermodynamic quantities of Fe_2TiAl at any temperature and under pressures ranging from the calculated E–V data at $T = 0$ and $P = 0$. Here, the thermodynamic properties of Fe_2TiAl are calculated in a temperature range from 0 K to 1200 K and in a pressure range from 0 GPa to 250 GPa. The investigation on the heat capacity of crystals, as one of the thermal properties, is an old topic of the condensed matter physics.[27] Knowledge of the heat capacity of a substance not only provides an essential insight into its vibrational properties but also acts as a limit on many applications. In Table 2 listed are the values of heat capacity and Debye temperature at different temperatures (200, 300, 400, 600, 800, 1000, and 1200 K) and different pressures (0, 50, 100, 150, 200, 250 GPa). From Table 2, it can be found that as pressure increases from 0 to 250 GPa, the heat capacity values reduce 54.3%, 44.6%, 30.5%, 15.9%, 9.6%, 6.3%, 4.5%, and Debye temperature values increase 113.2%, 114.3%, 115.5%, 118.2%, 121.1%, 124.2%, and 127.4% at temperatures of 200, 300, 400, 600, 800, 1000, and 1200 K, respectively.

Table 2. Values of heat capacity C_v (J·mol^{-1}·K^{-1}) and Debye temperature Θ (K) of the Fe_2TiAl at different values of temperature T (K) and pressure P (GPa).

T/K		P/GPa					
		0	50	100	150	200	250
200	C_v	75.562	60.965	51.407	44.381	38.948	34.559
	Θ	609.05	828.84	980.18	1101.77	1205.57	1298.32
	γ	1.906	1.576	1.484	1.440	1.410	1.386
300	C_v	82.064	70.146	61.765	55.24	49.944	45.484
	Θ	605.73	827.51	979.22	1101.04	1205.00	1297.85
	γ	1.915	1.577	1.484	1.440	1.410	1.386
400	C_v	89.332	81.368	75.320	70.285	65.954	62.114
	Θ	601.89	825.81	977.92	1099.99	1204.15	1297.12
	γ	1.924	1.578	1.485	1.441	1.411	1.386
600	C_v	95.058	91.006	87.753	84.892	82.305	79.907
	Θ	593.51	821.91	974.84	1097.39	1201.96	1295.16
	γ	1.945	1.582	1.486	1.441	1.411	1.386
800	C_v	97.159	94.751	92.789	91.027	89.401	87.869
	Θ	584.69	817.70	971.45	1094.48	1199.45	1292.87
	γ	1.969	1.586	1.488	1.442	1.412	1.387
1000	C_v	98.141	96.550	95.252	94.075	92.979	91.937
	Θ	575.59	813.35	967.93	1091.43	1196.79	1290.43
	γ	1.994	1.589	1.489	1.443	1.413	1.388
1200	C_v	98.672	97.544	96.625	95.788	95.004	94.256
	Θ	566.28	808.89	964.35	1088.31	1194.05	1287.90
	γ	2.021	1.594	1.491	1.444	1.413	1.388

Figure 4 shows the relationships between heat capacity at constant volume C_v and temperature at different pressures. It can be seen from Fig. 4 that when $T < 600$ K, C_v increases rapidly with temperature increasing at a given pressure and decreases with pressure increasing at a given temperature. At sufficiently low temperatures, C_v is proportional to T^3,[32] which is because only the long wavelength vibration modes of the lattice exist and these modes could be approximated by treating the lattice as a continuum. However, at high temperatures, the anharmonic effect on heat capacity C_v is suppressed and C_v is close to Dulong–Petit limit.[33] The heat capacity C_v exhibits a strong dependence on both temperature and pressure when temperature is smaller than 600 K. These results show that the interactions among atoms in Fe_2TiAl have great effects on heat capacity C_v especially at low temperatures. But at intermediate temperatures, the temperature dependence of C_v is governed by the details of vibrations of the atoms. Figures 5(a) and 5(b) show the variations of the Debye temperature $\Theta(T)$ with temperature. From the figure it is found that the Debye temperature $\Theta(T)$ increases with P increasing at a given temperature and decreases with temperature rising. From Figs. 4 and 5 it can also be seen that $C_v(T)$ and $\Theta(T)$ of Fe_2TiAl are quite significant. Because high Debye temperature means low heat capacity at a given temperature, and this allows a significant response to thermal pulse.[2] In fact, the anharmonic effect of pressure on C_v is very small at higher temperatures. However, heat capacity C_v is 82.06 J/mol·K at zero pressure and ambient temperature in this work. Moreover, the corresponding Debye temperature Θ obtained at the same condition above is 605.73 K. Unfortunately, to our knowledge, there are no experimental or other theoretical data of C_v and $\Theta(T)$ of Fe_2TiAl for comparison with our calculation results. There-

fore our work and results are first attempt in this research area and direction.

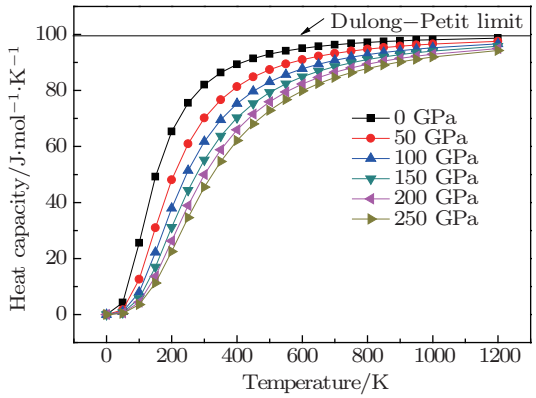
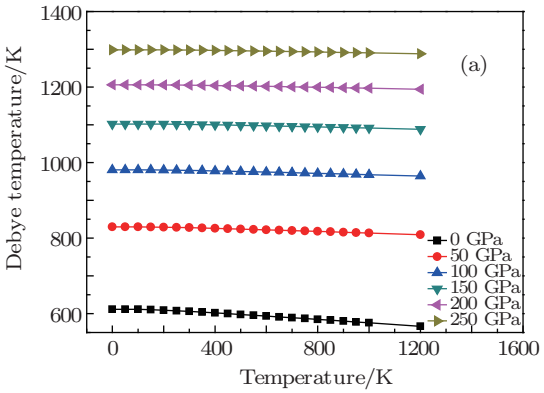


Fig. 4. (color online) Variations of heat capacity C_v with temperature under different pressures.



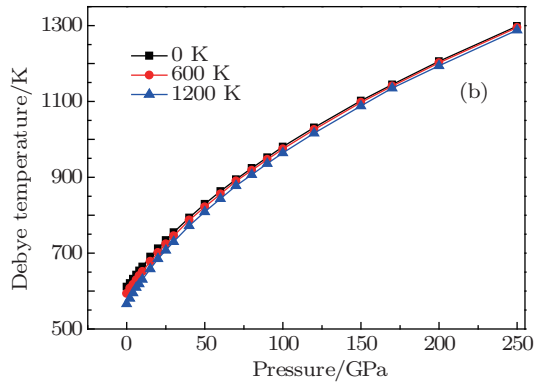


Fig. 5. (color online) Debye temperature values versus temperature (a) and pressure (b) of Fe_2TiAl.

The dependences of the thermal expansion α of Fe_2TiAl pressure and temperature are shown in Fig. 6. As shown in Fig. 6, we can see that for a given temperature, α almost decreases exponentially with pressure increasing, while higher the temperature, the faster the decrease of thermal expansion α with pressure is, and the decrease becomes slower as pressure increases. However, for a given pressure, α increases rapidly with temperature rising at low temperatures especially at zero pressure, then increases slowly at higher temperatures. When $T > 500$ K, and the tendency of increase becomes moderate, which indicates that the effects of temperature dependence of a is smaller than that of pressure dependence at high temperatures. Furthermore, the effect of temperature on the thermal expansion α under low temperature is greater.

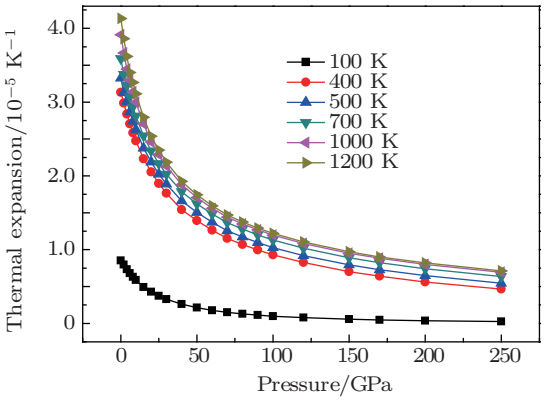


Fig. 6. (color online) Variations of thermal expansion with pressure at different temperatures of Fe_2TiAl.

The Grüneisen parameter is an important constant for Fe_2TiAl, which describes the anharmonic effect in the vibrating lattice and gives the volume dependence of the Debye temperature Θ, and it can correctly predict the anharmonic properties of one material, such as the thermal expansion α and the temperature dependence of phonon frequency and line-width. We calculated the Grüneisen parameters when pressure and temperature are plotted in Fig. 7, from which we can find that the Grüneisen parameter γ increases with temperature rising and decreases with the pressure increasing. When temperature T is 1200 K, the value $\gamma = 1.388$ (250 GPa) is much smaller than the value $\gamma = 2.021$ (0 GPa), which means that the influence of pressure on γ is significant at high temperatures.

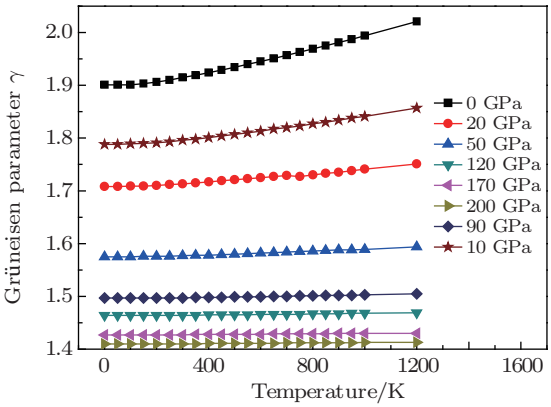


Fig. 7. (color online) Plots of Grüneisen parameter γ versus temperature under different pressures for Fe_2TiAl.

4. Conclusions

In this paper, we calculated the structure, elastic, and thermodynamic properties of Fe_2TiAl at different temperatures and pressures using the pseudo-potential plane-wave method

and the quasi-harmonic Debye model. The obtained lattice parameters at ambient pressure are in agreement with the experimental values. The elastic constants and bulk modulus each indicate a nearly linear increase with pressure rising at zero temperature and almost keep unchanged at zero pressure, and the effects of pressure on elastic constants are stronger than those of temperature. By using the quasi-harmonic Debye model, the pressure and temperature dependences of Debye temperature, heat capacity, and thermal expansion are obtained successfully. The Debye temperature increases with pressure increasing and decreases with temperature rising. The values of heat capacity C_v at different pressures are found to increase with temperature increasing and approach to the Dulong–Petit limit at high temperatures. Debye temperature Θ decreases with temperature rising, and increases with pressure increasing. Furthermore, thermal expansion α rises with temperature increasing and the increasing trend will become slow at high temperatures and high pressures.

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