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Thermodynamic properties of Fe₂B under high pressure from first-principles calculations

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Abstract

Equation of state (EOS) and other thermodynamic properties of Fe₂B are studied using first- principles calculations based on the plane wave full potential density functional theory method within the generalized gradient approximation (GGA) for exchange and correlation. It is demonstrated that the ratio c/a of about 1.271 is the most stable structure for the Fe₂B, which is consistent with the experimental data. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of the relative volume V/V_0 on pressure P , cell volume V , and on temperature T , are successfully obtained. The variations of the Debye temperature $\theta(V)$, the thermal expansion α , and the heat capacity C_V as a function of pressure P and temperature T , are investigated systematically in the ranges of 0-50 GPa and 0-1000 K.

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Keywords: Equation of state, thermodynamic properties, first- principles, Fe₂B, quasi-harmonic Debye model

1. Introduction

Prediction of good thermodynamic properties of materials is the focus of solid-state science and industrial research. It is particularly the key of applying in some modern technologies which make materials undergo the ultra high-pressure and high temperature environment. For these technologies, not only the high-performance materials but also more accurate theoretical models and computational methods are needed [1].

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The stable phase of Fe₂B, under ambient conditions, has a body-centered tetragonal structure of the CuAl₂ type with unit cell parameters of: $a = 5.109 \text{ \AA}$ and $c = 4.249 \text{ \AA}$, is ferromagnetic with a magnetic moment of about $1.9 \mu_B$ per Fe ion at 20 K and with the Curie temperature of approximately 1015 K [2, 3]. It has been reported that the Fe–B system amorphizes by rapid quenching [4] and by ion-beam mixing [5].

In our work, structure, heat capacity and thermal expansion of Fe₂B, are studied in detail by first-principles and quasi-harmonic Debye model. Since not many theoretical work on this has been published, the results obtained in this work may be useful for other groups working on or with Fe₂B.

2. Theoretical method

The zero-temperature energy calculations are performed using the WIEN2k package [6], which is based on the density functional theory. Exchange and correlation functional is given by the generalized-gradient approximation (GGA96) of Perdew et al. [7]. The PWs cut-off is used with the highly recommended condition RMTKmax = 9, where RMT is the average of the Muffin-tin spheres and Kmax is the plane waves (PWs) cut-off. The sphere radii used in the calculations are 2.17 and 1.92 a.u. for Fe and B, respectively. The k-integration over the Brillouin zone was performed using a mesh of 10 x10x10 k-points in the irreducible wedge of the Brillouin zone. To ensure proper convergence of the self consistency calculation, the calculated total energy of the crystal converged to less than <0.5 mRy.

To investigate the thermodynamic properties of Fe₂B, the quasi-harmonic Debye model [8], is applied in which the non-equilibrium Gibbs function $G^*(V, P, T)$ can be written in the form of:

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

where $E(V)$ is the total energy per unit cell, P corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature, and A_{vib} is the vibrational term, which can be written using the Debye model of the phonon density of states as [9, 10]:

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

where n is the number of atoms per formula unit, $D(\theta/T)$ represents the Debye integral, and for an isotropic solid, θ is expressed as [10]:

$$\theta = \frac{\hbar}{k} \left[6\pi^2 V^{\frac{1}{3}} n \right]^{\frac{1}{3}} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (3)$$

where M is the molecular mass per unit cell, B_s , the Poisson σ is taken as 0.25 [13], and the adiabatic bulk modulus, is approximated by the static compressibility[9]:

$$B_s \cong B(V) = V \frac{d^2 E(V)}{dV^2} \quad (4)$$

in which $f(\sigma)$ is given by references 11 and 12. Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ is a function of $(V; P, T)$ can be minimized with respect to volume V ,

$$\left[\frac{\partial G^*(V; P, T)}{\partial V} \right]_{P, T} = 0 \quad (5)$$

By solving Eq. (5), one can obtain the thermal equation-of-state (EOS) $V(P, T)$. The heat capacity C_V , and the thermal expansion coefficient α are given by [14]:

$$C_V = 3nk \left[4D \left(\frac{\theta}{T} \right) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (6)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (7)$$

where γ is the Grüneisen parameter defined as:

$$\gamma = - \frac{d \ln \theta(V)}{d \ln V} \quad (8)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperatures and pressures of Fe_2B from the calculated $E-V$ data at $T=0$ and $P=0$. By using the method above, the thermodynamic properties of Fe_2B can be successfully obtain.

3. Results and discussion

The total energy is obtained as a function of volume and fitted to the Murnaghan equation of state [15] (Fig. 1) to obtain the equilibrium lattice constant and bulk modulus. The calculated lattice cell volume and the bulk modulus are $V_0 = 353.96 \text{ (u.a)}^3$ and $B = 229.34 \text{ GPa}$, respectively. The experimental bulk modulus is $B = 194 \text{ GPa}$ [16].

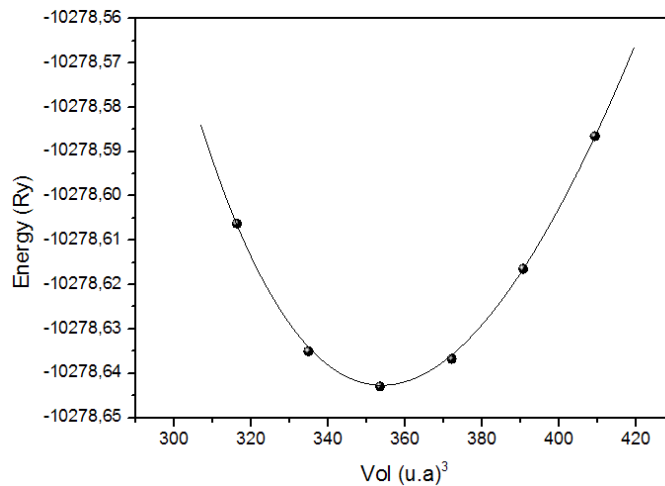


Fig. 1. Total energy as function of cell volume of Fe_2B .

The thermal properties are determined in the temperature range from 0 to 1300 K, where the quasi-harmonic model remains fully valid, whereas, the pressure effect is studied in the 0–50 GPa range.

The temperature effects on the cell volume are shown in Fig. 2. The cell volume increases with increasing temperature but the rate of increase is very moderate. Furthermore, it is noted, from Fig. 3, that the relationships between bulk modulus and pressure are all nearly linear at various temperatures of 0, 300, 500, 700, and 1000 K, respectively. The bulk modulus increases with pressure at a given temperature and decreases with temperature at a given pressure.

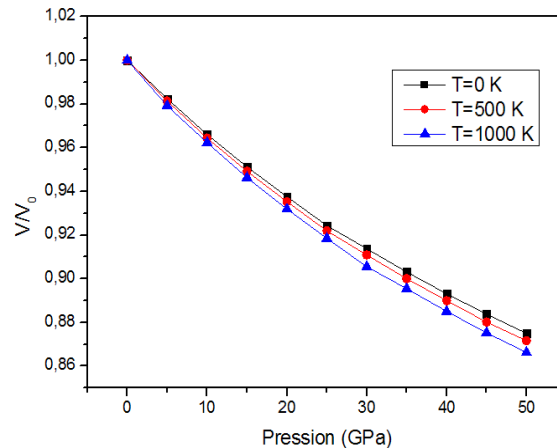


Fig. 2. Pressure and temperature dependence of the relative volume V/V_0 of the Fe_2B at temperatures of 0, 500, and 1000 K, respectively.

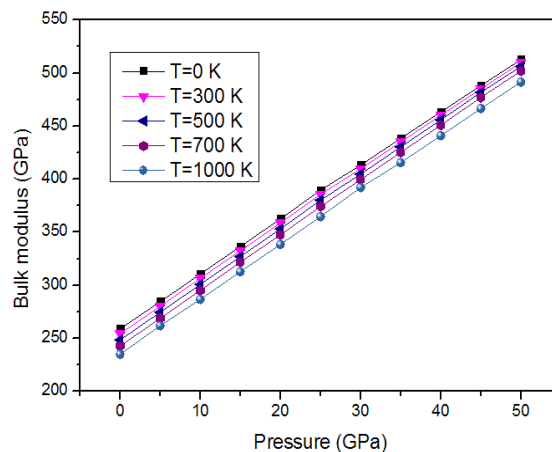


Fig. 3. Bulk modulus as a function of pressure at temperatures of 0, 300, 500, 700 and 1000 K.

The investigation on the heat capacity of crystals is a well established topic of condensed matter physics [17–19]. Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory [19]. At high temperatures, the constant-volume heat capacity C_v tends to the Petit and Dulong limit [20]. At sufficiently low temperatures, C_v is proportional to T^3 [19]. At intermediate temperatures, however, the temperature dependence of C_v is governed by the details of vibrations of the atoms. Fig. 4 represent the heat capacity, $C_v(T)$, as function of the temperature. These two quantities indicate a sharp increase up to ~ 600 K which is due to the anharmonic

approximation of the Debye model here. However, at higher temperature, the anharmonic effect on C_v is suppressed, and C_v is very close to the Dulong–Pettit limit, common to all solids at high temperatures. It can be seen from Fig. 3 that as pressure increases, the heat capacity C_v decreases as well as the Debye

Temperature θ increases. The heat capacity C_v in this work is 54.06 J/mol K at zero pressure and ambient temperature. Moreover, the Debye temperature θ obtained here is 792.48 K.

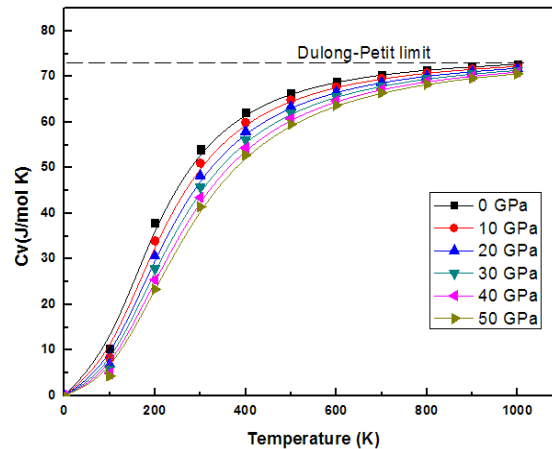


Fig. 4. Heat capacity C_v versus temperature at pressures of 0-50 GPa.

Finally, in Fig. 5, we have plotted our results for the thermal expansion coefficient α of Fe_2B . We remark that for a given pressure, α increases rapidly with temperature at low temperatures especially at zero pressure, then gradually increase slowly at higher temperatures. As pressure increases, the increasing of α with temperature becomes smaller. While for a given temperature, α decreases rapidly with increasing pressure.

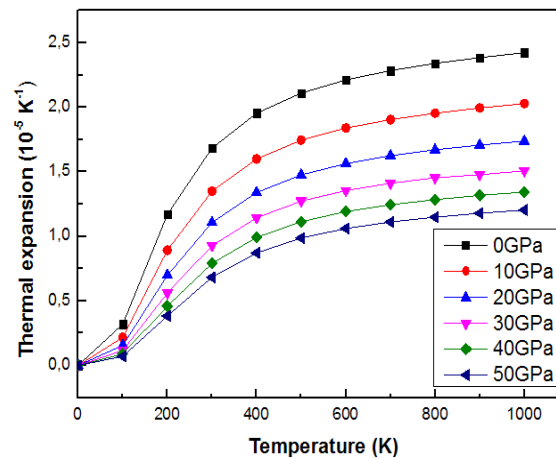


Fig. 5. The thermal expansion as a function of temperature at pressure of 0-50 GPa.

4. Conclusion

Structural properties of Fe₂B at temperature $T = 0$ K have been calculated using the FP-LAPW method within the generalized-gradient approximation in the frame of density functional theory. It is found that the cell volume is in a good agreement with the few available experimental and theoretical data. The thermodynamic properties of Fe₂B are predicted using the quasi-harmonic Debye model. C_v is found to increase with temperature and is close to the Dulong–Petit limit at high temperatures. Furthermore, the thermal expansion coefficient rises with temperature and its increasing trend will get slow at high temperature and high pressure.

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