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First-principles calculation of elastic and thermodynamic properties of Ni_2MnGa Heusler alloy*

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The equilibrium lattice parameter, heat capacity, thermal expansion coefficient and bulk modulus of Ni_2MnGa Heusler alloy are successfully obtained using the first-principles plane-wave pseudopotential (PW-PP) method as well as the quasi-harmonic Debye model. We analyse the relationship between bulk modulus B and temperature T up to 800 K and obtain the relationship between bulk modulus B and pressure at different temperatures. It is found that the bulk modulus B increases monotonically with increasing pressure and decreases with increasing temperature. The pressure dependence of heat capacity C_v and thermal expansion α at various temperatures are also analysed. Finally, the Debye temperature of Ni_2MnGa is determined from the non-equilibrium Gibbs function. Our calculated results are in excellent agreement with the experimental data.

Keywords: shape memory alloy, Debye temperature, thermodynamic properties, Ni_2MnGa
PACC: 7115M, 6740K, 6155H

1. Introduction

Magnetically driven actuator Heusler alloy Ni_2MnGa has aroused great interest in recent years because of its potential application as a magnetically driven shape memory alloy that is more efficient than temperature or stress driven shape memory devices.[1−4] Ni_2MnGa is technologically much more promising than other materials currently in commercial use. In the high temperature austenitic phase, the structure of Ni_2MnGa has been found to have cubic $L2_1$ Heusler structure (space group FM-3M) from x-ray and neutron diffraction studies.[5,6] Upon cooling, it undergoes a martensitic transformation to a modulated approximately tetragonal structure. The $L2_1$ structure may conveniently be considered as four interpenetrating fcc sublattices with atoms of Ga, Mn, Ni and Ni at locations (0, 0, 0), (0.5, 0.5, 0.5), (1/4, 1/4, 1/4), (3/4, 3/4, 3/4), respectively.

The elastic properties of solids are closely related to many fundamental solid-state properties, such as equation of state (EOS), thermal expansion, melting temperature and specific heat. A study of the elastic properties and thermodynamic properties for materials is well motivated by, for example, the understanding one thereby gains about the chemical bonds and the cohesion of material. Moreover, the elastic constants are also related to thermal properties according to the Debye theory. Because these effects are related to elastic and thermodynamic properties, there are good reasons to investigate the elastic properties of Ni_2MnGa. Since the elastic properties of Ni_2MnGa at high temperatures and pressures are not clear, here we make a first-principles calculation on the elastic modulus of Ni_2MnGa by using a recently developed non-empirical Debye-like model (quasi-harmonic Debye model),[7] in which the phononic effects are considered.

2. Theoretical method

2.1. Total energy calculations

Firstly, we make a first-principles total energy calculation in which the plane-wave pseudopotential (PW-PP) method is used.[8] The generalized gradi-

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ent approximation (GGA) of PBE[9] is used for the exchange-correlation energy functional and the ultrasoft pseudopotentials introduced by Vanderbilt[10] are applied to the interaction of the electron with the ion core. Initial convergence tests lead to the choice of 500 eV for the plane wave cutoff energy, $E_{\rm cut}$. For the Brillouin-zone sampling, we use the $12 \times 12 \times 12$ Monkhorst–Pack k-point mesh.[11] The electronic degrees of freedom are converged to within 10^{-6} eV/cell and the force components on each atom are relaxed to less than 10^{-5} eV/Å (1 Å = 0.1 nm).

2.2. Thermodynamic properties

Then, the quasi-harmonic Debye model is employed to calculate the equation of state (EOS) and the thermodynamic properties which are constructed from the Helmholtz free energy at the temperature below melting point in the quasi-harmonic approximation. This method is well established and many high quality papers have been published in recent years.[12,13] The non-equilibrium Gibbs function of the crystal phase $G^*(V;P,T)$ can be written in the form of[14]

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

where $E(V)$ is the total energy per unit cell; the second term, PV, corresponds to the constant hydrostatic pressure condition. The third term, $A_{\rm vib}$, is the vibrational Helmholtz free energy, which can be written as[15,16]

$$\begin{aligned} &A_{\rm vib}(\Theta_D;T) \\ &= nkT\left[\frac{9}{8}\frac{\Theta_D}{T} + 3\ln(1-{\rm e}^{-\Theta_D/T}) - D(\Theta_D/T)\right], \end{aligned} \qquad (2)$$

where Θ_D is the Debye temperature, $D(\Theta_D/T)$ represents the Debye integral, n is the number of atoms per formula unit. By solving the equation

$$\left(\frac{\partial G^*(V;p,T)}{\partial V}\right)_{p,T} = 0, \qquad (3)$$

one could obtain the isothermal bulk modulus B,

$$\begin{aligned} B_T(p,T) &= -V\left(\frac{\partial p}{\partial V}\right)_T \\ &= V\left(\frac{\partial^2 G^*(V;p,T)}{\partial V^2}\right)_{p,T}. \end{aligned} \qquad (4)$$

According to the quasi-harmonic Debye model, the heat capacity C_v and the thermal expansion α can be obtained by

$$C_v = 3nk\left[4D(\Theta_D/T) - \frac{3\Theta_D/T}{{\rm e}^{\Theta/T}-1}\right], \qquad (5)$$

$$\alpha = \frac{\gamma C_v}{B_T V}, \qquad (6)$$

where γ is the Grüneisen parameter. The Debye temperature Θ_D was given in Refs.[7, 17]. The zero pressure bulk modulus B_0 is determined by fitting the calculated energy-volume $(E-V)$ data to the Birch–Murnaghan EOS[18]

$$\begin{aligned} &\Delta E(V) \\ &= E - E_0 \\ &= B_0 V_0\left[\frac{V_n}{B_0'} + \frac{1}{1-B_0'} + \frac{V_n^{1-B_0'}}{B_0'(B_0'-1)}\right], \end{aligned} \qquad (7)$$

where E_0 is the equilibrium energy. The pressure P versus the normalized volume $V_n (= V/V_0$, where V_0 is the equilibrium volume at zero pressure) is obtained by

$$p = -\frac{{\rm d}E}{{\rm d}V} = \frac{B_0}{B_0'}\left[V_n^{-B_0'} - 1\right]. \qquad (8)$$

Using the methods mentioned above, we can successfully obtain the elastic and thermodynamic properties of Ni_2MnGa.

3. Results and discussion

The obtained relationship between primitive cell volume and total energy is illustrated in Fig.1.

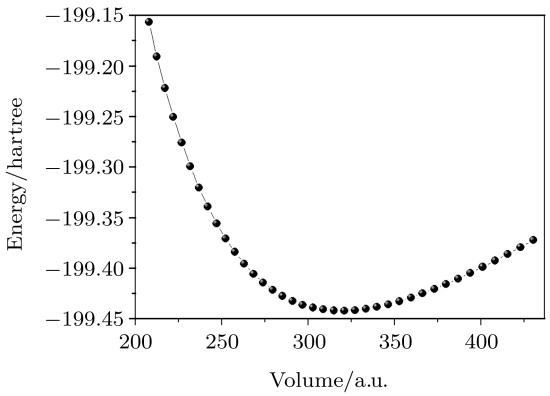


Fig.1. Energy-volume curves for Ni_2MnGa, a.u. represents atomic units (1 hartree= 1.1×10^{-19} J).

From Fig.1, it is found that the lattice constant $a = 0.5814$ nm has the minimum energy, which corresponds to the most stable structure of cubic Ni_2MnGa at $P = 0$ and $T = 0$. Our calculated results are in excellent agreement with experimental data 0.5825 nm[1]

and 0.582 nm.[19] It is clear that the most stable structure of Ni_2MnGa corresponds to the total energy -199.4423 hartree (1 hartree$= 1.1 \times 10^{-19}$ J) and the primitive cell volume $V_0 = 319.22$ a.u.^{3} When $V < 319.22$ a.u.^{3}, as V increases, the total energy decreases dramatically. When $V > 319.22$ a.u.^{3}, the relationship between total energy and volume V is the opposite.

Now, we investigate the pressure dependence of bulk modulus B with temperature varying from 0 to 800 K. The relationships between bulk modulus B and pressure P at different temperatures are also analysed and plotted in Fig.2.

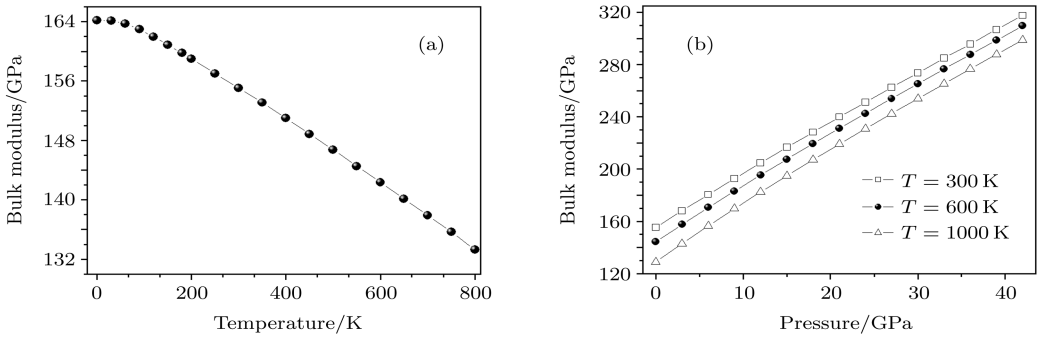


Fig.2. Bulk modulus B as a function of temperature T at zero pressure (a) and relationships between bulk modulus B as functions of pressure at $T = 300$, 600 and 1000 K (b).

At 300 K, we obtain the bulk modulus $B = 155.1$ GPa, which is in agreement with the value obtained by Ayuela *et al* (156 GPa),[20] Worgull *et al* (146 GPa)[2] and Zayak *et al* (155.42 GPa).[21] From Fig.2(a), we can find that when $T < 120$ K, B nearly keeps constant, the lattice parameter a nearly keeps constant. When $T > 120$ K, the bulk modulus B decreases dramatically as T increases, which indicates that the cell volume changes rapidly. It is the rapid volume variation that makes the bulk modulus B rapidly decrease. By fitting the $B - T$ data points to third-order polynomial, we obtain the following relationship,

$$B = 165.00524 - 2.541 \times 10^{-2}T - 2.72549 \times 10^{-5}T^2 + 1.14485 \times 10^{-8}T^3, \quad \text{for } T < 800\,\text{K}. \tag{9}$$

It is noted from Fig.2(b) that the relationships between bulk modulus B and pressure P are nearly linear at temperatures of 300, 600 and 1000 K. The bulk modulus B increases with pressure dramatically at a given pressure and decreases with T at a given temperature. These results are due to the fact that the effect of increasing pressure on Ni_2MnGa is the same as that of decreasing temperature on the material.

Using the quasi-harmonic Debye model described above, we can determine the heat capacity C_v and the thermal expansion coefficient α of Ni_2MnGa under simultaneous high pressure and temperature conditions, as shown in Figs.3 and 4.

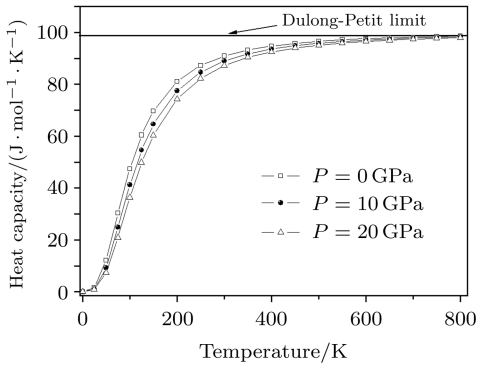


Fig.3. Heat capacity C_v of Ni_2MnGa at various pressures and temperatures.

The calculated relationships between heat capacities and temperatures at different pressures are plotted in Fig.3. It is clear that when $T < 400$ K, the heat capacity C_v increases with temperature at a given pressure and decreases with pressure at a given temperature. The heat capacity C_v is strongly dependent on both temperature T and pressure P when $T < 400$ K. This is due to the anharmonic approximation of the Debye approximation used here. However, when $T > 400$ K, the anharmonic effect on heat capacity C_v is suppressed. C_v is very close to the Dulong–Petit limit, which is common to all solids at high temperatures. These results show the fact that the interactions between ions in Ni_2MnGa have great effect on heat capacity C_v especially at low temperatures. Unfortunately, there are no theoretical results or experimental data to check our calculated results.

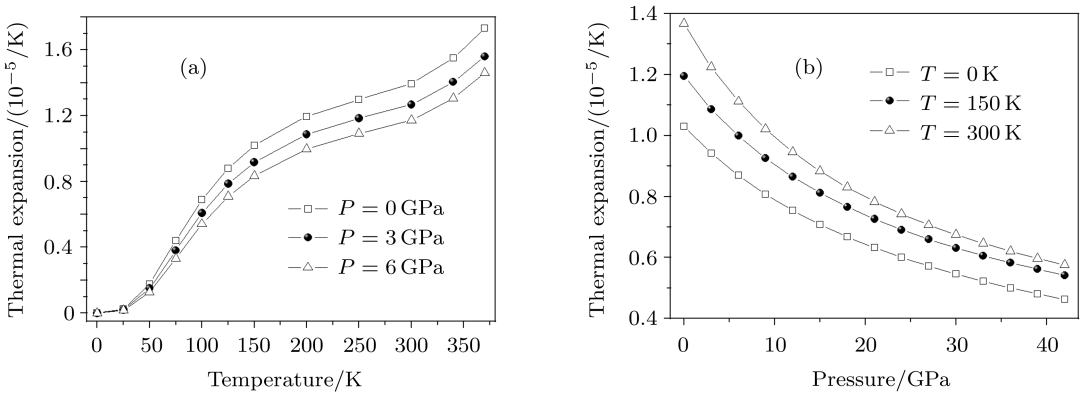


Fig.4. Thermal expansion versus temperature at $P = 0$, 3 and 6 GPa (a) and thermal expansion versus pressure at $T = 0$, 150 and 300 K (b).

In Fig.4(a), the variations of thermal expansion coefficient α and temperature and pressure are clearly seen. The thermal expansion α increases with T^3 at low temperatures and gradually approaches a linear increase at higher temperatures. It is noteworthy that the higher temperature dependence of the thermal expansion α is not linear at the temperature 300 K. It shows the fact that the thermal expansion α increases more quickly when $T > 300$ K. The reason why α increases more quickly at $T > 300$ K is the rapid decrease of bulk modulus B.

In Fig.4(b), we found that for a given temperature, α decreases dramatically with increasing pressure. The higher the temperature is, the faster the thermal expansion α decreases. At 300 K, the value $\alpha_1 = 0.64 \times 10^{-5}/\,\mathrm{K}$ (39 GPa) is much smaller than the value $\alpha_2 = 1.36 \times 10^{-5}/\,\mathrm{K}$ at zero pressure; which implies that the pressure influence on α is significant at higher temperatures. When the pressure is above 40 GPa, the thermal expansion α at 300 K is just a little larger than that at 0 K, which means that the temperature dependence of α is very weak at high pressures. Our calculated value for α equals $1.36\times10^{-5}/\,\mathrm{K}$ at 300 K, which is in agreement with the value $\alpha = 1.34 \times 10^{-5}/\,\mathrm{K}$ ($T = 300$ K) obtained by a strain gage technique.[22] At 370 K, we obtain the thermal expansion $\alpha = 1.73 \times 10^{-5}/\,\mathrm{K}$, which is in agreement with the experimental data ($\alpha = 1.76 \times 10^{-5}/\,\mathrm{K}$).[22] These results are in agreement with the results of Debye theory, which applies to many kinds of materials.

The Debye temperature Θ_D is another important fundamental parameter of solids, which is closely related to specific heat, elastic constants and melting temperature. Finally, the pressure dependence of the Debye temperature Θ_D and heat capacity C_v with pressure increasing from 0 to 42 GPa are analysed and plotted in Fig.5.

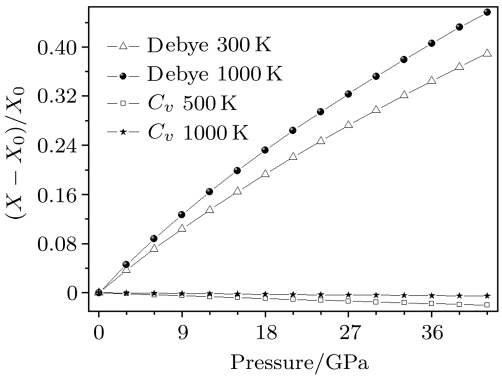


Fig.5. Variations of thermodynamic parameters X(X: Debye temperature or specific heat) with pressure P. They are normalized by $(X - X_0)/X_0$, where X and X_0 are the Debye temperature or heat capacity under any pressure P and zero pressure P_0 at the temperatures of 300, 500 and 1000 K.

At 300 K, we obtain the Debye temperature $\Theta_D = 332.1$ K. The calculated Θ_D is in agreement with the experimental measurements for Ni_2MnGa (321.9 K).[23] At 1000 K, we obtain the Debye temperature $\Theta_D = 306.2$ K, which is in relatively good agreement with the experimental data (318±7 K).[24] It is found that the Debye temperature Θ_D decreases with the temperature. It is shown that when the temperature is constant, the Debye temperature Θ_D increases almost linearly as pressure increases. However, C_v decreases with the applied pressures, which is due to the fact that the effect of increasing pressure on Ni_2MnGa is the same as decreasing its temperature.

4. Conclusions

The equilibrium lattice parameter, heat capacity C_v, thermal expansion coefficient α, bulk modulus and Debye temperature of Ni_2MnGa Heusler alloy are investigated using the first-principles plane-wave pseudopotential (PW-PP) method as well as the quasi-harmonic Debye model. For the first time we have analysed the temperature dependence of bulk modulus and obtained the relationships between bulk modulus and pressure at different temperatures. It is found that the bulk modulus B increases monotonically as pressure increases. The pressure dependences of heat capacity C_v and thermal expansion α at various temperatures are analysed. Finally, the Debye temperatures of Ni_2MnGa at different pressures are also successfully obtained. Our results are in excellent agreement with the experimental data.

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