CHIN. PHYS. LETT. Vol. 26, No. 1 (2009) 016201

First-Principles Calculations of Elastic Properties of Cubic Ni_2MnGa *

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(Received 15 July 2008)

Dependence of bulk modulus on both pressure and temperature, the elastic constants C_{ij} and the pressure and temperature dependence of normalized volume V/V_0 of cubic Ni_2MnGa 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 and temperature up to 800 K and obtain the relationships between bulk modulus B and pressures at different temperatures. It is found that the bulk modulus B increases monotonically with increasing pressure. Moreover, the temperature dependences of the Debye temperature are also analysed. The calculated results are in agreement with the available experimental data and the previous theoretical results.

PACS: 62.20.Dc, 81.05.Bx

Magnetically driven actuator materials such as ternary Heusler alloy Ni_2MnGa have generated tremendous interest in recent years because of their potential applications as magnetically driven shape memory alloys that are more efficient than temperature or stress driven shape memory devices.[1−4] Ni_2MnGa is the only ferromagnetic Heusler alloy which undergoes a martensitic transformation. From the technological point of view, Ni_2MnGa is much more promising than other materials presently in commercial use. In the high temperature austenitic phase, the structure of Ni_2MnGa has been found to be 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 crystal structure with an approximate 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.

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 for materials is well motivated by, for example, the understanding one thereby gains about the chemical bonds and the cohesion of material. The elastic properties of Ni_2MnGa have been mainly attributed to internal strains. Moreover, the elastic constants are also related to thermal properties according to the Debye theory. Because these effects are related to elastic properties, there are good reasons to calculate the elastic properties of the Ni_2MnGa shape memory alloy. Compared to other parameters, elastic properties of Ni_2MnGa, such as elastic constants, have received less experimental attention, partially because of the difficulty of preparing suitable samples. Therefore, there are only rare studies of the elastic properties were performed experimentally. Due to the unclear of elastic properties for Ni_2MnGa under higher temperatures and pressures, here we make a first-principles calculation on the elastic modulus of Ni_2MnGa by using a quasi-harmonic Debye model,[7] in which the phononic effect is considered.

Firstly, we make a first-principles total energy electronic structure calculation. In our electronic structure calculation, we adopt the plane wave pseudopotential (PW-PP) method.[8] The generalized gradient approximation of PBE96[9] was used for the exchange-correlation energy functional. Initial convergence test guided the choice of 500 eV for the cutoff energy. For the Brillouin-zone sampling, we use the $12\times12\times12$ Monkhorst-Pack mesh,[10] which is enough to achieve the self-consistent convergence of total energy to 1×10^{-6} eV/atom. All total energy electronic structure calculations are implemented by the CASTEP code.[11]

Then, the quasi-harmonic Debye model is employed to calculate the equation of state (EOS) and the elastic properties which are constructed from the Helmholtz free energy at the temperature below the melting point in the quasi-harmonic approximation. The zero pressure bulk modulus B_0 is determined by fitting the calculated energy-volume $(E-V)$ data to the Birch-Murnaghan EOS[12]

*Supported by the National Natural Science Foundation of China under Grant No 60777012, and the Programme for Science and Technology Innovation Talents in Universities of Henan Province under Grant No 2008HASTIT008.
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$$\Delta E(V) = E - E_0$$
$$= B_0 V_0 \left[\frac{V_n}{B_0'} + \frac{1}{1 - B_0'} + \frac{V_n^{1-B_0'}}{B_0'(B_0' - 1)} \right], \quad (1)$$

where E_0 is the equilibrium energy. The pressure P versus the normalized volume V_n (i.e. V/V_0 with V_0 being the equilibrium volume at zero pressure) is obtained by

$$p = -\frac{dE}{dV} = \frac{B_0}{B_0'} \left[V_n^{-B_0'} - 1 \right]. \quad (2)$$

In addition, the bulk modulus B is also investigated under various pressures and temperatures using the quasi-harmonic Debye model. In the quasi-harmonic Debye model, the non-equilibrium Gibbs energy of the crystal phase $G^*(V; P, T)$ of cubic Ni_2MnGa can be written as[13]

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}(V; T), \quad (3)$$

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_{vib} is the vibrational Helmholtz free energy, which can be written as[14,15]

$$A_{\text{vib}}(\Theta_D; T) = nkT \left[\frac{9}{8} \frac{\Theta_D}{T} + 3 \ln \left(1 - e^{-\Theta_D/T} \right) - D(\Theta_D/T) \right], \quad (4)$$

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 following equation

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

one could obtain the isothermal bulk modulus B,

$$B(p, T) = V \left(\frac{\partial^2 G^*(V; p, T)}{\partial V^2} \right)_{p,T}. \quad (6)$$

Another important fundamental parameter of solids is the Debye temperature Θ_D, which is closely related to specific heat, elastic constants, thermal coefficient and melting temperature. The Debye temperature Θ_D is expressed as[16]

$$\Theta_D = \frac{h}{2\pi k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}}, \quad (7)$$

where M is the molecular mass per formula unit cell; B_S is the adiabatic bulk modulus, which is approximated calculated by the static compressibility[16,17]

$$B_S \cong B(V) = V \left[\frac{d^2 E(V)}{dV^2} \right]; \quad (8)$$

$f(\sigma)$ was given in Refs. [18,19].

In Fig. 1, we present the normalized volume-pressure diagrams of Ni_2MnGa at 300, 600 and 900 K.

The obtained primitive cell volume V dependences on pressure P at different temperatures are illustrated in Fig. 1. It is noted that as the pressure P increases, the value V/V_0 decreases at a given temperature, and the normalized volume V/V_0 of higher temperature is less than that of lower temperature at the same pressure. When temperature T increases, the curve of $V/V_0 - P$ becomes steeper, indicating that the Ni_2MnGa alloy is compressed much easier with increasing temperature.

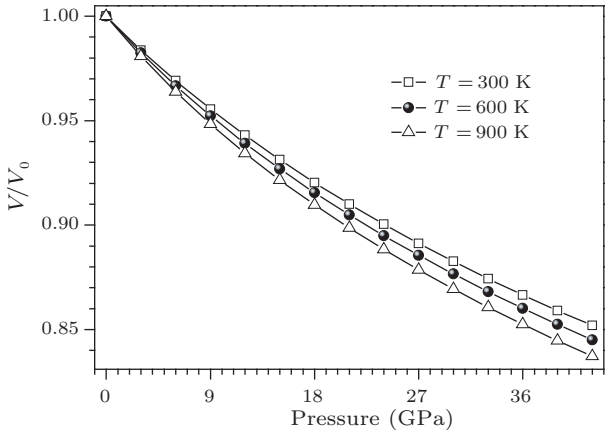


Fig. 1. Normalized volume $V/V_0 - P$ diagrams of cubic Ni_2MnGa at $T = 300$, 600, 900 K.

We now investigate the dependence of bulk modulus B on temperature T and pressure P. To investigate the elastic properties of Ni_2MnGa under high pressures and high temperatures, we apply the quasi-harmonic Debye model. The relationships of the bulk modulus B as a function of temperature T up to 800 K and the relationships between bulk moduli B and pressure P at different temperatures are plotted in Fig. 2.

At 300 K, we obtain the bulk modulus $B = 155.1$ GPa, which is in agreement with the values 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 constants, 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_0 rapidly decreases. By fitting the $B - T$ data points to third-order polynomial, we obtain the relationship

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

From Eq. (9) we obtain the slope of the $B - T$ curve, as shown in Fig. 2(a),

$$K = \left(dB/dT \right)_{p=0}$$

$$= -2.541 \times 10^{-2} - 5.45098 \times 10^{-5} T + 3.43455 \times 10^{-8} T^2. \quad (10)$$

It is noted from Fig. 2(b) that the relationships between bulk moduli B and pressure P are nearly linear at temperatures of 300, 900 and 1200 K, respectively. The bulk modulus B increases with pressure dramatically at a given pressure and decreases with T at a given pressure. 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 this shape memory alloy.

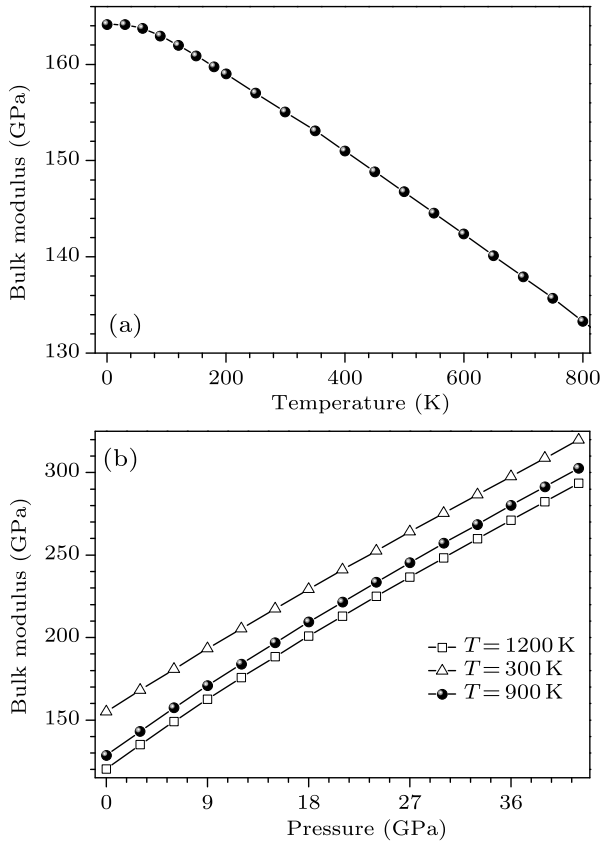


Fig. 2. Bulk modulus B as a function of temperature T at $P = 0$ (a) and relationships between bulk modulus B as a function of pressure at $T = 300$, 900, 1200 K (b).

For the cubic structure, there are three independent elastic constants, i.e. C_{11}, C_{12} and C_{44}. In order to calculate the elastic constants under various pressures, we employ the CASTEP code. For the cubic polycrystalline sample, the shear modulus G_H can be determined from single crystal elastic constants according to the Voigt–Reuss–Hill scheme.[22] The zero pressure bulk modulus B_0, elastic shear constant C', elastic longitudinal constant C_L and polycrystalline shear modulus G_H are given by

$$B_0 = 1/3(C_{11} + 2C_{12}), \quad (11)$$

$$C' = \frac{1}{2}(C_{11} - C_{12}),\ C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}), \quad (12)$$

$$G_V = \frac{1}{5}(2C' + 3C_{44}),\ G_R = \left[\frac{1}{5}\left(\frac{2}{C'} + \frac{3}{C_{44}}\right)\right]^{-1}, \quad (13)$$

$$G_H = \frac{1}{2}(G_V + G_R). \quad (14)$$

Table 1. Calculated elastic constants C_{ij}, bulk modulus B_0 (GPa) and shear modulus G_H for Ni_2MnGa.

	Ni_2MnGa				
C_{11}	152(expt)[2]	139.4[21]	156(expt)[23]	213(expt)[24]	159.5(calc)
C_{12}	143	122.6	143	87	147
C_{44}	103	91	98	92	102
C'	4.5	8.4	6.5	63	6.25
C_L	250.5	222	147.5	242	255.2
B_0	146	128.2	147.3	129	151.6
G_H	37.1	38.2	38.1	79.1	39.0

The reason why we analyse the elastic constants C_L and C' is that they can be directly measured in experiments and can be used to characterize the structure stability of a crystal. From Table 1, one can see that our calculated results are in agreement with the theoretical elastic constants obtained from the phonon dispersion curves[21] and the experimental values obtained from ultrasonic pulse echo technique measurements.[2] The values of C_{11} and C_{12} in the electromagnetic generation technique (EMG) study[24] are in error because the elastic constant $C' = 1/2(C_{11} - C_{12})$ is incorrect by a factor of 16.[2] The calculated polycrystalline shear modulus G_H is in agreement with the experimental data. The calculated zero temperature bulk modulus B_0 is in agreement with the result obtained by the quasi-harmonic Debye model ($B = 155.1$ GPa at $T = 300$ K).

Table 2. Elastic constants C_{ij} (GPa) and bulk modulus B (GPa) under various pressures P(GPA) at $T = 0$.

P	B	C_{11}	C_{12}	C_{44}
0.2	152.2	160.3	148.2	102.3
0.4	153.3	161.1	149.4	102.6
0.6	154.4	161.9	150.6	102.9
0.8	155.4	162.7	151.8	103.2
1.0	156.5	163.5	153.0	103.5
1.2	157.6	164.3	154.2	103.8

In Table 2, we present the pressure dependences of the elastic constants C_{ij} and bulk modulus B. From Table 2, we can find that all the elastic constants C_{ij} and bulk modulus B increase monotonically when the pressure is enhanced. The elastic constant C_{11} increases more quickly compared with C_{12}, C_{44} and B. Moreover, C_{44} increases slowly with the elevated pressure compared with C_{11}, C_{12} and B. For the cubic lattice, Born's rule must be true, i.e. $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{44} > 0$. In Table 2, it is clear that the Ni_2MnGa crystal is stable under pressure. Unfortunately, no experimental data or theoretical results are available to check our calculated results under pressure.

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[25]). At 1050 K, we obtain the Debye temperature $\Theta_D = 306.2$ K, which is relatively in agreement with the experimental data (318 ± 7 K[26]). It is shown that the Debye temperature Θ_D decreases with applied temperatures. As the temperature increases, the Debye temperature Θ_D decreases more quickly at $T > 700$ K. By fitting the data point to third-order polynomial, we obtain the equation

$$\Theta_D = 339.23348 - 1.817 \times 10^{-2}T - 1.8882 \times 10^{-5}T^2 + 5.76154 \times 10^{-9}T^3. \quad (15)$$

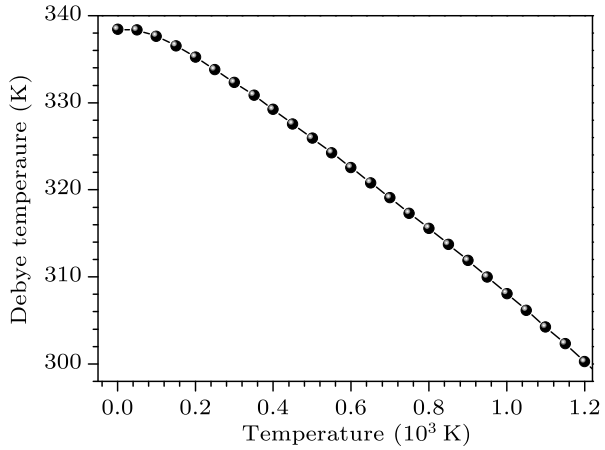


Fig. 3. Relationships of Debye temperature Θ_D with temperatures at pressure 0 Pa.

In summary, the temperature and pressure dependences of bulk modulus B, the pressure dependence of the normalized volume V/V_0 and the high pressure elastic constants C_{ij} of Ni_2MnGa shape memory alloy are successfully obtained using the first-principles plane-wave pseudopotential (PW-PP) method in the GGA-PBE generalized gradient approximation as well as the quasi-harmonic Debye model. For the first time we analyse the bulk modulus of Ni_2MnGa up to 800 K and the relationships between bulk modulus B and pressure at different temperatures are also obtained. Moreover, the temperature dependences of Debye temperature also analysed. Our calculated results are in agreement with the available experimental data. The methods reported here seems to be helpful to investigate the elastic properties of solids.

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