First-Principles Study of the Structural, Elastic, and Mechanical Properties of Ni_3Ga Compound under Pressure

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There was employed the density functional theory plane-wave pseudopotential method with local density approximation and generalized gradient approximation to investigate the structural, elastic and mechanical properties of the intermetallic compound Ni_3Ga. The calculated equilibrium lattice constant and bulk modulus are in good agreement with the experimental values. The elastic constants were determined from a linear fit of the calculated stress–strain function according to Hooke's law. From the elastic constants, the bulk modulus B, anisotropy factor A, shear modulus G, Young's modulus E and Poisson's ratio υ for Ni_3Ga compound are obtained. Our results for the bulk modulus B, anisotropy factor A, shear modulus G, Young's modulus E and Poisson's ratio υ are consistent with the experimental values. The sound velocities and the Debye temperature are also predicted from elastic constants. The dependences of the elastic and mechanical properties of Ni_3Ga compound on pressure were investigated for the first time. It was found that the cubic Ni_3Ga compound is mechanically stable according to the elastic stability criteria and it is not elastically isotropic. By analyzing the ratio B/G, it was concluded that Ni_3Ga compound is ductile in nature.

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1. Introduction

Intermetallics have a wide spectrum of properties ranging between metallic and non-metallic. Some intermetallics are interesting functional materials, others have attracted attention as structural materials for high-temperature applications. There are a large number of engineering alloys that find applications because of some special physical or chemical properties — for example, magnetic behaviour, superconductivity, or chemical stability in corroding atmospheres. Intermetallics are used in a wide range of industries such as semiconductors, superconductors and the aerospace industry [1].

In the last years, intermetallics with $L1_2$ structure were of particular interest, both from the point of view of their fundamental properties and their practical applications as materials with excellent chemical, mechanical and physical properties. Intermetallic compounds Ni_3Al, Ni_3Ga, and Ni_3Mn provide a class of systems exhibiting many interesting mechanical and electronic properties that make them attractive for structural applications at elevated temperatures [2].

The Ni_3Ga compound has been studied, both experimentally as well as theoretically. First-principles total-energy electronic structure calculations based on the full-potential linear muffin-tin-orbital method have been used to study the electronic and elastic properties of the Ni_3X (X = Al, Ga, Mn) [2]. The electronic structures, mechanical and magnetic properties of Ni_3Ga, Ni_3Al, and Ni_3In have been studied by spin-density functional theory and also by X-ray absorption near-edge spectra [3, 4]. Many experimental works [5–7] have been conducted to investigate the electronic structures of the Ni_3Al and Ni_3Ga. The optical properties of Ni_3Ga, Ni_3Al, and Ni_3In have been investigated by Hsu and Wang [8]. However, the high-pressure behaviours are less often reported in the literature. In order to fully take advantage of the properties of Ni_3Ga for more technological applications, theoretical explorations of the structural, elastic and electronic properties are necessary. In this paper, we present a systematic study on the equilibrium structure of Ni_3Ga compound. Then the elastic constants were calculated under pressure and the mechanical stability was evaluated, also the temperature of Debye was estimated by using first-principles calculations based on density functional theory (DFT).

The rest of the paper is organized as follows. The computational method is given in Sect. 2. The numerical results and discussion are given in Sect. 3, and finally a conclusion is presented in Sect. 4.

2. Computational method

Our first-principles calculations are performed with the plane-wave pseudopotential (PWPP) total energy method implemented with the Cambridge Serial Total Energy Package (CASTEP) simulation program [9]. This is based on DFT [10, 11] which is, in principle, an exact theory of the ground state. We have used two approximations. First, the local density approximation (LDA) developed by Ceperley and Adler and parameterized by Perdew and Zunger [12, 13], as well as the generalized gradient approximation (GGA), with the functional of Wu and Cohen, known as WC [14], are made for elec-

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tronic exchange-correlation potential energy. Second, the Coulomb potential energy caused by electron–ion interaction is described using the Vanderbilt-type ultrasoft scheme [15], in which the orbitals of Ni ($3d^8 4s^2$), Ga ($3d^{10} 4s^2 4p^1$), are treated as valence electrons. The cut-off energy for the plane-wave expansion is 300 eV and the Brillouin zone sampling was carried out using the $8 \times 8 \times 8$ set of Monkhorst–Pack mesh [16].

The structural parameter a_0 of Ni_3Ga was determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [17]. This method usually provides the fast way of finding the lowest energy structure.

Full geometry optimization was performed at a fixed value of applied hydrostatic pressure in the range 0–30 GPa. This procedure allows us to produce an equation of state (EOS). This is similar to the experimental procedure for measuring the EOS. The calculated cell volumes were then used to construct the EOS, which was fitted to a third order Birch–Murnaghan [18] to obtain the bulk modulus, B_0, and its pressure derivative, B_0'. In the structural optimization process, the energy change, maximum force, maximum stress, and maximum displacement are set as 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively.

The elastic constants were determined from first--principles calculations by applying a given homogeneous strain (deformation) with a finite value and calculating the resulting stress. The total energy is converged to 5.0×10^{-6} eV/atom in the self-consistent calculation.

3. Results and discussion

3.1. Structural properties

The atomic structure of Ni_3Ga compound is known to crystallize in a cubic lattice of Cu_3Au structure type with the space group $Pm\text{-}3m$ and the equilibrium lattice parameter has a value of 3.58 Å [19]. Two inequivalent atomic sites, the gallium (Ga) atom is positioned at (0, 0, 0) and the nickel (Ni) at (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2).

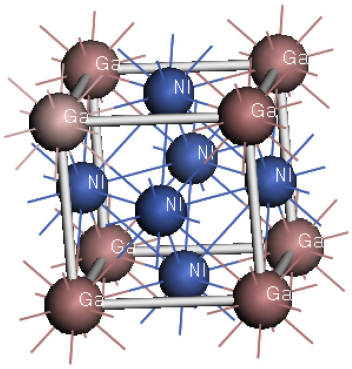

Fig. 1. The cubic structure of Ni_3Ga.

The initial unit cell structural model of the Ni_3Ga compound is built according to the experimental data [19], as shown in Fig. 1. The calculated lattice parameter a_0 of

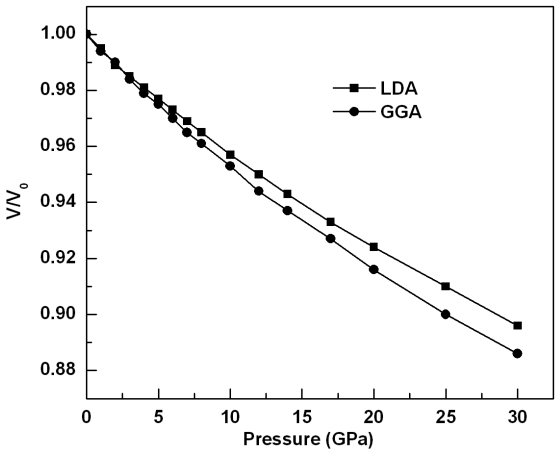

Fig. 2. Pressure dependence of the relative unit cell volume V/V_0 for Ni_3Ga compared with LDA and GGA.

TABLE I

Calculated, experimental and other values of the equilibrium lattice constant a_0 [Å], bulk modulus B_0 [GPa] and bulk derivative B_0' in cubic Ni_3Ga compound.

	a_0	B_0	B_0'
this work:			
LDA	3.5206	207.05	5.19
GGA	3.5697	185.73	4.86
experiment	3.5800[a]	146[a]	
other	3.4700[b]	249[b]	
	3.5900[c]	183.6[c]	

[a]Ref. [19]; [b]Ref. [2]; [c]Ref. [3].

Ni_3Ga compound using the PP-PW method within both the LDA and the GGA, approximations is in Table I along with the available experimental and theoretical data. The calculated lattice constant a_0 is only 1.6% and 0.2% smaller than the experimental value using LDA and GGA, respectively. Our calculated equilibrium lattice parameter a_0 is in a good agreement with the experimental data. The calculated unit cell volume at values of applied hydrostatic pressure up to 30 GPa were used to construct the EOS, which was fitted to a third-order Birch–Murnaghan equation [18] as following:

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \times X \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\}, \quad (1)$$

with V_0 fixed at the value determined from the zero pressure data. The relative changes of unit cell volume V/V_0 as a function of external pressure P of Ni_3Ga compound for both approximations are shown in Fig. 2. We obtained, by least-squares fitting, the bulk modulus B_0 and its pressure derivative B_0' at zero pressure. These are listed in Table I. Our result for the bulk modulus B_0 using GGA approach is within 21% of the experimental

value, but it is in good agreement with the theoretical result in Ref. [3].

3.2. Elastic and mechanical properties

The elastic constants were determined from a linear fit of the calculated stress–strain function according to Hooke's law [20]. The cubic crystal has three independent elastic constants, C_{11}, C_{12}, and C_{44}. The bulk modulus B is related to the elastic constants by

$$B = \frac{C_{11} + 2C_{12}}{3}. \tag{2}$$

TABLE II

Calculated, experimental and other values of the elastic constants C_{ij} [GPa], bulk modulus B [GPa], anisotropy factor A, shear modulus G [GPa], Young's modulus E [GPa], Poisson's ratio ν and B/G in cubic Ni_3Ga compound.

	C_{11}	C_{12}	C_{44}	B	A	G	E	v	B/G
this work:									
LDA	288.86	192.53	127.74	224.64	2.65	86.41	134.86	0.40	2.60
GGA	264.14	169.99	116.39	201.37	2.47	80.96	131.02	0.39	2.49
experimental	191[a]	123[a]	108[a]	146[a]	3.17[a]	68[a]	176[a]	0.39[a]	2.15[a]
other	296[b]	226[b]	202[b]	249[b]	5.73[b]	103[b]	270[b]	0.43[b]	2.42[b]
				183.6[c]					

[a]Ref. [21]; [b]Ref. [2]; [c]Ref. [3].

In Table II, the calculated elastic constants and the bulk modulus of Ni_3Ga at zero pressure are presented, where we also compare the recent calculations and experimental measurement. The two theoretical approaches overestimate the elastic constants C_{ij}. The GGA overestimates the C_{11} and C_{12} values by 27% than the experimental values [21]. The C_{44} value within GGA is 7% higher than the experimental value [21]. The C_{11}, C_{12} and C_{44} elastic constants obtained within GGA are much closer to the experimental values than the LDA values and the other theoretical calculations in Ref. [2]. The calculated values of the bulk modulus B from the elastic constants, using LDA and GGA have nearly the same values as the ones obtained from the fit to a Birch–Murnaghan EOS (B_0). This might be an estimate of the reliability and accuracy of our calculated elastic constants for Ni_3Ga compound. The Zener anisotropy factor A is a measure of the degree of anisotropy in solid [22]. It takes the value of 1 for an isotropic material. It provides a measure of the degree of elastic anisotropy, when the A values are smaller or greater than unity. The Zener anisotropy factor A of Ni_3Ga compound is calculated by the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \tag{3}$$

As shown in Table II, the calculated Zener anisotropy factor is larger than 1, which indicates that this compound is not elastically isotropic. The elastic constants C_{ij} are estimated from first-principles calculations for monocrystal Ni_3Ga. However, the prepared materials are in general polycrystalline, and therefore it is important to evaluate the corresponding moduli for the polycrystalline phase. For this purpose we have applied the Voigt–Reuss–Hill (VRH) approximation [23–25]. For the cubic system, the Reuss and Voigt bounds on the shear modulus are given by

$$G_{\mathrm{R}} = \frac{5C_{44}\left(C_{11} - C_{12}\right)}{4C_{44} + 3\left(C_{11} - C_{12}\right)}, \tag{4}$$

$$G_{\mathrm{V}} = \frac{C_{11} - C_{12} + 3C_{44}}{5}. \tag{5}$$

Finally, the VRH mean value is obtained by

$$G = \frac{1}{2}\left(G_{\mathrm{V}} + G_{\mathrm{R}}\right). \tag{6}$$

We also calculated Young's modulus E and Poisson's ratio v which are frequently measured for polycrystalline materials when investigating their hardness. These quantities are related to the bulk modulus and the shear modulus by the following equations [26]:

$$E = \frac{9BG}{3B + G}, \tag{7}$$

$$v = \frac{3B - E}{6B}. \tag{8}$$

The shear modulus G, Young's modulus E and Poisson's ratio v for Ni_3Ga compound, calculated from the elastic constants are listed in Table II. Our calculated shear moduli G are 19–27% larger than the one measured from the experiment [21]. For Young's modulus E, our values are 30–34% lower than the experimental result [21], and finally, for Poisson's ratio v, our values are well consistent with the experimental value [21]. One can see that our calculation results are closer to the experimental values than the other theoretical calculations in Ref. [2].

The ratio B/G is a simple relationship related to brittle or ductile behaviour of materials; it has been proposed by Pugh [27]. A high B/G ratio is associated with ductility, whereas a low value corresponds to the brittleness. The critical value separating ductile and brittle material is 1.75. The calculated results are listed in Table II. The results indicate that Ni_3Ga can be classified as ductile material at zero pressure.

3.3. Calculation of Debye temperature

Once the elastic constants are determined from first--principles calculations and having calculated Young's modulus E, bulk modulus B, and shear modulus G, we can calculate the Debye temperature, which is an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperature the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. One of the standard methods to calculate the Debye temperature θ_{D} is from elastic data, since θ_{D} may be estimated from the average sound velocity v_{m} by the following equation [28]:

$$\theta_{\mathrm{D}} = \frac{h}{k_{\mathrm{B}}}\left(\frac{3n}{4\pi V_{\mathrm{a}}}\right)^{1/3} v_{\mathrm{m}}, \tag{9}$$

where h is the Planck constant, k_{B} — Boltzmann's constant, n is the atoms number per molecule and V_{a} is the atomic volume. The average sound velocity v_{m} is given by [29]:

$$v_{\mathrm{m}} = \left[\frac{1}{3}\left(\frac{1}{v_{\mathrm{l}}^3} + \frac{2}{v_{\mathrm{t}}^3}\right)\right]^{-1/3}, \tag{10}$$

where v_{l} and v_{t} are the longitudinal and transverse sound velocity of an isotropic aggregate obtained using the shear modulus G and the bulk modulus B from Navier's equation [26]:

$$v_{\mathrm{l}} = \left(\frac{3B + 4G}{3\rho}\right)^{1/2} \tag{11}$$

and

$$v_{\mathrm{t}} = \left(\frac{G}{\rho}\right)^{1/2}. \tag{12}$$

The calculated Debye temperature and sound velocities as well as the density for Ni_3Ga compound are given in Table III. To the best of our knowledge, there are no experimental and other theoretical data for comparison, so we consider the present results as a prediction study which still awaits an experimental confirmation.

TABLE III

The calculated density ρ, the longitudinal, transverse and average sound velocities v_{l}, v_{t} and v_{m} calculated from elastic moduli, and the Debye temperatures θ_{D} calculated from the average sound velocity for Ni_3Ga compound.

	ρ [g cm^{-3}]	v_{l} [ms^{-1}]	v_{t} [ms^{-1}]	v_{m} [ms^{-1}]	Θ_{D} [K]
this work:					
LDA	9.4708	5990.35	3020.54	3386.78	457
GGA	9.1152	5825.30	2980.28	3338.66	445

3.4. High pressure behaviour of Ni_3Ga compound

In order to investigate the high pressure behaviour of Ni_3Ga compound, we have optimized the structural parameter of its cubic lattice at different pressure up to 50 GPa. In this study, we still used GGA approximation. We next study the pressure dependence of the elastic properties. In Fig. 3, we present the variation of the elastic constants (C_{11}, C_{12}, and C_{44}) and the bulk modulus B of Ni_3Ga with respect to the variation of pressure. We observe a linear dependence in all curves in the considered range of pressure. It is easy to observe that the elastic constants C_{11}, C_{12}, C_{44}, and the bulk modulus B increase when the pressure is enhanced in this compound.

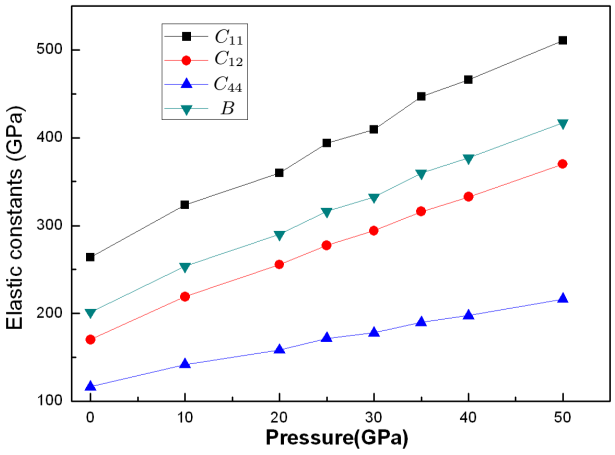

Fig. 3. GGA pressure dependence of the elastic constants C_{11}, C_{12}, and C_{44} and the bulk modulus B for Ni_3Ga.

For a cubic crystal under pressure P, the generalized elastic stability criteria [30, 31] are

$$K = C_{11} + 2C_{12} + P > 0, \quad K_1 = C_{44} - P > 0$$
$$\text{and} \quad K_2 = C_{11} - C_{12} - 2P > 0. \tag{13}$$

The obtained results are depicted in Fig. 4. As shown in Fig. 4, these criteria are satisfied in the studied pressure range up to 40 GPa. Consequently this compound is mechanically stable up to 40 GPa. The Zener anisotropy factor A of Ni_3Ga compound is calculated at various pressures and the results are shown in Fig. 5. As a result in Fig. 5, it can be seen that Ni_3Ga exhibits anisotropic elasticity with the change of pressure.

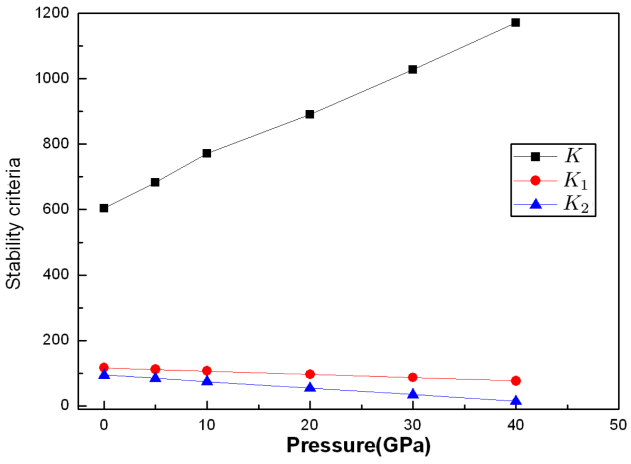

Fig. 4. Stability criteria vs. pressure.

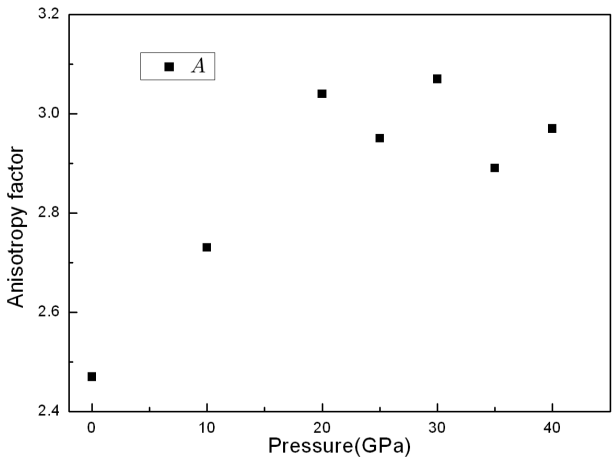

Fig. 5. Pressure dependence of the elastic anisotropy factor.

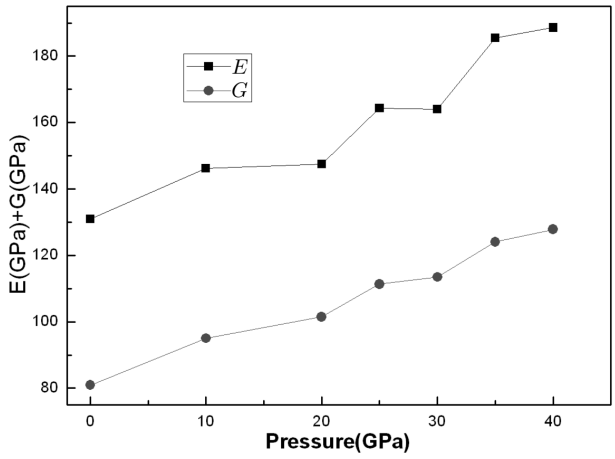

Fig. 6. Pressure dependence of shear modulus G and Young's modulus E of Ni_3Ga.

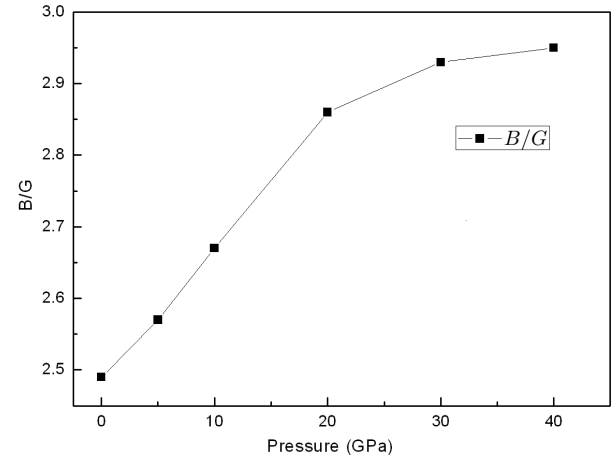

Fig. 7. Pressure dependence of the ratio of shear modulus to bulk modulus B/G for Ni_3Ga.

The shear modulus G, and Young's modulus E of Ni_3Ga at various pressures are also calculated and the results are depicted in Fig. 6. It can be seen from Fig. 6 that the pressure affects significantly the G and E moduli. The results indicate that the values of G and E increase with the increase of pressure. It is interesting to point out that the Ni_3Ga compound has a strongest mechanical behaviour. We also studied the effect of pressure on the B/G ratios and the results are shown in Fig. 7. It can be seen that the B/G ratios increase with an increase in pressure. As shown in Fig. 7, it is clear that Ni_3Ga compound remains in a ductile manner.

4. Conclusion

In this paper, the ground state properties as well as the high pressure behaviour of Ni_3Ga intermetallic compound have been studied by means of the density functional theory plane-wave pseudopotential method, within the LDA and GGA. The calculated equilibrium lattice parameter and bulk modulus of Ni_3Ga compound are in good agreement with the available experimental data. By comparison, it is found that the GGA calculated results give close results to the experimental values for elastic constants C_{11}, C_{12}, and C_{44}, bulk modulus B, shear modulus G, and Poisson's ratio ν. We find that the elastic constants of Ni_3Ga compound, obtained by the calculations satisfy the requirement of the mechanical stability in a cubic structure with applied pressure. The computed results indicate that Ni_3Ga compound is mechanically stable up to 40 GPa. It is found that the Zener factor A suggests that Ni_3Ga compound exhibits anisotropic elasticity at various pressures. The isotropic bulk modulus B, shear modulus G, and Young's modulus E of the Ni_3Ga compound were determined using the VRH averaging scheme. The results indicate that Ni_3Ga has the strongest mechanical behaviour. It is found that the Ni_3Ga compound remains in ductile nature in the entire pressure range studied. Our results suggest there are potential technological applications of such material in extreme environments.

Acknowledgments

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