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First-principles study of the elastic and mechanical properties of Ni_3Al under high pressure

S. BOUCETTA[1*], T. CHIHI[1], B. GHEBOULI[2], M. FATMI[3]

[1]Laboratoire d'Elaboration de Nouveaux Matériaux et Caractérisations (ENMC), Département de Physique, Université Ferhat Abbas, Sétif 19000, Algérie

[2]Laboratoire d'Etudes de Surfaces et Interfaces des Matériaux Solides (LESIMS), Département de Physique, Université Ferhat Abbas, Sétif 19000, Algérie

[3]Laboratoire de Physique et Mécanique des Matériaux Métalliques (LP3M), Département d'Optique et Mécanique de Précision, Université Ferhat Abbas, Sétif 19000, Algérie

A first-principles study of the structural and elastic properties of the intermetallic compound Ni_3Al was undertaken, exploiting density-functional theory and generalized gradient approximation (GGA). The elastic constants C_{11}, C_{12}, and C_{44} were shown to be sufficiently close to the density of the *k*-point mesh in the deformed Brillouin zone to conclude that the elastic anisotropy of the coefficient A increases as the pressure increases. Young's modulus of Ni_3Al along {100} is approximately two times higher than that along {111}. The computed elastic constants from first principles satisfy $C_{11} > C_{12} > C_{44}$, which are in good agreement with the experiment data. The cubic Ni_3Al possesses a bulk modulus of 312 GPa, comparable to that of cubic hafnium nitride. Theoretical calculations for Ni_3Al show that all elastic moduli increase monotonically as the pressure increases. These results suggest there are potential technological applications of such materials in extreme environments.

Keywords: *intermetallics; structural properties; elastic properties*

1. Introduction

Ni_3Al, an intermetallic compound, is representative of a class of systems exhibiting unique mechanical properties which make them attractive for structural applications. Hence Ni_3Al is a very promising material for high temperature and pressure applications [1]. In an early theoretical study on the Ni_3Al, Dobrina et al. [2] investigated its electronic structure and elastic properties by using the *ab initio* density func-

*Corresponding author, e-mail: boucetta_said02@yahoo.fr

tional theory and the FLMTO method. Sot and Kurzydłowski [3] studied the elastic properties of Ni_3Al, using the ab initio calculations for lower pressures. Hsu [21] studied electronic absorption spectra of Ni_3Al and Ni_3Ga. Sob et al. [22] investigated the magnetism of Ni_3Al and Fe_3Al under extreme pressure and shape deformation from ab initio study. Hsu and Wang [23] investigated optical properties of Ni_3Al, Ni_3Ga and Ni_3In. Guo et al. [24] studied the electronic structure, mechanical and magnetic properties of Ni_3Al, Ni_3Ga and Ni_3In from the first-principles and experimental studies. To the best of our knowledge, no other theoretical studies on Ni_3Al at high pressures have been reported.

In this paper, we report first-principles calculations of total energy electronic structure and the elastic constants of Ni_3Al. The elastic constants C_{ij} determine the response of the crystal to external forces, as characterised by the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, playing an important role in determining the strength of a material. The elastic constants are the measure of the shear and tensile strength of crystals in the long-wavelength limit. They provide valuable information on the bonding characteristics between adjacent atomic planes and the anisotropic character of the bonding. Here, we report a theoretical study of the equation of state, elasticity and mechanical properties of the intermetallic compound Ni_3Al.

2. Computational method

The use of computer simulation techniques is becoming more important in the understanding of the microscopic behaviour of materials. Our first-principles calculations are performed with the plane-wave pseudo potential (PWPP) method implemented with the CASTEP (Cambridge Serial Total Energy Package) simulation program [4]. This is based on the density functional theory (DFT) [5, 6] which is, in principle, an exact theory of the ground state. The generalized gradient approximation (GGA) method, proposed by Perdew and Wang, known as PW91 [7], is applied for determining the electronic exchange-correlation potential energy. The Coulomb potential energy caused by electron–ion interaction is described according to the ultrasoft scheme [8], in which the orbitals of Ni ($3d^8 4s^2$) and Al ($3s^2 p^1$), are treated as valence electrons. By the norm-conservation condition, the pseudo-wave function related to pseudopotential matches the plane wave function expanded with Kohn–Sham formation beyond the cut-off energy. Using high cut-off (660 eV) energy, accurate results can be obtained at the expense of long computational time. The cut-off energy for the plane wave expansion is 330 eV and the Brillouin zone sampling was carried out using an 8×8×8 set of the Monkhorst–Pack mesh [9].

The structural parameter a_0 of Ni_3Al was determined using the Broyden–Fletcher –Goldfarb–Shenno (BFGS) minimization technique. Therefore, the present parameters are sufficient to obtain well converged total energy and geometrical configurations.

3. Numerical results and discussion

3.1. Structural properties

The Ni_3Al is known to crystallize in a cubic lattice of Cu_3Au structure type with the space group $Pm\bar{3}m$, and the equilibrium lattice parameter is 3.572 Å [10–12]. Two inequivalent atomic sites, the aluminium atom is positioned at (0,0,0) and the nickel atoms at (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) (Fig. 1).

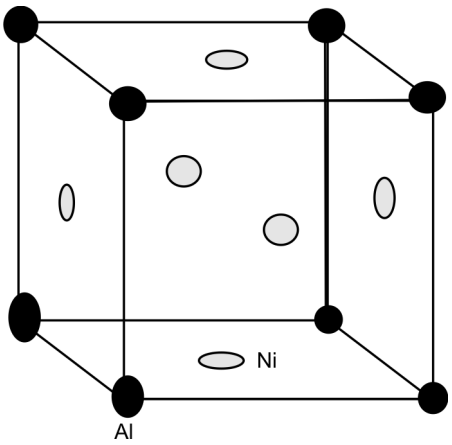

Fig. 1. The cubic structure of Ni_3Al

Table 1. Calculated and experimental values of the equilibrium lattice constant a_0 [Å], bulk modulus B_0 [GPa] and bulk derivative in cubic Ni_3Al compound.

a_0	B_0 [GPa]	B'$_0$	Source
3.558	130.13	8.67	This work
3.572[a] 3.56[b]	171[b]		Experiment
3.588[a] 3.48[b]	234[b]		Other

[a]Ref. [3].
[b]Ref. [2].

The lattice parameter of Ni_3Al calculated using the (PP-PW) method is given in Table 1, along with the available experimental and theoretical data. Our calculated equilibrium lattice parameter a_0 is in a good agreement with the experimental data. The calculated lattice constant a_0 is only 0.4% smaller than the experimental value. The calculated unit cell volume at an applied hydrostatic pressure in the range from 0 to 30 GPa were used to construct the equation of state (EOS), which was fitted to the third order Birch–Murnagham equation [13] (Fig. 2):

$$P=\frac{3}{2}B_0\left(\left(\frac{V}{V_0}\right)^{-7/3}-\left(\frac{V}{V_0}\right)^{-5/3}\right)\left(1+\frac{3}{4}\left(B'-4\right)\left(\left(\frac{V}{V_0}\right)^{-2/3}-1\right)\right)$$

With V_0 fixed at the value determined from the zero pressure data, we obtained by least-squares fitting the bulk modulus B_0 and its pressure derivative B_0' under zero pressure. These are listed in Table 1. We can see that the calculated value of the bulk modulus B_0 from the elastic constants $B_0 = (C_{11}+2C_{12})/3$ has nearly the same value as the one obtained from the EOS fitting. This might be an estimate of the reliability and accuracy of our calculated elastic constants for Ni_3Al.

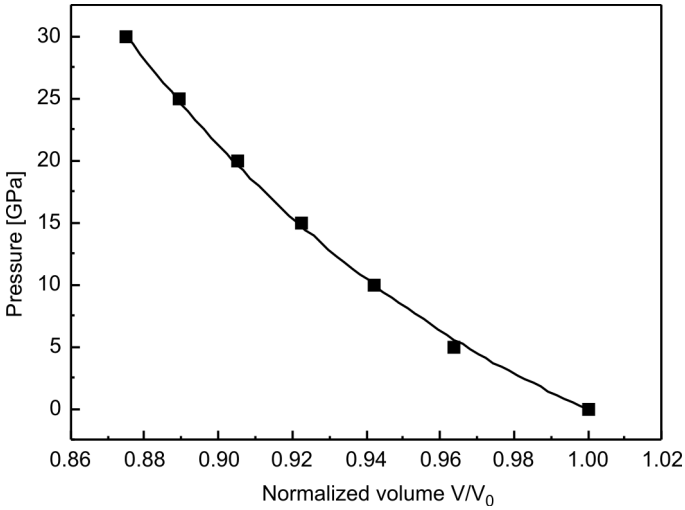

Fig. 2. Dependence of the calculated pressure on the normalized volume for Ni_3Al; the solid line is the plot of the Birch–Murnaghan equation of state with the parameters listed in Table 1

3.2. Elastic properties

The elastic constants are important parameters describing the response to an applied macroscopic stress. In Table 2, the calculated elastic constants and shear modulus of Ni_3Al under zero pressure are presented. We next study the pressure dependence of the elastic properties. In Figure 3, we present the variation of the elastic constants (C_{11}, C_{12} and C_{44}) and the bulk modulus B of Ni_3Al 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_{ij} and the bulk modulus B increase when the pressure is enhanced in this compound.

For a cubic crystal under a pressure P, the generalized elastic stability criteria [14, 15] are:

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

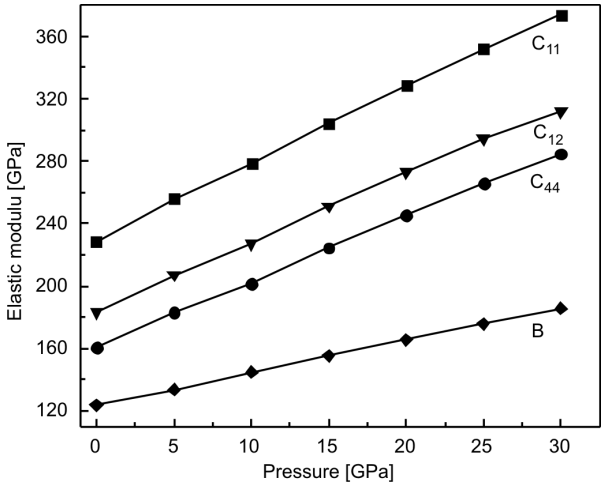

Fig. 3. Calculated pressure derivatives of the elastic constants C_{11}, C_{12} and C_{44} and the bulk modulus B_0 for Ni_3Al

Table 2. Calculated and experimental values of the elastic constants C_{ij} [GPa], shear moduli G [GPa], anisotropy factor A, Young's modulus E and Poisson's ratio ν in cubic Ni_3Al

C_{11}	C_{12}	C_{44}	G	A	E	ν	Source
228.4	160.41	123.75	34	3.64	96.04	0.41	This work
230[a] 221[b]	150[a] 146[b]	131[a] 124[b]	–	3.31[b]	–	0.40[b]	Experiment
230[a] 278[b]	139[a] 212[b]	123[a] 186[b]	–	5.64[b]	–	0.43[b]	Other

[a]Ref. [3].
[b]Ref. [2].

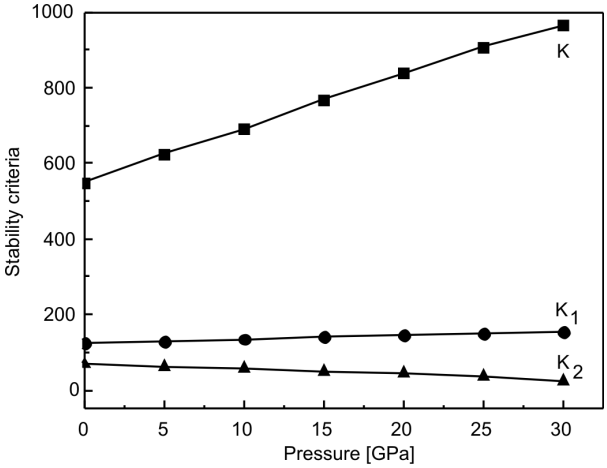

Fig. 4. Pressure dependences of the stability criteria

The obtained results are shown in Fig. 4. These criteria are satisfied in the studied pressure range. From our calculated C_{ij}, it is known that this compound is mechanically stable.

3.3. Mechanical properties

From the theoretical elastic constants, we computed the elastic wave velocities. The single crystal elastic wave velocities in different directions are given by the resolution of the Cristoffel equation [16]:

$$\left(C_{ijkl}n_j n_k - \rho v^2 \delta_{il}\right)u_l$$

where C_{ijkl} is the single crystal elastic constant tensor, n is the propagation direction, ρ is the density of material, u is the wave polarisation and v is the wave velocity. The solutions of this equation are of two types: a longitudinal wave with polarisation parallel to the direction of propagation v_l and two shear waves v_{T1} and v_{T2} with polarisations perpendicular to n. Another important parameter is the elastic anisotropy factor, A, which gives a measure of the anisotropy of the elastic wave velocity in a crystal. In a cubic crystal, the elastic anisotropy factor is given by [17]:

$$A = \frac{2C_{44} + C_{12}}{C_{11}} - 1$$

which is zero for an isotropic material. The plot of the elastic anisotropy factor is shown in Fig. 5.

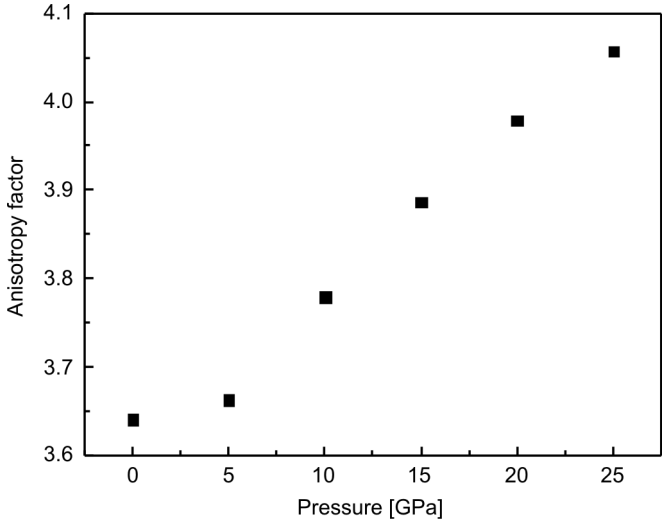

Fig. 5. Pressure dependence of the elastic anisotropy

The calculated elastic wave velocities along the [100], [110] and [111] directions for Ni_3Al under zero pressure are given in Table 3. Under zero pressure, longitudinal waves propagate faster along [111] and shear waves are slowest along [110] for Ni_3Al, which has a positive elastic anisotropy factor.

Table 3. The elastic wave velocities [$m \cdot s^{-1}$] for different propagation directions for Ni_3Al

Direction	v_L^{100}	v_{T1}^{100}	v_{T2}^{100}	v_L^{110}	v_{T1}^{110}	v_{T2}^{110}	v_L^{111}	v_{T1}^{111}	v_{T2}^{111}
Value	5733.18	4215.78	4215.78	6819.54	2211.83	4220.04	7077.49	3032.77	3032.77

Once the elastic constants are determined, we compare our results with experimental data, or predict what the elastic constants should be for a given experiment. For cubic systems, the isotropic bulk modulus B is given exactly by:

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

The bounds on the shear modulus are given by:

$$G_R = \frac{5C_{44}\left(C_{11} - C_{12}\right)}{4C_{44} + 3\left(C_{11} - C_{12}\right)}, \qquad G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}$$

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 relate to the bulk modulus and the shear modulus by the following equations [18]:

$$E = \frac{9BG}{3B + G}, \qquad v = \frac{3B - E}{6B}$$

The shear moduli G_R and G_V, Young's modulus E and Poisson's ratio v for Ni_3Al calculated from the elastic constants are listed in Table 2.

3.4. Calculation of the Debye temperature

Having calculated Young's modulus E, the bulk modulus B and the shear modulus G, we can calculate the Debye temperature, which is an important fundamental parameter closely related to many physical properties such as elastic constants, the specific heat and the melting temperature. At low temperatures, the vibrational excitation arises solely from acoustic mode. Hence, at low temperatures, the Debye temperature calculated from the 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

based on the elastic data, since θ_D may be estimated from the average sound velocity v_m by the following equation [19]:

$$\theta_D = \frac{h}{k_B}\left(\frac{3n}{4\pi V_a}\right)^{1/3} v_m$$

where h is Planck's constant, k_B Boltzmann's constant and V_a the atomic volume. The average sound velocity in the polycrystalline material is given by [20]:

$$v_m = \left(\frac{1}{3}\left(\frac{2}{v_l^2}+\frac{1}{v_t^3}\right)\right)^{-1/3}$$

where v_l and v_t are the longitudinal and transverse sound velocities of an isotropic aggregate obtained using the shear modulus G and the bulk modulus B from Navier's equation [18]:

$$v_l = \left(\frac{3B+4G}{3\rho}\right)^{1/2} \quad \text{and} \quad v_t = \left(\frac{G}{\rho}\right)^{1/2}$$

The calculated sound velocity and Debye temperature as well as the density for Ni_3Al are given in Table 4.

Table 4. The calculated density ρ, the longitudinal, transverse and average sound velocity v_l, v_l and v_m calculated from polycrystalline elastic modulus, and the Debye temperatures θ_D calculated from the average sound velocity for Ni_3Al

Parameter	ρ [g cm^{-3}]	v_l [m·s^{-1}]	v_t [m·s^{-1}]	v_m [m·s^{-1}]	Θ_D [K]
Value	6.94882	6712.24	3590.82	4010.63	516.84

4. Conclusion

In this paper, the elastic and mechanical properties of the Ni_3Al intermetallic compound have been studied based on density functional theory (DFT), and the generalised gradient approximation (GGA) method. It has been shown that the equilibrium lattice parameter of the Ni_3Al compound is in excellent agreement with the available experimental data. It has also been shown that the elastic constants of Ni_3Al compound, obtained from the calculations, satisfy the criterion of mechanical stability in a cubic structure under an applied pressure. The computed results for the bulk and shear moduli suggest that the hardness of this material increases upon increasing pressure.

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