



Full length article

Density functional study of elastic, mechanical and thermodynamic properties of MgCu with a CsCl-type structure

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Abstract

We have employed the density functional theory plane-wave pseudo potential method, with local density approximation and generalized gradient approximation to perform first-principles quantum mechanics calculations in order to investigate the structural, elastic and mechanical properties of the intermetallic compound MgCu with a CsCl-type structure. The calculated equilibrium lattice constant is in good agreement with the experimental and theoretical 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 , Poisson's ratio ν , and the ratio B/G for MgCu compound are obtained. Our calculated results for the bulk modulus B , and Young's modulus E are consistent with the experimental and theoretical data. The sound velocities and Debye temperature are also predicted from elastic constants. Finally, the linear response method has been used to calculate the thermodynamic properties. The temperature dependence of the enthalpy H , free energy F , entropy S , and heat capacity at constant volume C_v of MgCu crystal in a quasi-harmonic approximation have been obtained from phonon density of states and discussed for the first report.

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1. Introduction

Magnesium (Mg) alloys are among the lightest structural materials known and are used in a variety of applications, particularly in automotive industry and aerospace manufacturing [1]. In the last years, Mg-based alloys have been extensively studied and novel Mg-based intermetallic compounds have been prepared in Mg–Cu and Mg–Ni

systems. For example, MgCu with a CsCl-type structure, Mg₅₁Cu₂₀ with an Mg₅₁Zn₂₀-type structure, and Mg₄Ni with an FCC structure have been reported [2]. Among them, the MgCu phase with ordered structure is of interest, since the chemical composition of MgCu is the middle of Mg₂Cu and MgCu₂. Intermetallic compounds were of particular interest, both from the point of view of their fundamental properties and their practical applications as materials with excellent chemical, physical and mechanical properties [3].

The Mg–Cu system has been studied, both experimentally as well as theoretically [1,4–7]. In an early experimental study on the Mg–Cu system, H. Takamura et al. have synthesized a novel intermetallic compound of MgCu with a CsCl-type structure [4]. To the best of our knowledge, no ab initio study on MgCu compound has been reported. Thus, we have carried out a theoretical study of the structural, elastic and

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mechanical properties of the novel intermetallic compound of MgCu, in order to provide a sounder basis for further experimental and theoretical investigations. First-principles (ab initio) methods offer one of the most powerful tools carrying out theoretical studies of an important number of physical and chemical properties of materials with great accuracy.

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

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) total energy method implemented with the CASTEP (Cambridge Serial Total Energy Package) code [8]. This is based on the density functional theory (DFT) [9,10] 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 [11,12], as well as the generalized gradient approximation (GGA), in the scheme of Perdew–Burke–Ernzerhof, known as PBE [13], are made for electronic exchange–correlation potential energy. Second, Coulomb potential energy caused by electron–ion interaction is described using the Vanderbilt-type ultrasoft scheme [14], in which the orbitals of Mg ($2P^63s^2$), Cu ($3d^{10}4s^1$), are treated as valence electrons. The cut-off energy for the plane-wave expansion is 400 eV and the Brillouin zone sampling was carried out using the $8 \times 8 \times 8$ set of Monkhorst–Pack mesh [15]. Therefore, the present parameters are sufficient in leading to well converged total energy and geometrical configuration.

The structural parameter a_0 of MgCu was determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [16]. 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 equation of state (EOS), which was fitted to a third order Birch–Murnaghan [17] 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 1.0×10^{-6} eV/atom in the self-consistent calculation.

3. Results and discussion

3.1. Structural properties

The atomic structure of MgCu compound is known to crystallize in a cubic lattice of CsCl-type structure with the space group Pm-3m (221) and the equilibrium lattice parameter has a value of 3.161 Å [4]. The initial unit cell structural model of the MgCu compound is built according to the experimental data [4], as shown in Fig. 1. The results of calculated lattice parameter a_0 of MgCu intermetallic compound using the (PP-PW) method within both the LDA and the GGA approximations are listed in Table 1, along with the available experimental and theoretical data. One can see from Table 1 that the calculated lattice constant a_0 is 2.7% smaller than the experimental value using LDA and it is only 0.06% higher than the experimental value using GGA. Our calculated equilibrium lattice parameter a_0 in GGA approximation is in a good agreement with the experimental and theoretical data. The calculated unit cell volume at values of applied hydrostatic pressure up to 30 GPa were used to construct the equation of state (EOS), which was fitted to a third-order Birch–Murnaghan equation [17] as following:

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

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 MgCu compound for both

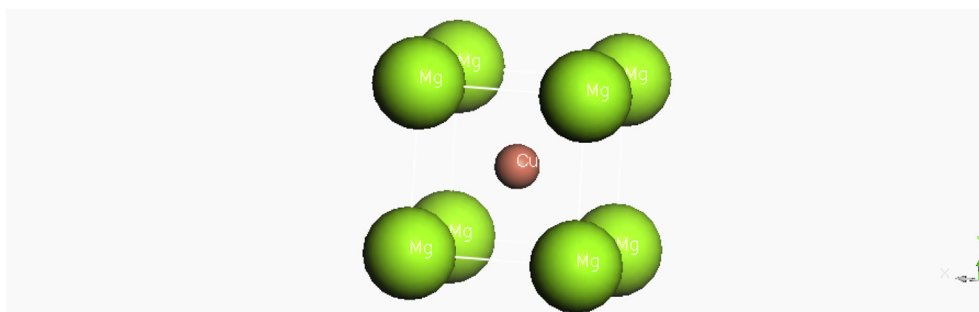


Fig. 1. Crystal structure of MgCu.

Table 1

Calculated, experimental and other values of the equilibrium lattice constant a_0 , bulk modulus B_0 and bulk derivative B_0' in cubic structure of MgCu compound.

		a_0 (Å)	B_0 (GPa)	B_0'
This work:	LDA	3.073	75.25	7.40
	GGA	3.163	69.52	4.13
Exp [4]		3.161	—	—
Cal [4]		3.153	68.7	—

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 1. Our results for the bulk modulus B_0 using LDA and GGA approach are within 8.7% and 1.17% of the theoretical value [4] respectively. The value obtained with GGA is in good agreement with the theoretical result in ref. [4]. There is no experimental data for the comparison.

3.2. Elastic properties

The elastic properties of the material are important if the material is subjected to external forces (pressure, temperature) or to lattice mismatch heteroepitaxy. The elastic properties of solids are of great importance because they relate to various fundamental solid-state phenomena such as equation of state, brittleness, ductility, anisotropy, propagation of elastic waves and normal mode oscillations. The response of material to pressure is governed by an elastic constant. The elastic constants of solids provide a link between the mechanical and dynamic information concerning the nature of the forces operating in solids, especially for the stability and stiffness of materials. The elastic constants were determined from a linear fit of the calculated stress-strain function according to Hook's law [18]. The cubic crystal has three independent elastic constants, C_{11} , C_{12} and C_{44} . The isotropic bulk modulus B is

calculated from the theoretical values of elastic constants by the relation:

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

In Table 2, the calculated elastic constants and the bulk modulus of MgCu compound at zero pressure are presented. For a cubic crystal, the obtained elastic constants meet the requirements of mechanical stability criteria: $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{11} > B > C_{12}$. From Table 2, one can see that the elastic constants of MgCu compound satisfy all of these conditions, suggesting that the structure of MgCu is mechanically stable. To the best of our knowledge, there are no experimental and other theoretical data in literature for the elastic constants (C_{ij}) of MgCu for comparison, so we consider the present results as prediction study which still awaits an experimental confirmation. For the bulk modulus, the calculated values of 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) in LDA and GGA approximations.

Once the elastic constants are obtained, the most important parameters for estimating mechanical properties of compounds such as elastic anisotropy factor (A), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) are determined. They have an important implication in engineering science.

The Zener anisotropy factor A is a measure of the degree of anisotropy in solid [19]. 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 MgCu compound is calculated by the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (3)$$

As shown in Table 2 that the calculated Zener anisotropy factor A is larger than 1, which indicates that this compound is weakly anisotropic. The elastic constants C_{ij} are estimated from first-principles calculations for monocrystal MgCu. 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 approximation [20–22]. For the cubic system, the Reuss and Voigt bounds on the shear modulus are given by:

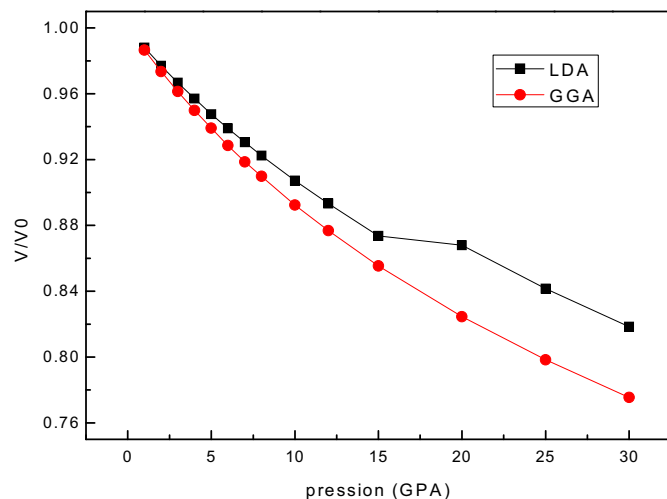


Fig. 2. Pressure dependence of the relative unit cell volume V/V_0 for MgCu compound compared with LDA and GGA.

Table 2

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 of MgCu compound.

	C_{11}	C_{12}	C_{44}	B	A	G	E	ν	B/G
This work:									
LDA	128.14	61.06	85.09	83.42	2.54	58.58	88.72	0.32	1.42
GGA	119.47	44.74	72.26	69.65	1.93	55.46	95.10	0.27	1.26
Exp [5]	—	—	—	—	—	—	96.8	—	—
Other [4]	—	—	—	68.7	—	—	—	—	—

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (4)$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (5)$$

Finally, the VRH mean value is obtained by:

$$G = \frac{1}{2}(G_V + G_R) \quad (6)$$

We also calculated Young's modulus E and Poisson's ratio ν 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 [23]:

$$E = \frac{9BG}{3B + G} \quad (7)$$

$$\nu = \frac{3B - E}{6B} \quad (8)$$

The shear modulus G , Young's modulus E and Poisson's ratio ν for MgCu compound, calculated from the elastic constants are listed in Table 2. Using GGA approximation, our calculated Young's modulus E is 1.7% smaller than the one measured from the experiment for MgCu thin film [5]. Our value for the parameter E is well consistent with the experimental value [5]. We are not aware of any experimental measurement or theoretical result for the shear modulus and Poisson's ratio of MgCu intermetallic compound to testify our results, so we consider the present results as a prediction study.

The ratio B/G is a simple relationship related to brittle or ductile behaviour of materials; it has been proposed by Pugh [24]. 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 2. The results of both approximations LDA and GGA indicate that MgCu compound can be classified as brittle material at zero pressure.

3.3. Thermodynamic properties

It is important to determine precisely the Debye temperature Θ_D , which is connected directly with thermal vibration of atoms. The Debye temperature corresponds in the Debye theory to a maximum phonon frequency. In addition, it reflects the structural stability, the strength of bonds and it is 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 [25]:

$$\Theta_D = \frac{h}{k_B} \left(\frac{3n}{4\pi V_a} \right)^{1/3} v_m \quad (9)$$

where h is Plank's constant, k_B Boltzmann's constant and V_a the atomic volume. The average sound velocity in the polycrystalline material is given by Ref. [26]:

$$v_m = \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-1/3} \quad (10)$$

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 [23]:

$$v_l = \left(\frac{3B + 4G}{3\rho} \right)^{1/2} \quad (11)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (12)$$

The calculated Debye temperature and sound velocities as well as the density for MgCu intermetallic compound in both approximations LDA and GGA are given in Table 3. 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 for the first time, which still awaits an experimental confirmation.

In order to evaluate the temperature dependence of the enthalpy H , free energy F , entropy S , and heat capacity at constant volume C_v of a crystal in a quasi-harmonic approximation, we need to calculate the phonon density of states (PDOS), which can be obtained by performing phonon calculations. In this work, the phonon contribution to the free energy F , the phonon contribution to the enthalpy H , the entropy S , and the specific heat C_v at temperature are shown in Fig. 3. The calculated value of zero point energy at 0 GPa is 0.0598 eV. From Fig. 3(a), we can see that the free energy decreases gradually with increasing temperature. In Fig. 3(b) and (c), as temperature increases, the calculated enthalpy H , and entropy S increase continually. At ambient temperature, the heat capacity C_v is 11.21 Cal/Cell.K and it tend to the asymptotic limit (so called the Dulong-Petit limit) of $C_v = 11.85$ Cal/Cell.K = $3nNk_B$ at higher temperatures, as is shown in Fig. 3(d). The experimental thermodynamic data cannot be found, therefore it is difficult to evaluate the magnitude of errors between theory and experiment. Our calculated results can be seen as a prediction study for future investigations.

Table 3

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 MgCu compound.

	ρ (g cm ⁻³)	v_l (ms ⁻¹)	v_t (ms ⁻¹)	v_m (ms ⁻¹)	Θ_D (K)
This work					
LDA	5.0286	5667.59	3413.18	3774.44	461
GGA	4.6081	5582.26	3469.17	3823.36	454

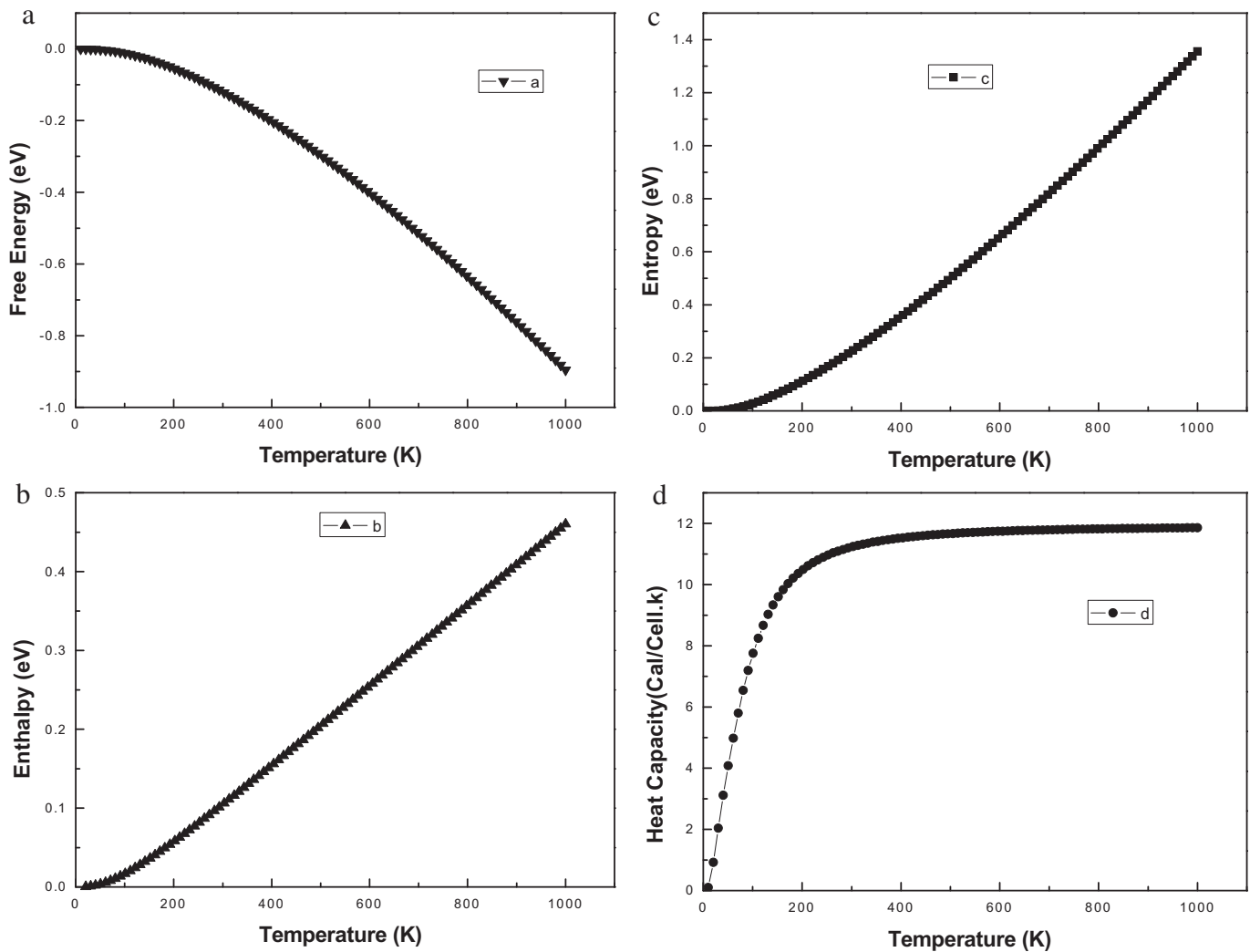


Fig. 3. (a) Temperature dependence of the free energy for MgCu. (b) Temperature dependence of the enthalpy for MgCu. (c) Temperature dependence of the entropy for MgCu. (d) Temperature dependence of the heat capacity at constant volume for MgCu.

4. Conclusions

In summary, the structural, elastic, mechanical, and thermodynamic properties of MgCu intermetallic compound with a CsCl-type structure have been investigated for the first time by means of the DFT within LDA and GGA approximations. The optimized lattice parameter a_0 is in good agreement with the available experimental and theoretical data. The elastic constants C_{ij} , the bulk modulus B , the shear modulus G , and the Young's modulus E are calculated. It is found that our calculated bulk and Young's moduli are in perfect consistent with the experimental and theoretical data. The Zener factor A , and the B/G ratio are also estimated. The Zener factor suggests that MgCu compound exhibits anisotropic elasticity. The ratio B/G shows a brittle manner for the MgCu compound. Finally, from the knowledge of the elastic constants and the sound velocities, and through the quasi-harmonic Debye model using the calculated PDOS the thermodynamic properties have been predicted successfully.

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References

- [1] R.H. Tabor, S. Curtarolo, G. L.W. Hart, Phys. Rev. B 84 (2011) 084101.
- [2] H. Watanabe, Y. Goto, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 45 (2004) 1350–1353.
- [3] J.H. Westbrook, R.L. Fleischer, Intermetallic Compounds-principles and Practices, Wiley, New York, 1995.
- [4] H. Takamura, H. Kakuta, Y. Goto, H. Watanabe, A. Kamegawa, M. Okada, J. Alloys Compd. 404–406 (2005) 372–376.
- [5] H.S. Chou, J.C. Huang, Y.H. Lai, L.W. Chang, X.H. Du, J.P. Chu, T.G. Nieh, J. Alloys Compd. 483 (2009) 341–345.
- [6] Z. Ma, Y. Liu, L. Yu, Q. Cai, Nanoscale Res. Lett. 7 (2012) 390.
- [7] M. Mezbahul-Islam, D. Kevorkov, M. Meradj, J. Chem. Thermodynamics 40 (2008) 1064–1076.
- [8] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys. Condens. Matter 14 (2002) 2717.
- [9] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.

- [10] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 113.
- [11] D.M. Ceperley, B.J. Alder, *Phys. Rev. Lett.* 45 (1980) 566.
- [12] J.P. Perdew, A. Zunger, *Phys. Rev. B* 23 (1981) 5048.
- [13] J.P. Perdew, K. Burke, M. Ernzerhoff, *Phys. Rev. Lett.* 77 (1996) 3865.
- [14] D. Vanderbilt, *Phys. Rev. B* 41 (1990) 7892.
- [15] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B* 13 (1976) 5188.
- [16] T.H. Fischer, J. Almlof, *J. Phys. Chem.* 96 (1992) 9768.
- [17] F. Birch, *J. Geophys. Res.* 83 (1978) 1257.
- [18] J.F. Nye, *Propriétés Physiques des Matériaux*, Dunod, Paris, 1961.
- [19] C. Zener, *Elasticity and Anelasticity of Metals*, University of Chicago Press, Chicago, 1948.
- [20] W. Voigt, *Lehrbuch de Kristallphysik* (Teubner) (1928). Leipzig.
- [21] A. Reuss, *Z. Angew. Math. Mech.* 9 (1929) 49.
- [22] R. Hill, *Proc. Phys. Soc. London, Sect. A* 65 (1952) 349.
- [23] E. Schreiber, O.L. Anderson, N. Soga, *Elastic Constants and Their Measurements*, McGraw-Hill, New York, 1973.
- [24] S.F. Pugh, *Philos. Mag.* 45 (1954) 823.
- [25] P. Wachter, M. Filzmoser, J. Rebisant, *J. Phys. B* 293 (2001) 199.
- [26] O.L. Anderson, *J. Phys. Chem. Solids* 24 (1963) 909.