Review

# Elastic and mechanical properties of Mg₃Rh intermetallic compound: An ab initio study

S. Boucetta [a],*, G. Uğur [b]

[a] Laboratoire d'Elaboration de Nouveaux Matériaux et Caractérisations (ENMC), Département de Physique, Université Ferhat Abbas SETIF 1, Sétif 19000, Algeria
[b] Faculty of Science, Department of Physics, Teknikokullar, Gazi University, Ankara 06500, Turkey

## Abstract

In this work, density functional theory plane-wave pseudo potential method, with local density approximation (LDA) and generalized gradient approximation (GGA) are used to investigate the structural, elastic, mechanical and thermodynamic properties of the intermetallic compound Mg₃Rh. Comparison of the calculated equilibrium lattice constants and experimental data shows very good agreement. 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 $B$, shear modulus $G$, Young's modulus $E$, Poisson's ratio $\sigma$, anisotropy factor $A$, the ratio $B/G$ and the hardness parameter $H$ for Mg₃Rh compound are obtained. Our calculated elastic constants indicate that the ground state structure of Mg₃Rh is mechanically stable. The calculation results show that this intermetallic crystal is stiff, elastically anisotropic and ductile material. The sound velocities and Debye temperature are also predicted from elastic constants. This is the first quantitative theoretical prediction of these properties.
© 2016 Production and hosting by Elsevier B.V. on behalf of Chongqing University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Mg₃Rh; Elastic properties; Mechanical properties; Ab initio

## 1. Introduction

Research on Mg based alloys is of particular interest due to its low density (~1.74 g/cm³) and high specific strength and stiffness than many other engineering materials, including aluminium, steel and polymer-based composites. Magnesium also possesses many other attractive properties, such as a high damping capacity, electromagnetic shielding, thermal conductivity, good machinability and high recycling potential [1]. Magnesium alloys are among the lightest structural materials known and are used in a variety of applications, particularly in automobile industry and aerospace manufacturing [2]. The above-mentioned features have motivated us to study these alloys.

Magnesium forms a wide range of ordered intermetallic compounds with the transition metals (TM). The binary transition metal magnesium compound Mg₃Rh has been synthesized from the elements in sealed niobium tubes and investigated on the basis of X-ray powder diffraction, and it crystallizes in Cu₃P type structure [3].

To date, no studies have been reported on this compound in literature; in other words, to the best of our knowledge, the intermetallic compound Mg₃Rh has been studied neither experimentally nor theoretically. Thus, in this work we have carried out a systematic theoretical investigation on the structural, elastic and mechanical properties of Mg₃Rh alloy, in order to provide a sounder basis and data for further experimental and theoretical studies. The results of this work are compared with available experimental and theoretical values, which can provide a theoretical guidance to design a new kind of magnesium alloy. The rest of this paper is organized as follows: the computational method is described in Section 2, the numerical results and discussions are given in Section 3 and finally a conclusion is presented in Section 4.

## 2. Computational method

Our first-principles quantum mechanics calculations are performed with the plane-wave pseudo-potential (PW–PP) total energy method implemented with the CASTEP (Cambridge

* Corresponding author. Laboratoire d'Elaboration de Nouveaux Matériaux et Caractérisations (ENMC), Département de Physique, Université Ferhat Abbas SETIF 1, Sétif 19000, Algeria. Tel.: +213 36 87 35 51.
E-mail address: sd.boucetta@gmail.com (S. Boucetta).

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. We have used two approximations. First, the local density approximation (LDA) developed by Ceperley and Adler and parameterized by Perdew and Zunger [7,8], as well as the generalized gradient approximation (GGA), with the functional of Wu and Cohen, known as WC [9], 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 [10], in which the orbitals of Mg ($2p^6 3s^2$) and Rh ($4d^8 5s^1$) are treated as valence electrons. The cut-off energy for the plane-wave expansion was chosen at 340 eV and the Brillouin zone sampling was carried out using the $4 \times 4 \times 4$ set of Monkhorst–Pack mesh [11].

The structural parameter ($a$) of $Mg_3Rh$ was determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [12]. This method usually provides the fast way of finding the lowest energy structure.

In the structural optimization process, the energy change, maximum force, maximum stress and maximum displacement are set as $1.0 \times 10^{-5}$ 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 according to Hook's law [13]. The total energy is converged to $1.0 \times 10^{-6}$ eV/atom in the self-consistent calculation.

## 3. Results and discussion

### 3.1. Structural properties

The binary transition metal magnesium compound $Mg_3Rh$ crystallizes in a structure-type $Cu_3P$ with the space group $P6_3cm$ and the equilibrium lattice parameters have the values of ($a = 7.905$ Å, and $c = 8.256$ Å) [3]. The unit cell structural model of the $Mg_3Rh$ compound is built according to the experimental data [3], as shown in Fig. 1. The crystal structure was optimized at first. The obtained results of calculated lattice
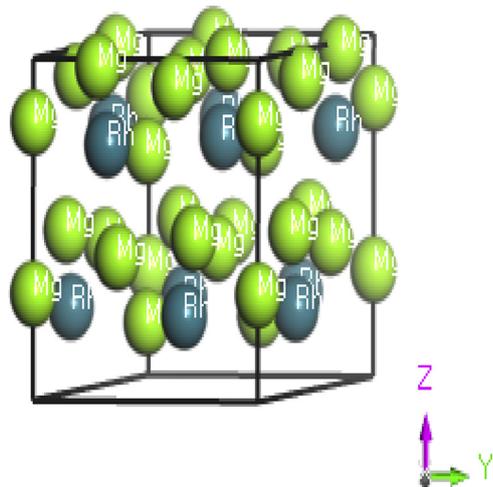


Fig. 1. Crystal structure of $Mg_3Rh$.

Table 1
Equilibrium lattice parameters and unit cell volume of the $Mg_3Rh$ compound.

| Source | | $a$ (Å) | $c$ (Å) | $c/a$ | $V$ (Å$^3$) |
|---|---|---|---|---|---|
| This work: | LDA | 7.771 | 8.129 | 1.046 | 425.12 |
| | GGA-WC | 7.913 | 8.264 | 1.044 | 448.11 |
| Exp [3]. | | 7.905 | 8.256 | 1.044 | 446.80 |
| Cal. | | – | – | – | – |

parameters of $Mg_3Rh$ intermetallic compound using the (PW–PP) method within both the LDA and the GGA-WC approximations for ground states are listed in Table 1, together with the available experimental and theoretical data for comparison. One can see from the present results in Table 1 that the computed lattice constants $a$ and $c$ are, respectively, 1.7% and 1.5% smaller than the experimental values using LDA. They are only 0.01% higher than the experimental values using GGA-WC. Our calculated equilibrium lattice parameters agree very well with the reported experimental data, mostly the equilibrium lattice constants calculated with GGA-WC functional are close to the previous experimental data. The optimized cell volume shows increase of 0.3% as compared to experimental value. Thus, the first-principles calculation in this work is sufficiently reliable to reproduce the equilibrium crystal structure of $Mg_3Rh$ intermetallic compound.

### 3.2. Elastic and mechanical properties

Elastic constants are very important material parameters. The elastic constants can provide information on the stability, stiffness, brittleness, ductility, and anisotropy of a material. The elastic constants give also important information concerning the nature of the forces operating in solids. Moreover, knowledge of the values of elastic constants is crucial for a sound understanding of the mechanical properties of the relevant material [14].

The full elastic stiffness constants are evaluated to use the stress–strain method, in which the relationship between stress and strain is expressed by the Hook's law, $\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$, where $\sigma_{ij}$ is the stress tensor, $\varepsilon_{kl}$ is the strain tensor and $C_{ijkl}$ is the elastic constants tensor.

The elasticity of a hexagonal crystal is specified by six different elastic coefficients ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$), but only five of them are independent since $C_{66} = (C_{11}-C_{12})/2$. In this work, the elastic constants calculated for $Mg_3Rh$ compound at zero pressure and temperature are presented in Table 2. For a hexagonal crystal, the obtained elastic constants meet the requirements of mechanical stability criteria [15]:

$$C_{11} > 0, \quad C_{44} > 0, \quad C_{11} - C_{12} > 0, \quad (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \tag{1}$$

Table 2
Elastic constants $C_{ij}$ (inGPa) of the $Mg_3Rh$ compound.

| Source | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ |
|---|---|---|---|---|---|---|
| *This work:* | | | | | | |
| *LDA* | 106.34 | 66.08 | 52.20 | 106.53 | 25.64 | 20.13 |
| *GGA-WC* | 110.58 | 65.76 | 47.18 | 90.89 | 23.11 | 22.41 |
| *Experiment* | – | – | – | – | – | – |

From Table 2, one can verify that the elastic constants of Mg$_3$Rh compound satisfy all of these conditions, suggesting that the structure of Mg$_3$Rh is mechanically stable. The present calculated results of elastic constants show high values of $C_{11}$ and $C_{33}$ suggesting a large tensile modulus along [100] and [001] directions. To the best of our knowledge, there are no experimental and other theoretical data in literature for the elastic constants ($C_{ij}$) of Mg$_3$Rh for comparison; therefore, it is difficult to evaluate the magnitude of errors between theory and experiment. Our calculated results can be considered as a reference for further study.

The most important parameters for estimating mechanical properties of materials such as bulk modulus ($B$), shear modulus ($G$), Young's modulus ($E$) and Poisson's ratio ($\sigma$) are obtained from results of the calculated single-crystal elastic constants $C_{ij}$ using the Voigt–Reuss–Hill (VRH) averaging scheme [16]. The Voigt–Reuss–Hill approximation gives the effective values of the bulk and shear moduli. For the hexagonal system, the Voigt bounds [17] of the bulk modulus $B_V$ and shear modulus $G_V$ are:

$$B_V = \frac{2}{9}\left(C_{11} + C_{12} + \frac{C_{33}}{2} + 2C_{13}\right) \quad (2)$$

and

$$G_V = \frac{1}{30}\left(7C_{11} - 5C_{12} + 12C_{44} + 2C_{33} - 4C_{13}\right) \quad (3)$$

The Reuss bounds [18] of the bulk and shear moduli are:

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} \quad (4)$$

and

$$G_R = \frac{5}{2}\left\{\frac{\left[(C_{11} + C_{12})C_{33} - 2C_{13}^2\right]C_{44}C_{66}}{3B_V C_{44}C_{66} + \left[(C_{11} + C_{12})C_{33} - 2C_{13}^2\right](C_{44} + C_{66})}\right\} \quad (5)$$

Finally, the bulk modulus $B$ and shear modulus $G$, based on Hill approximation, are arithmetic average of Voigt and Reuss elastic moduli. They are expressed as following:

$$B = \frac{1}{2}(B_V + B_R) \quad (6)$$

and

$$G = \frac{1}{2}(G_V + G_R) \quad (7)$$

Young's modulus ($E$) and Poisson's ratio ($\sigma$) can be calculated by using Hill's elastic moduli ($B$) and ($G$), which are given as:

$$E = \frac{9BG}{3B + G} \quad (8)$$

$$\sigma = \frac{3B - 2G}{2(3B + G)} \quad (9)$$

The calculated results for these moduli and Poisson's ratio for the Mg$_3$Rh compound are presented in Table 3. The bulk modulus is usually assumed to be a measure of resistance to volume change by applied pressure. The larger the value of bulk modulus of compound, the stronger resistance to volume change by an applied pressure. The two constants $E$ and $G$ are all that are needed to fully characterize the stiffness of an isotropic material. The present calculated results of these moduli demonstrate that the Mg$_3$Rh compound is stiff. The Poisson's ratio ($\sigma$) defined as the ratio of transverse strain to the longitudinal strain is used to reflect the stability of the material against shear and provides information about the nature of the bonding forces. It takes the value: $-1 < \sigma < \frac{1}{2}$. No real material is known to have a negative value of $\sigma$. So this inequality can be replaced with $0 < \sigma < \frac{1}{2}$. The low value of Poisson's ratio indicates a large compression of volume and when $\sigma = 0.5$ no volume change occurs. The bigger the Poisson's ratios, the better the plasticity. The present calculated result of the Poisson's ratio shows that the Mg$_3$Rh intermetallic compound is of good plasticity. The $\sigma = 0.25$ and $\sigma = 0.5$ are the lower limit and upper limit for central forces in solids, respectively. The obtained value of Poisson's ratio ($\sigma$) of Mg$_3$Rh is larger than the lower limit value ($\sigma = 0.25$), which indicates that the interatomic forces of Mg$_3$Rh are central forces.

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 Mg$_3$Rh compound is calculated by the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (10)$$

As shown in Table 3, the calculated Zener anisotropy factor $A$ is larger than 1 for both approximations LDA and GGA-WC, which indicates that the Mg$_3$Rh compound is anisotropic material.

The ratio $B/G$ is a simple relationship related to brittle or ductile behaviour of materials. It has been proposed by Pugh [20]. 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 3. In this work, the obtained results of the ratio $B/G$ in both approximations LDA and GGA-WC indicate that Mg$_3$Rh compound can be classified as ductile material

Table 3
Bulk modulus ($B$), shear modulus ($G$), Young's modulus ($E$), Poisson's ratio ($\sigma$), Zener factor ($A$), ratio of bulk modulus to shear modulus ($B/G$) and hardness parameter ($H$) of the Mg$_3$Rh compound.

| Source | B(GPa) | G(GPa) | E(GPa) | $\sigma$ | A | B/G | H(GPa) |
|---|---|---|---|---|---|---|---|
| This work: | | | | | | | |
| LDA | 73.23 | 23.92 | 64.71 | 0.353 | 1.27 | 3.06 | 2.34 |
| GGA-WC | 69.29 | 23.71 | 63.85 | 0.346 | 1.03 | 2.92 | 2.44 |
| Experiment | – | – | – | – | – | – | – |

at zero pressure and zero temperature. Another parameter indicating the brittleness or ductility of the material is the Cauchy relation defined as: $C_P = C_{12} - C_{44}$. The material is expected to be ductile, if the value of this expression is positive; on the other hand, if its value is negative, the material is brittle [21]. At zero pressure, we found 40.44 GPa and 42.65 GPa for Cauchy pressure within both the LDA and the GGA-WC approximations respectively. From these values and according to above criterion, the studied compound is ductile. Thus, the ductile nature of Mg$_3$Rh compound can be related to a metallic character in its bonds.

Furthermore, hardness is also one fundamental physical parameter when considering the mechanical properties of polycrystalline Mg$_3$Rh intermetallic. The hardness parameter ($H$) denoting the resistance of the physical object against compression of the contacting parts is applied [22], so here we calculate the hardness of Mg$_3$Rh by using the approach as expressed below:

$$H = \frac{(1-2\sigma)E}{6(1+\sigma)} \tag{11}$$

The hardness associated to this polycrystalline intermetallic crystal in both approximations LDA and GGA-WC are listed in Table 3. One can see in Table 3, the Mg$_3$Rh compound has a low hardness. It turns out that the Mg$_3$Rh compound is a low stiff material. The low hardness of this crystal can be attributed to the low density of crystal structure.

### 3.3. Thermodynamic properties

The Debye temperature ($\Theta_D$) of a material is a suitable parameter to describe phenomena of solid-state physics which are associated with lattice vibrations. The Debye temperature corresponds in the Debye theory to a maximum phonon frequency. In addition, it reflects the structural stability and 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 ($\Theta_D$) is from elastic data, since $\Theta_D$ may be estimated from the average sound velocity $v_m$ by the following equation [23]

$$\Theta_D = \frac{h}{k_B} \left( \frac{3n}{4\pi V_a} \right)^{\frac{1}{3}} v_m \tag{12}$$

where h is Plank's constant, $k_B$ Boltzmann's constant, n is the number of atoms per formula unit and $V_a$ the atomic volume. The average sound velocity in the polycrystalline material is given by the following equation [24]

$$v_m = \left[ \frac{1}{3} \left( \frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-\frac{1}{3}} \tag{13}$$

where $v_l$ and $v_t$ are the longitudinal and transverse sound velocities of an isotropic aggregate, obtained using the shear

Table 4
Density ($\rho$), longitudinal, transverse and average sound velocities ($v_l$, $v_t$ and $v_m$), and the Debye temperature ($\Theta_D$) of the Mg$_3$Rh compound.

|  | $\rho$ (g cm$^{-3}$) | $v_l$ (ms$^{-1}$) | $v_t$ (ms$^{-1}$) | $v_m$ (ms$^{-1}$) | $\Theta_D$ (K) |
|---|---|---|---|---|---|
| This work: |  |  |  |  |  |
| LDA | 4.12 | 5051.27 | 2409.53 | 2710.06 | 310.16 |
| GGA-WC | 3.91 | 5080.01 | 2462.51 | 2767.30 | 311.24 |
| Exp. | 3.92 | – | – | – | – |

modulus $G$ and the bulk modulus $B$ from Navier's equation [25]:

$$v_l = \left( \frac{3B + 4G}{3\rho} \right)^{1/2} \tag{14}$$

and

$$v_t = \left( \frac{G}{\rho} \right)^{1/2} \tag{15}$$

The calculated Debye temperature ($\Theta_D$) and sound velocities ($v_m, v_l, v_t$) as well as the density ($\rho$) for Mg$_3$Rh compound in both approximations LDA and GGA-WC are listed in Table 4. 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.

### 4. Conclusions

In this ab initio study, the structural, elastic, mechanical, and thermodynamic properties of Mg$_3$Rh intermetallic compound have been investigated by means of the DFT within LDA and GGA-WC functional. Our results for the optimized lattice parameters ($a$) and ($c$) are in good agreement with the available experimental data. The elastic constants $C_{ij}$, and related polycrystalline mechanical parameters such as bulk modulus $B$, shear modulus $G$, Young's modulus $E$ and Poisson coefficient $\sigma$ are calculated using Voigt–Reuss–Hill approximations. The Mg$_3$Rh compound is mechanically stable according to the elastic stability criteria, while no experimental results of elastic moduli for comparison. The calculated Zener factor indicates that Mg$_3$Rh compound is elastically anisotropic. The values of the ratio $B/G$ and Cauchy pressure ($C_{12}-C_{44}$) show a ductile manner for the Mg$_3$Rh compound. The polycrystalline intermetallic Mg$_3$Rh turns out to be a low stiff material according to the calculated hardness parameter ($H$). Finally, from the knowledge of the elastic constants and the average sound velocities, the Debye temperature has been predicted successfully.

### Acknowledgements

### References

[1] C.X. Shi, J. Magnes. Alloys 1 (2013) 1.

[2] K.U. Kainer, Magnesium-Alloys and Technology, Wiley-VCH, Weinheim, 2003.

[3] V. Hlukhyy, U.C. Rodewald, R.-D. Hoffmann, R. Pottgen, Z. Naturforsch. 59b (2004) 251.

[4] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, et al., J. Phys. Condens. Matter 14 (2002) 2717.

[5] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.

[6] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 113.

[7] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.

[8] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.

[9] Z. Wu, R.E. Cohen, Phys. Rev. B 73 (2006) 235116.

[10] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.

[11] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.

[12] T.H. Fischer, J. Almlof, J. Phys. Chem. 96 (1992) 9768.

[13] J.F. Nye, Propriétés Physiques des Matériaux, Dunod, Paris, 1961.

[14] K. Tanaka, M. Koiwa, Intermetallics (Barking) 4 (1996) S29–S39.

[15] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, Phys. Rev. B 76 (2007) 054115.

[16] R. Hill, Proc. Phys. Soc., London, Sect. A 65 (1952) 349.

[17] W. Voigt, Lehrbuch de Kristallphysik, Terubner, Leipzig, 1928.

[18] A. Reuss, Z. Angew. Math. Mech. 9 (1929) 49.

[19] C. Zener, Elasticity and Anelasticity of Metals, University of Chicago Press, Chicago, 1948.

[20] S.F. Pugh, Philos. Mag. 45 (1954) 823.

[21] D.G. Pettifor, Mater. Sci. Technol. 8 (1992) 345.

[22] H.C. Cheng, C.F. Yu, W.H. Chen, J. Alloys Compd. 546 (2013) 286–295.

[23] P. Wachter, M. Filzmoser, J. Rebisant, Physica B Condens. Matter 293 (2001) 199.

[24] O.L. Anderson, J. Phys. Chem. Solids 24 (1963) 909.

[25] E. Schreiber, O.L. Anderson, N. Soga, Elastic Constants and Their Measurements, McGraw-Hill, New York, 1973.