Revue des Energies Renouvelables Vol. 18 N°3 (2015) 503 – 512
DOI: https://doi.org/10.54966/jreen.v18i3.525

Hydrogen storage: Investigation of the elastic properties of Mg_7NbH_{16} hydride

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(reçu le 22 Juillet 2014 – accepté le 31 Septembre 2015)

Abstract - *Structural, mechanical and electronic structure properties of Mg_7NbH_{16} were investigated using the norm-conserving pseudo-potentials and plane waves (PP-PW) within the general gradient approximation (GGA) in the frame of density functional theory (DFT). The computed equilibrium lattice constants are in excellent agreement with the available experimental and theoretical data. The elastic constants C_{ij} of Mg_7NbH_{16} were calculated for the first time. The Mg_7NbH_{16} compound is found to be mechanically stable. The bulk modulus of single crystals has been derived using elastic constants. The results are discussed and compared with the calculated bulk modulus reported in the literature. The polycrystalline elastic moduli (namely: the shear modulus, Young's modulus, Poisson's ratio, Lamé's coefficients, sound velocities and the Debye temperature) were derived from the obtained single-crystal elastic constants. According to the obtained results, Mg_7NbH_{16} can be classified as ductile material. The shear anisotropic factors and the elastic anisotropy are also discussed. A Debye temperature of 619 K was also determined using theoretical elastic constants.*

Résumé - *Dans ce travail, nous avons étudiés les propriétés structurelles, mécaniques et électroniques de Mg_7NbH_{16}, en utilisant la méthode des pseudo-potentiels combinée aux ondes planes (PP-PW) dans le cadre de la théorie de la densité fonctionnelle (DFT). Les paramètres de maille calculés sont en excellent accord avec les données expérimentales et théoriques disponibles. Les constantes élastiques C_{ij} de Mg_7NbH_{16} ont été calculées pour la première fois. Le composé Mg_7NbH_{16} est mécaniquement stable. Le module de compression a été obtenu en utilisant les constantes élastiques. Les résultats sont discutés et comparés avec le module de compression rapporté dans la littérature. Les modules élastiques polycristallins (le module de cisaillement, le module de Young, le coefficient de Poisson, les coefficients de Lamé, les vitesses du son et de la température de Debye) ont été dérivés à partir des constantes élastiques monocristallines obtenues. Nos résultats montrent que le Mg_7NbH_{16} peut être classé comme matériau ductile. Les facteurs d'anisotropie de cisaillement et l'anisotropie élastique ont été calculés. Enfin, nous avons déterminé la température de Debye de Mg_7NbH_{16} (619 K) à l'aide des constantes élastiques théoriques.*

Keywords: Magnesium alloys - Mechanical properties - Density functional theory - Hydrogen storage.

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1. INTRODUCTION

The main problem in extending the application of hydrogen (H_2) as a clean source of energy, resides in the choice of the storability and portability. Hydrogen is often stored in gaseous or liquid forms [1]. However, the storage of H_2 in the form of metallic hydrides is the safest method and presents numerous advantages, e.g. (i) relatively large H_2 storage capacity, compared with the gaseous and liquid forms (ii) good reversibility of hydrogenation/dehydrogenation with many metallic hydrides [2], etc.

The choice of the hydrides is based on their storage capacities, their good reversibility and their large reactivity [1]. Magnesium hydride, MgH_2, satisfies some of the above requirements. It has high storage capacity (up to 7.6 wt %), good cyclability, lightweight and it is relatively inexpensive. But, there are many problems limiting the direct use of MgH_2, including: high desorption temperature [3], slow reaction kinetics of H_2 sorption/desorption [4], high oxidability in air [5] and high thermodynamic stability.

It is well known that the addition of a small amount of transition metals such as Ti, V, Mn, Fe, Ni, Cu, Nb and Pd [5-10] can improve drastically the kinetic parameters of H_2 diffusion in MgH_2 as well as decreases the temperature of H_2 desorption.

Indeed, several research works reported in the literature were devoted to study Mg-Nb-H system with a small amount of Niobium [9-17]. Okada *et al.* [12] have investigated Mg–Nb–H system under a pressure of 5 GPa by using a cubic-anvil-type apparatus. The authors determined the hydrogen content from the fusion extraction analysis and found to be 5.8 mass%, corresponding to $Mg_{6.2}NbH_{14}$. This later showed the lowest dehydrogenation temperature of 595 K with an endothermic reaction.

Experimentally, an FCC type hydride Mg_7NbH_{16} [13, 14] have been successfully synthesized by reacting MgH_2 and Nb in a high-pressure anvil cell at 8 GPa and 600 K and the structure was characterized with high-energy synchrotron X-ray powder diffraction. The authors found that Mg_7NbH_{16} has a structure identical to that of Mg_7TiH_{16} [8], i.e. Ca_7Ge-type. Moser *et al.* [15] found from powder X-ray diffraction using synchrotron radiation, that the hydrogen atoms are located in the two possible tetrahedral sites, one coordinates three Mg atoms and one Nb atom whereas another coordinates four Mg atoms.

Shelyapina *et al.* [16] have carried out, within the framework of the full-potential and linearized augmented plane-wave method, the electronic structure of Mg_7NbH_{16}. The authors have discussed the bonding of this material, using the calculated electronic structure, heat of formation and relative stability.

Xiao *et al.* [17] have performed first-principles calculations on the face-centered cubic (FCC) Mg_7NbH_{16}. The authors have analyzed the stability of Mg_7NbH_{16} using the cohesive energies and electronic densities of state as well as calculated the enthalpies of formation for Mg_7NbH_{16} which was used to investigate the possible path ways for the formation reaction. However, a huge value of bulk modulus was found, i.e. $B = 488.8\ \text{GPa}$, which is comparable to that of diamond.

Nonetheless, no information about mechanical properties of Mg_7NbH_{16} is available, except the bulk modulus for this material is studied theoretically [17].

The knowledge of the elastic constants of complex hydrides compounds is necessary for many practical applications related to the mechanical properties of a solid, and closely related to many fundamental solid-state properties [18, 19], such as equation of state, specific heat, thermal expansion, Debye temperature, melting point, etc.

In this study, bulk modulus and the elastic constants of Mg_7NbH_{16} were calculated for the first time using the density functional theory (DFT) with general gradient approximation (GGA) functional. Moreover, shear and Young's moduli, Poisson ratio, Lamé's coefficients, sound velocities and the Debye temperature were also calculated. So far and up to the knowledge of the authors, no experimental values or previous theoretical calculations for the elastic constants of Mg_7NbH_{16} compound have been reported in the literature. Thus the results presented in this work are novel and represent the first theoretical prediction for the above quantities.

2. CALCULATION DETAILS

In this study, all the computations have been carried out using ABINIT code [20] that is based on pseudo potentials and plane waves within density functional theory (DFT) [21]. It relies on an efficient fast Fourier transform algorithm [22] for the conversion of wave functions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate-gradient method [23] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [24]. Generalized gradient approximation (GGA-PBE) to DFT [25], were performed. Fritz–Haber–Institute GGA pseudo potentials [26] are used to represent atomic cores.

The convergence of the calculations with respect to the plane wave cut-off and k-point mesh, were carefully tested. An energy cut-off of 50 Hartree and a 6 × 6 × 6 grid for k-point were used. The self consistency has been achieved with a tolerance in the total energy of 0.01 meV.

All structural degrees of freedom including unit-cell parameters and shape as well as atomic positions were relaxed. The relaxations of cell geometry and atomic positions were carried out using a conjugate gradient algorithm until the Hellman–Feynman forces on all atoms, were less than 0.05 meV/Å.

The elastic constants tensor was subsequently obtained using the linear-response method, implemented in the ABINIT code. The linear response is used to calculate the second derivative of the total energy with respect to the strains.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

The high pressure phase of Mg_7NbH_{16} crystallizes within a face-centered cubic structure analogous to the Ca_7Ge type (space group $Fm3m$, no. 225), with a unit cell containing 96 atoms [13, 15]. Moreover, in this structure there are three possible metallic sites: $4a$, $4b$ and $24d$.

Nb atoms occupy $4a$ (0, 0, 0) sites, Mg atoms occupy $4b$ (0.5, 0.5, 0.5) and $24d$ (0.25, 0.25, 0.25) sites, H_2 atoms are located in two different tetrahedral sites $32f$ between the close packed layers of Mg and Nb atoms (where $4a$, $4b$ and $24d$ are the Wyckoff symbols given in **Table 1**).

The H_2 atoms are at interstitial sites but slightly displaced from the center of the corresponding tetrahedrons. Indeed, the ideal positions of H_2 atoms would be $x = 1/8$ and $x = 1/3$ both in $32f$ site but the coordinates are distorted from these positions as can be seen in **Table 1** [13, 15]. The tetrahedral environment of one H1-atom consists of one Nb-atom and three Mg ($24d$)-atoms.

The tetrahedral environment of H_2 consists of one Mg($4b$)-atom and tree Mg($24d$)-atoms. The atomic positions were relaxed; which results in lowering the total energy. The final structure obtained within PBE GGA approximations is given in **Table 1**.

Table 1: Optimized crystal structure of Mg_7NbH_{16}, compared to the experimental structure [13, 15] and to the calculated [16, 17]

Perovskite	Cell parameters (A°)		Atomic position		
	Exp	Cal-GGA		Exp.	Theory: GGA
Mg_7NbH_{16}	a=9.548[a] a=9.566[b]	a=9.5376 a=9.322[c] a=9.396[d]	Mg(4b)	(0.5, 0.5, 0.5)[a,b]	(0.5, 0.5, 0.5)
			Mg(24d)	(0, 0.25, 0.25)[a,b]	(0, 0.25, 0.25)
			Nb(4a)	(0, 0, 0)[a,b]	(0, 0, 0)
			H_1(32f)	(0.127,0.127,0.127)[a] (0.130,0.130,0.130)[b]	(0.120,0.120,0.120) (0.119,0.119,0.119)[c]
			H_2(32f)	(0.360,0.360,0.360)[a] (0.368,0.368,0.368)[b]	(0.372,0.372,0.372) (0.371,0.371,0.371)[c]

a - [13], b - [15], c - [16], d - [17]

The relaxed structure in this study is in good agreement with the structure resolved experimentally by X-ray synchrotron radiation [13, 15]. The deviation between the experimental and the calculated unit-cell parameter is estimated by less than 2 % using GGA.

Also, the obtained results are in good agreement with the previous works of Shelyapina *et al.* [16] using linear augmented plane wave and Xiao *et al.* [17] using the projector augmented wave (PAW) method. It can be noticed that GGA underestimate the lattice parameter. The obtained results show that this method is reliable and the optimized lattice constants will be used to calculate other properties.

3.2 Mechanical properties (elastic properties)

3.2.1 Single-crystal elastic constants

The elastic properties define the behavior of a solid that undergoes stress, deforms, and then recovers to return to its original form [18-19]. To investigate the mechanical stability description of Mg_7NbH_{16} structure, a set of zero-pressure elastic constants was determined from the stress of the strained approach using ABINIT code, taking into account the ionic relaxations in response to strain perturbations [18, 19]. The calculated elastic constants are listed in **Table 2**.

Table 2: Calculated elastic constants, elastic compliance constants, Zener factor (A_{Zener}) and elastic wave velocities for different propagation directions for Mg_7NbH_{16}.

Elastic Constants (GPa)	Elastic compliance Constants (10^{-2} GPa^{-1})	A_{zener}	Elastic wave velocities (m/s)
$C_{11}=157.25$	$S_{11}=0.006632$	0.294	$\nu_L^{100}=8361$, $\nu_{1T}^{100}=2950$, $\nu_{2T}^{100}=2950$
$C_{44}=19.58$	$S_{44}=0.05100837$		$\nu_L^{110}=7003$, $\nu_{1T}^{110}=2950$, $\nu_{2T}^{110}=5437$
$C_{12}=24.23$	$S_{12}=-0.00088539$		$\nu_L^{111}=6487$, $\nu_{1T}^{111}=4755$, $\nu_{2T}^{111}=4755$

The mechanical stability in a cubic crystal requires that the three independent elastic constants C_{ij} should satisfy the well-known Born stability criteria [27]:

$$C_{11}>0\,,\ C_{44}>0\,,\ (C_{11}+2C_{12})>0\,,\ (C_{11}-C_{12})>0\,,\ C_{12}<\frac{C_{11}+2C_{12}}{3}<C_{11}$$

The calculated elastic constants C_{ij} satisfy Born stability criteria. Thus, the cubic phase of Mg_7NbH16 is mechanically stable.

The shear elastic constant C_{44} (which reflects the resistance to shear deformation) is very smaller than C_{11} (which is related to the unidirectional compression along the principal crystallographic directions). This indicates the weak resistance to shear deformation compared to the resistance to the unidirectional compression.

It is important to calculate elastic anisotropy for structural hydrides in order to improve their mechanical durability for mobile application (H2 storage) [18, 19], since it is highly correlated with the possibility to induce microcracks within these hydrides.

The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The elastic anisotropy behaviour of a cubic crystal can be measured by the Zener ratio A_{Zener} [28]:

$$A_{Zener} = \frac{2\,C_{44}}{(C_{11} - C_{12})} \tag{1}$$

For a completely isotropic material $C_{11} = C_{12} + 2C_{44}$, so $A_{Zener} = 1$. The deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. If $A_{Zener} < 1$, the crystal is stiffest along $< 100 >$ cube axes, and when $A_{Zener} > 1$, it is stiffest along the $< 111 >$ body diagonals [29]. The calculated value of A_{Zener} listed in **Table 2**, indicates that Mg_7NbH_{16} compound is highly anisotropic. Also, Mg_7NbH_{16} is stiffest along the $< 100 >$ cube axes.

To the best of authors' knowledge, there are, till now, no available experimental data about the elastic constants of Mg_7NbH_{16} compound. Thus this research work and the obtained results could provide a useful reference for future studies.

Experimentally, one can measure the sound wave velocities along certain directions within a crystal, and then fit them into the Christoffel equation [29] to get the elastic constants. Inversely, if the elastic tensor is known, one can get their propagation properties by the same equation.

Therefore, we have estimated the elastic wave velocities in the [100], [110] and [111] directions were estimated from the calculated single crystal elastic constants C_{ij}. These velocities are calculated from the resolution of the Christoffel equation [29]:

$$\left(C_{ijkl} \cdot n_j \cdot n_k - \rho \cdot \nu^2 \cdot \delta_{il}\right) \cdot u_l = 0 \tag{2}$$

where C_{ijkl} is the single crystal elastic constants tensor, n is the wave propagation direction, ρ is the density of material, u is the wave polarization and ν is the wave velocity. The solutions of Christoffel equation are of two types: a longitudinal wave with polarization parallel to the direction of propagation (ν_L) and two shear waves (ν_{T1}) and (ν_{T2}) with polarization perpendicular to n.

The calculated elastic waves velocities in the [100], [110] and [111] directions for Mg_7NbH_{16}, are reported in **Table 2**. It can be seen that the fastest longitudinal waves propagate along the [100] direction and the slowest ones propagate along the [111] direction.

While, the fastest and slowest transverse waves propagate along the [110] and [100] directions, respectively. These results give a theoretical guidance for future experiments.

3.2.2 Polycrystalline elastic moduli

It is not possible to measure the individual elastic constants $C_{i\,j}$ when single crystal samples are not available. Instead, the polycrystalline bulk modulus (B) and shear modulus (G) may be determined [18, 19, 30]. Frequently, for such calculations, two main approximations are used, namely Voigt (V) [31] and Reuss (R) [32] schemes. In these approaches, the Voigt approximation is the upper limit of the actual effective modulus, while the Reuss approximation corresponds to the lower limit of this parameter [19]. Thus, for the cubic structure, in terms of Voigt approximation, bulk (B_V) and shear (G_V) moduli can be expressed by:

$$B_V = (1/3)\left[C_{11} + 2C_{12}\right] \tag{3}$$

$$G_V = (1/5)\left[C_{11} + 3C_{44} - C_{12}\right] \tag{4}$$

In terms of the Reuss approximation, bulk (B_V) and shear (G_V) moduli can be expressed by:

$$B_R = (1/3)\left[S_{11} + 2S_{12}\right] \tag{5}$$

$$G_R = 5/\left[4S_1 - 4S_{12} + 3S_{44}\right] \tag{6}$$

The elastic moduli of the polycrystalline material can be approximated by Hill’s (which takes the arithmetic average of the Voigt [31], and Reuss approximations [32]) and for shear moduli will be presented by:

$$G = (G_R + G_V)/2 \tag{7}$$

Similarly, for bulk moduli:

$$B = (B_R + B_V)/2 \tag{8}$$

Both Young’s modulus (E) and Poisson’s ratio (ν) are given by the following equations [31]:

$$E = \frac{9B.G}{3B + G} \tag{9}$$

$$\nu = \frac{3B - 2G}{2.(3B + G)} \tag{10}$$

The Lamé constants λ and ν (the first Lamé constant represents the compressibility of the material while the second Lamé constant reflects its shear stiffness) are defined as:

$$\lambda = \frac{E.\nu}{(1 - 2\nu).(1 + \nu)} \tag{11}$$

$$\mu = \frac{E}{(1 + \nu)} \tag{12}$$

The calculated values of bulk, shear and Young's moduli, as well as Poisson's ratio and Lamé constants of the cubic Mg_7NbH_{16} structure are given in **Table 3** for Voight, Reuss and Hill approaches. The calculated bulk moduli (68.57 GPa), from the elastic constants, is in enormous disagreement with the calculated value reported by Xiao *et al.* [17]. Indeed, the authors reported a huge value for the bulk modulus of Mg_7NbH_{16} (about 488 GPa) which is not expected from a soft Mg-rich compound. No experimental data are available for comparison.

Table 3: Calculated bulk modulus B (B_V , B_R denotes Voigt bulk modulus and Reuss bulk modulus), shear modulus G (G_V and G_R denote Voigt shear modulus and Reuss shear modulus), Young's modulus E , Poisson's ratio ν and Lamé constants of Mg7NbH16 compound

B_R GPa	B_V GPa	G_R GPa	G_V GPa	G GPa	B GPa	E GPa	ν GPa	λ GPa	μ GPa
68.57	68.57	27.27	38.35	32.81	68.57	84.89	0.29	45.31	32.81
					488.8[17]				

The calculated shear moduli from single crystal elastic constants of Mg_7NbH_{16} is smaller than that of the $KMgH_3$ [18] and $NaMgH_3$ [19] and larger than that of Mg_7TiH_{16} [29] calculated previously. In general, the small value of shear moduli is an indication of the less pronounced directional bonding between atoms [31].

Pugh [33] introduced the proportion of bulk to shear modulus of polycrystalline phases (B/G) as a measure of ductility by considering that the shear modulus G represents the resistance to plastic deformation while the bulk modulus B B represents the resistance to fracture [18, 19, 31]. Higher B/G value is generally associated with higher ductility and the critical value which separates ductile and brittle materials is 1.75, i.e. if $B/G > 1.75$, the material behaves in a ductile manner, otherwise the material behaves in a brittle manner [18, 19]. In the case of Mg_7NbH_{16} the value of B/G (2.09) is greater than 1.75 and therefore Mg_7NbH_{16} compound can be classified as ductile material.

The values of the Poisson ratio (ν) are minimal for covalent materials (typically $\nu = 0.1$), and there is little difference between G and B ($G = 1.1\,B$). A typical value of ν for ionic materials is 0.25 and $G = 0.6\,B$; for metallic materials ν is typically 0.33 and $G = 0.4\,B$ G = 0.4 B [34].

In this study, the value of ν for Mg_7NbH_{16} is about 0.29, i.e. metallic contributions in intra atomic bonding should be assumed for this compound. Also, the calculated value of $G = 0.48\,B$, which also indicates that the metallic bonding is suitable for Mg_7NbH_{16}. This confirms the result reported by Shelyapina *et al.* [16] and Xiao *et al.* [17] about the chemical bonding.

3.2.3 Debye Temperature

The Debye temperature (T_{Debye}) is linked to many physical properties such as specific heat, elastic constants, and melting point [18, 19, 31]. Debye temperature can be calculated from the elastic constants, using the average sound velocity (ν_m) by the following equation [35]:

$$T_{Debye} = \frac{h}{k}\left(\frac{3n}{4\pi}\cdot\left(\frac{N_A\,\rho}{M}\right)\right)^{1/3} \times \nu_m \qquad (13)$$

where h is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, ρ is the density of molecule, M is the molecular weight and n is the number of atoms in the molecule.

The average sound velocity (ν_m) in polycrystalline materials is given by [35]:

$$\nu_m = \left(\frac{1}{3} \cdot \left(\frac{2}{\nu_t^3} + \frac{1}{\nu_l^3} \right) \right)^{-1/3} \tag{14}$$

where ν_t and ν_l are the transverse and longitudinal elastic wave velocities of the polycrystalline materials and are given by Navier's equation [36]:

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

$$\nu_l = \left(\frac{B + (4G/3)}{\rho} \right)^{1/2} \tag{16}$$

The calculated ρ, ν_l, ν_t, ν_m and T_{Debye} are listed in **Table 4**. In the absence of any measured data in the literature, no comparison could be discussed. Hence, the results reported in this study can be considered as a prediction for the mechanical properties of Mg_7NbH_{16} compound and will testify future experimental work.

Table 4: Molecular mass (M), density (ρ), longitudinal (ν_l), transverse (ν_t), average elastic wave velocity (ν_m) and the Debye temperatures (T_{Debye}) calculated of Mg_7NbH_{16}

M g/mol	ρ g/m^3	ν_l m/s	ν_t m/s	ν_m m/s	T_{Debye} K
279.17	2.249	7166.383	3819.370	4262.736	619.753

4. CONCLUSION

The structural and mechanical properties of Mg_7NbH_{16} are calculated within the density functional theory. The calculated lattice parameters using GGA are in good agreement with the experimental data. The density of states indicates that this hydride exhibits a metallic character.

To the best knowledge of authors, there are no available experimental data about the elastic constants of Mg_7NbH_{16} compound. The results obtained in this study could provide a useful reference for future studies.

The calculated Zener factor indicates that Mg_7NbH_{16} compounds is highly anisotropic. Also, Mg_7NbH_{16} is stiffest along the <100> cube axes. Using Hill's approximation, the ideal polycrystalline aggregates bulk modulus, shear modulus, Young's modulus, Poisson's ratio and Lamé constants, are calculated.

For Mg_7NbH_{16}, the value of B/G is greater than 1.75, and therefore Mg_7NbH_{16} can be classified as ductile material. The calculated Poisson's ratio confirms again the metallic bonding of Mg_7NbH_{16}.

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