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Structural and Elastic properties of LiBH₄ for hydrogen storage applications

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Abstract- We have investigated the structural and elastic properties of LiBH₄ in orthorhombic structure using both the norm-conserving pseudopotentials and full potential within the general gradient approximation (GGA) in the frame of density functional theory. The Orthorhombic LiBH₄ phase is found to be mechanically stable at an ambient pressure. The calculated linear bulk moduli are found to be in good agreement with the experiments. The shear modulus, Young's modulus, and Poisson's ratio for ideal polycrystalline LiBH₄ are also calculated. According to our results the LiBH₄ can be classified as brittle material.

Keywords- Hydrogen storage, LiBH₄, Elastic properties, Bulk moduli, DFT.

I-INTRODUCTION

Complex hydrides for solid-state hydrogen storage are one of the future solutions polluiant-free for storage and the transport of energy. Among the candidates, LiBH₄ was selected considering its high gravimetric hydrogen capacity (18.5 wt %). This material has thermodynamic and kinetic insufficiently established to be included in future applications.

At ambient condition LiBH₄ exhibits an orthorhombic structure (α-LiBH₄) with the space groupe Pnma (no. 62) [1,2,3] in which each $[BH_4]^-$ anion is surrounded by four lithium Li^+ and each Li^+ by four $[BH_4]^-$, both in tetrahedral configurations. The unit cell parameters of this structure are a= 7.17858(4), b=4.43686(2), c=6.80321(4) Å [4].

At about 384 K (110.58°C) [5] α-LiBH₄ undergoes a structural transition into a high-temperature phase (β-LiBH₄) but conflicting results have been reported concerning the symmetry of the phase formed [2], it was believed to belong to the tetragonal class [6,7]. Although recent experimental studies [4,8,9] agree that the structure of β- LiBH₄ is hexagonal with space group P6₃mc (no. 186). Ab-initio-calculation based density functional theory showed that this structure to be unstable [10,11]. Łodziana and Vegge [10] proposed a new structure with a monoclinic Cc symmetry to occur at about 3Gpa. Frankcombe et al [11] suggests that LiBH₄ should transform first into a P2₁/c phase at 1GPa, then into the Cc structure near 2.2 GPa. At high pressure, two structurally different polymorphs are identified with space group symeties Ama2 (no. 40) and Fm-3m (no. 225). Talyzin et al [3] showed a phase transition from ambiant pressure α-LiBH₄ to a high-pressure β- LiBH₄ phase at 0.5-1.4 GPa and room temperature (co-existance of both ambient and high pressure phase at 1.1 GPa, while at 1.4 GPa the phase transformation is complete) and the β- LiBH₄ phase seems to remain stable up to 8.9 GPa. The second transformation, from Ama2 phase to Fm-3m phase, starts at 10 GPa [1].

Knowledge of the elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermo- elastic stress, internal strain, sound velocities, and fracture toughness.

Elastic constants for most pure metals are available over a wide range of temperature in the literature. In contrast, data for complex hydrides compounds are much more limited.

Only the bulk modulus for the LiBH₄ is studied theoretically and experimentally [2,3,12]. However, there is a difference between the experimental values of the bulk modulus found in the literature.

In this work, we calculate the bulk modulus and the elastic constants of the LiBH₄ for the first time.

This paper is organized as follows: the computational methods are described firstly. Structural and elastic

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properties of $LiBH_4$ are presented in detail later. Finally, a brief conclusion is given.

II-CALCULATION METHOD

In the present work, we use two different approaches to examine the elastic properties of the $LiBH_4$. in order to estimate the bulk modulus and structural properties,We apply the most recently developed Vienna package WIEN2k [13,14] for the full-potential augmented plane-waves plus local orbitals (FP-APW+lo) method within the density functional theory (DFT) [15,16], for which the electron exchange correlation energy, is described in the generalized gradient approximation (GGA) using the Perdew–Burke–Enzerhof functional parameterization [17]. The APW + lo method expands the Kohn–Sham orbitals in atomic like orbitals inside the atomic muffin-tin (MT) spheres and plane waves in the interstitial region. The details of the method have been described in the literature [18–20]. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut off $l_{max} = 10$, and in Fourier series in the interstitial region. We use a parameter RMT $K_{max} = 3.5$, which determine the matrix size, where RMT denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane-wave expansion. All of the calculations were carried out at the theoretical equilibrium lattice constants. We choose the muffin-tin radii of H, Li and B to be 0.65, 2.3, and 1.2 a.u. respectively. The K integration over the Brillouin zone is performed using the Monkhorst–Pack scheme [21] with 3x6x4 grid of K-points. The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal is converged to less than 0.1 mRyd.

Also, In this study, we use the ABINIT code [22] based on pseudopotentials and planewaves in density functional theory (DFT) [16]. It relies on an efficient fast Fourier transform algorithm [23] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate-gradient method [24] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [25].We performed generalized gradient approximation (GGA-PBE) to DFT [17]. Fritz–Haber–Institute GGA pseudopotentials [26] are used to represent atomic cores.

We carefully tested the convergence of our calculations with respect to the plane-wave cut-off and k-point mesh. An energy cutoff of 50 Hartree and a 6x6x6 grid for k-point were used.
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.

III- RESULTS AND DISCUSSION

III.1- STRUCTURAL PROPERTIES

We relaxed the atomic positions; this relaxation lowered the total energy. The final structure obtained within the PBE GGA approximations is given in Table 1.
Our relaxed structure is in good agreement with the reported structure from the experiment. The deviations between the experimental and the calculated unit-cell parameters a, b and c, are estimated by less than 1.8% using PP-PW and 0.28% using FP-LAPW.
These deviations are acceptable and are typical for the state-of-art approximation of the density functional theory. We also note that in our case both PP-PW and FP-LAPW underestimate the lattice parameters, and FP-LAPW is more accurate than PP-PW. These results show our method is reliable and we will use the optimized lattice constants to calculate other properties.
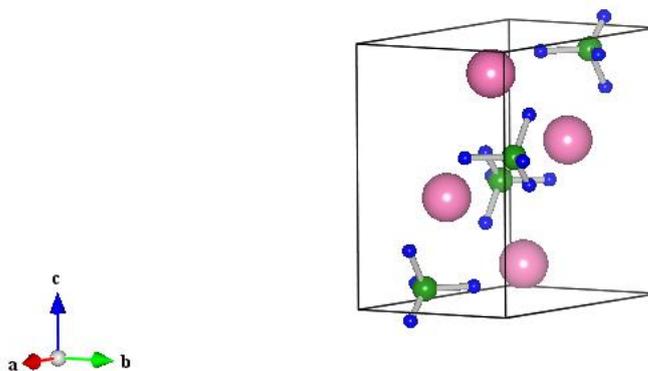

Fig 1: Crystal structure of α-$LiBH_4$.

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	Experiment [4]	FP-LAPW	PP-PW
Wyckoff Positions	Li (0.1568, 0.25, 0.1015) B (0.3040, 0.25, 0.4305) H1 (0.900, 0.25, 0.956) H2 (0.404, 0.25, 0.280) H3 (0.172, 0.054, 0.428)	Li (0.1566, 0.25, 0.1078) B (0.3087, 0.25, 0.4250) H1 (0.911, 0.25, 0.930) H2 (0.401, 0.25, 0.2722) H3 (0.2076, 0.0277, 0.426)	Li(0.1587,0.25,0.1090) B (0.3081, 0.25, 0.4234) H1 (0.911, 0.25, 0.929) H2 (0.404, 0.25, 0.2704) H3 (0.2059,0.0248,0.423)
Cell Parameters	a= 7.179 Å b= 4.437 Å c= 6.803 Å	a= 7.159 Å b= 4.425 Å c= 6.784 Å	a= 7.052 Å b= 4.358 Å c= 6.682 Å

TABLE.1 : Optimized unit-cell dimensions and atom coordinates for $LiBH_4$.

III.2- CALCULATION OF BULK MODULUS AND ITS PRESSURE DERIVATIVE FROM E(V)

The bulk modulus, B_0, and its pressure derivative B'_0 can be deduced from the variation of the total energy with volume.

In the present study, the total energies are calculated at several volumes around the equilibrium and are fitted to the Murnaghan's equation of state using FP-LAPW methods only. We used the relaxed atomic positions given in table.1 (FP-LAPW column). The structural optimization, total energy curves for $LiBH_4$ obtained from our GGA calculations are shown in Fig. 2. From this figure it is clear that the equilibrium structural parameters obtained from our GGA calculations are in very good agreement with the corresponding experimental values (see also table 1).

By fitting the total energies to the Murnaghan equation of states, we found the bulk modulus and its pressure derivative for $LiBH_4$, in the Orthorhombic structure, to be 50.95 GPa and 3.126 respectively. Our calculated bulk modulus is in good agreement with the experimental value of Talyzin et al [3] (45 GPa) but in disaccord with the value of Filinchuk et al [1] (14.4 GPa).

To more elucidate this confusion, we calculate, next, the elastic properties of $LiBH_4$.

III.3- MECHANICAL PROPERTIES (ELASTIC PROPERTIES):

The elastic properties define the behavior of a solid that under- goes stress, deforms, and then recovers and returns to its original shape after stress ceases.

To investigate the mechanical stability description of the $LiBH_4$ structures, 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.

The calculated elastic constants are listed in Table.2. For stable orthorhombic crystals, the nine independent elastic constants C_{ij} should satisfy the well-known Born stability criteria [27], i.e.,
$C_{11}>0, C_{22}>0, C_{33}>0, C_{44}>0, C_{55}>0, C_{66}>0,$
$[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,$
$(C_{11}+C_{22}-2C_{12})>0,$
$(C_{11}+C_{33}-2C_{13})>0,$
$(C_{22}+C_{33}-2C_{23})>0.$

Clearly, the calculated elastic constants C_{ij} satisfy Born stability criteria. Thus, the orthorhombic phase of $LiBH_4$ is mechanically stable at ambient pressure. To the best of our knowledge, there are hitherto no available experimental data about the elastic constants of $LiBH_4$. We hope our work could provide a useful reference for future study.

A problem arises when single crystal samples are not available, since it is then not possible to measure the individual elastic constants C_{ij} . Instead, the polycrystalline bulk modulus B and shear modulus G may be determined.

Usually, for such calculations two main approximations are used, namely Voigt (V) [28] and Reuss (R) [29] 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.

Thus, orthorhombic phase (such as $LiBH_4$), in terms of the Voigt approximation:
$B_v =(1/9)[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})]$
$G_v =(1/15)[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})]$

In terms of the Reuss approximation:
$B_R=1/[(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{13}+S_{23})]$
$G_R=15/[4(S_{11}+S_{22}+S_{33})-4(S_{12}+S_{13}+S_{23})+3(S_{44}+S_{55}+S_{66})]$
Where, the S_{ij} are the elastic compliance constants (The compliance matrix S_{ij} is the inverse of the matrix C_{ij}).

The elastic moduli of the polycrystalline material can be

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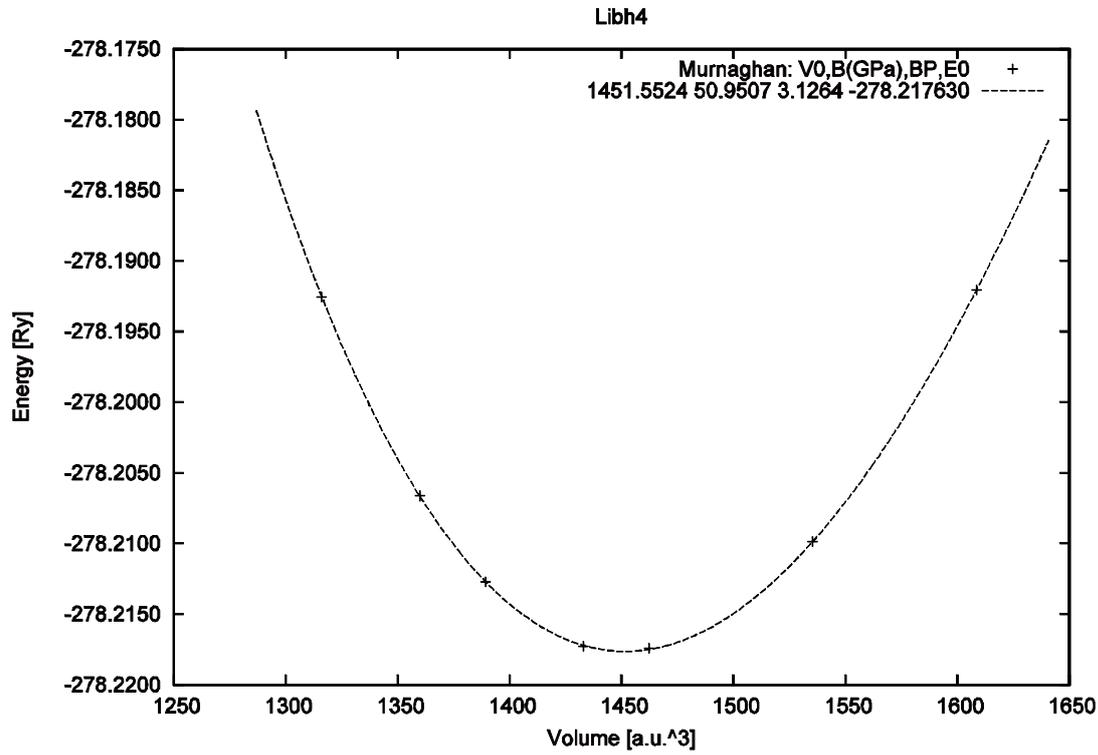Ghardaïa – Algérie 15, 16 et 17 Octobre 2012

Fig 2: Total energy vs unit-cell volume for α-LiBH$_4$.

C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{23}$	B$_R$	B$_v$	G$_R$	G$_V$	G	B	E	ν
93.26	114.13	118.35	29.81	60.53	59.74	35.53	31.52	03.80	51,88	51,94	58,48	47,01	52,74	51,91	118,20	0,12

TABLE.2 : The elastic constants C$_{ij}$ (in GPa), bulk modulus B, Young's modulus E, shear modulus G and Poisson's ratio ν for LiBH$_4$.

Where, the S$_{ij}$ are the elastic compliance constants (The compliance matrix S$_{ij}$ is the inverse of the matrix C$_{ij}$).
The elastic moduli of the polycrystalline material can be approximated by Hill's average and for shear moduli it is
G = (G$_R$+G$_V$)/2
 and for bulk moduli it is
 B = (B$_R$+B$_V$)/2
The Young's modulus E and Poisson's ratio ν [28] are given by
E = (9BG)/(3B+G) and ν=(3B-2G)/[2(3B+G)]
Our calculated bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of orthorhombic LiBH$_4$ structures are summarized in Table 2 according to the Voight, Reuss and Hill approaches.

The calculated bulk moduli, from the elastic constants, agree well with those directly obtained from the fitting of the Murnaghan EOS given above using FP-LAPW and in the range of the experimental value of Talyzin et al [3].
Pugh [30] introduced the quotient 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 represents the resistance to fracture. Higher B/G value is associated with higher ductility and the critical value which separates ductile and brittle materials is1.75,i.e. if B/G > 1.75, the material behaves in a ductile manner, otherwise the material behaves in a brittle manner. In the case of

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$LiBH_4$ the value of B/G is smaller than 1.75, and therefore $LiBH_4$ can be classified as brittle material.

IV- CONCLUSION:

Based on the first principles calculations, we have investigated the mechanical and structural properties of $LiBH_4$.

Our calculated lattice parameters are in good agreement with the experimental data .

We also calculated the strain energies for nine different distortions of $LiBH_4$ using GGA in the theoretically optimized crystal structure in order to calculate elastic constants.

To the best of our knowledge, there are no available experimental data about the elastic constants of $LiBH_4$. We hope our work could provide a useful reference for future study.

Using Hill's approximation, the ideal polycrystalline aggregates bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, are calculated.

In the case of $LiBH_4$ the value of B/G is smaller than 1.75, and therefore $LiBH_4$ can be classified as brittle material.

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