

Electronic properties of lightweight intermetallic Li-Al hydrides in the γ -phase

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An *ab initio* electronic structure study of the potential light-weight hydrogen storage materials LiAlH₄ and Li₃AlH₆, in their γ -phase, is presented. Electronic band structures and total and partial densities of states for both compounds are calculated by using the WIEN2k simulation code. We estimate an energy bandgap of ca. 3.82 eV for the γ -LiAlH₄ semiconductor and no gap in the γ -Li₃AlH₆ metal-like compound. In the latter, the valence band is formed by two distinct energy bands originating from hydrogen orbitals hybridization with metal atomic orbitals. Optical properties such as the refractive index $n(\omega)$, the reflectivity $R(\omega)$, the absorption coefficient $I(\omega)$, and energy-loss function $L(\omega)$ are determined from the complex dielectric function $\varepsilon(\omega)$ for incident photon energies in the 0-40 eV interval. It is found that these quantities are isotropic for cubic γ -Li₃AlH₆, while they are similar but distinguishable in the orthorhombic γ -LiAlH₄ compound. The γ -Li₃AlH₆ hydride, as an anode in lithium ion cells, is more Li reversible than the γ -LiAlH₄. Results are discussed and compared with available published data.

Keywords: Ab initio calculations; WIEN2k; Electronic properties; Intermetallic hydrides; Hydrogen storage.

1. INTRODUCTION

Hydrogen storage in metallic hydrides is the subject of intensive research, both fundamental and applied, with the aim of discovering suitable compounds which will fit in the envisioned sustainable economy utilizing hydrogen, a clean and procurable combustible, as an energy vector [1-9]. Among complex hydrides, AMH₄ compounds form an extensive family, where A stands for an alkali metal (A=Li, Na, K from the first column of the periodic table) and M stands for a third column element (M=B, Al, Ga). Lithium-Aluminium hydrides, also known as alanates, which are serious

hydrogen storage candidates owing to their fair weight and high H tenor, form several compounds depending on ambient preparation conditions [10]. These have acquired a growing importance as anode materials in solid-state lithium ion batteries due to the particular conductivity of Li^+ ions [11]. The actual phase formed depends on temperature and, more practically, on applied pressure. Vajeeston et al [12] identify three phases for our first studied LiAlH_4 compound: a monoclinic α -phase below 2.6 GPa, followed by a tetragonal β -phase up to 33.8 GPa when an orthorhombic γ -phase sets in. The latter has a $Pnma$ space group with 4 formula units per unit cell, allowing the Al atom to see an irregular octahedral surrounding. The building block of all these phases is a negatively charged tetrahedron of four H atoms surrounding an Al atom (in its center), $[\text{AlH}_4]^-$, bonded to a positively charged Li^+ ion [12]. Our second studied intermetallic compound, Li_3AlH_6 , is reported to have four different phases, with various space groups, which also depend on ambient conditions, especially on pressure [13]. The transitions $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \delta$ occur at 18.64, 28.85, and 68.79 GPa, respectively. In the α -phase compound, the structure is constituted by isolated $[\text{AlH}_6]^{-3}$ octahedral ion units connected on two corners and two edges to Li^+ ions [13]. These authors report that these phases have not been entirely unraveled and several models have been suggested to explain accessible experimental diffraction data. The space group $Fd\bar{3}$ was found to account for the γ - Li_3AlH_6 hydride [13, 14].

In this work, we investigate by *ab initio* calculations the structure of the less-studied high pressure γ -phase for both alanate compounds LiAlH_4 and Li_3AlH_6 in order to gain new insight into these systems. In the following, first principles computations of band structures, partial and total densities of states, and optical properties (dielectric function, refractive index, reflectivity, absorption coefficient, energy-loss function) are reported and discussed in the light of available published literature. In addition, an electrochemical investigation is carried out to determine which hydride is more Li reversible.

2. COMPUTATIONAL METHODS

The calculated results in this paper were obtained using the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) [15-18] method within the framework of density functional theory (DFT) [17, 18] as implemented in the WIEN2k code [19, 20]. This method uses the muffin-tin geometry separating space into distinct spheres and an interstitial region. For the exchange correlation potential, we used the generalized gradient approximation as defined by Perdew et al. [21-24]. We used the scalar relativistic approach.

In the calculation, the H ($1s^1$), Li ($1s^2 2s^1$) and Al ($2p^6 3s^2 3p^1$) states are treated as valence electrons. The muffin-tin radii R_{MT} , which are chosen such that the MT spheres do not overlap, are taken to be 0.8 Bohr for H, 1.5 Bohr for Al and 1.1 Bohr for Li in the γ - LiAlH_4 phase (Fig. 1a) [12], and 0.8 Bohr for H, 1.5 Bohr for Li and 1.7 Bohr for Al in the γ - Li_3AlH_6 phase (Fig. 1b) [13].

The basis functions were expanded up to $R_{\text{MT}} \times K_{\text{max}} = 7$, where R_{MT} is the smallest of all MT sphere radii and K_{max} is the maximum value of the wave vector K . The number of K -points which ensures total energy convergence in the whole Brillouin zone, was 1000 for the orthorhombic γ - LiAlH_4

structure and 1000 for the cubic γ -Li₃AlH₆ structure. The self-consistent calculations are considered to be converged when the total energy becomes stable within 0.1 mRyd.

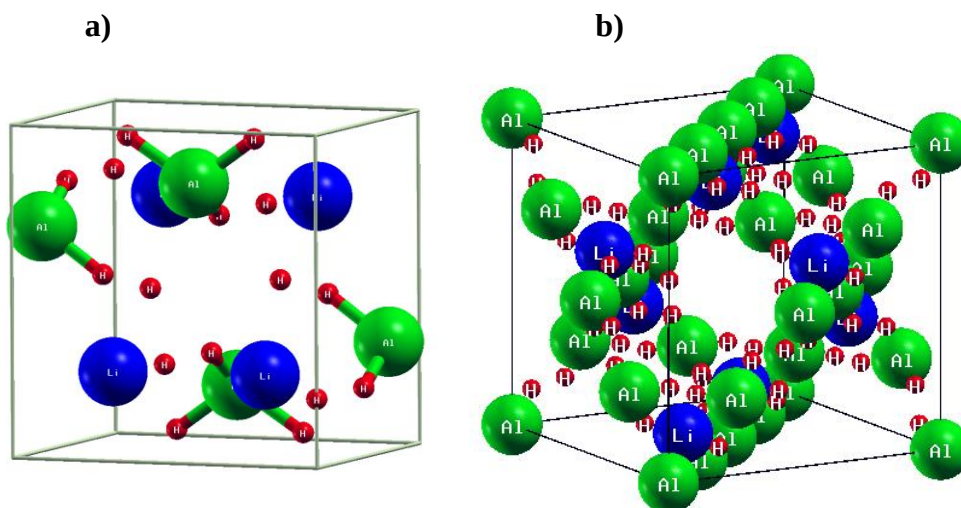


Figure 1. a) γ -LiAlH₄ phase structure (*Pnma* space group) and b) γ -Li₃AlH₆ phase structure (*Fd $\bar{3}$* space group).

3. RESULTS AND DISCUSSION

3.1 Structural properties

The total energy vs. volume curves $E(V)$ were fitted to the Murnaghan equation of state (EOS) [25], for both calculated γ -LiAlH₄ and γ -Li₃AlH₆ structures. Table 1 displays optimized structural parameters for both γ -LiAlH₄ and γ -Li₃AlH₆ structures along with other data from the literature. Lattice parameters and internal atomic positions identified at the equilibrium position are listed, together with available experimental data and previous theoretical works for comparison purposes.

Table 1. Optimized structural parameters for γ -LiAlH₄ and γ -Li₃AlH₆ from our calculations and other works

Structure	Lattice constants (in Å)	Atom coordinates
γ -LiAlH ₄ (<i>Pnma</i>)	$a = 6.5196^x (6.4667)^y$ $b = 5.3916^x (5.3478)^y$ $c = 6.6471^x (6.5931)^y$	Li: 0.2465; 0.25; 0.2474 ^x (0.2428; 0.25; 0.2467) ^y Al: 0.5157; 0.25; 0.8228 ^x (0.5120; 0.25; 0.8221) ^y H1: 0.2984; 0.25; 0.9591 ^x (0.3067; 0.25; 0.9617) ^y H2: 0.7147; 0.25; 0.9614 ^x (0.7162; 0.25; 0.9631) ^y H3: 0.4934; 0.0208; 0.2947 ^x (0.4889; 0.9833; 0.2943) ^y
γ -Li ₃ AlH ₆ (<i>Fd$\bar{3}$</i>)	$a = 13.2406^w (13.9015)^z$	Li: 1/8 ; 1/8 ; 1/8 ^x (1/8 ; 1/8 ; 1/8) ^z Al: 0 ; 0 ; 0 ^x (0 ; 0 ; 0) ^z H: 0.0634; 0.9867; 0.1125 ^x (0.1125; 0.0634; 0.9867) ^z

^w: This work.

^x: Our previously calculated value at equilibrium from Ref. [26].

^y: Calculated value from Ref. [12].

^z: Calculated value from Ref. [13].

Table 2. Equilibrium volume V_0 (Bohr³/f.u), bulk modulus B_0 (GPa) and its corresponding pressure derivative B_0' for γ -LiAlH₄ (Pnma) and γ -Li₃AlH₆ (Fd $\bar{3}$) compared with other calculations.

Structure	V_0 ; B_0 (GPa) ; B_0'	
	This work	Other work
γ -LiAlH ₄ (Pnma)	1758.50 ; 14.26 ; 5.40	none ; 14.25 ; 4.85 ^y
γ -Li ₃ AlH ₆ (Fd $\bar{3}$)	3917.66 ; 22.35 ; 3.88	none ; 37.63 ; 3.94 ^z

^y: Calculated value from Ref. [12].^z: Calculated value from Ref. [13].

Optimized lattice parameters show a slight increase of 0.3 % when compared to the previous theoretical work of Vajeeston et al [12, 13]. To our knowledge, no experimental values exist in the literature. In Table 2, the calculated equilibrium volume V_0 for one formula unit, the bulk modulus B_0 , and the pressure derivative B_0' are displayed for both γ -LiAlH₄ and γ -Li₃AlH₆ structures. We can observe that our calculated B_0 and B_0' values agree well with those reported elsewhere [12, 13].

In the following, we are going to use these equilibrium values to investigate electronic and optical properties of both γ -LiAlH₄ (Pnma) and γ -Li₃AlH₆ (Fd $\bar{3}$) structures.

3.2 Electronic properties

3.2.1 Band structures

a. γ -LiAlH₄ (Pnma)

The calculated band structures in Fig. 2 exhibit a finite energy gap between the valence and conduction bands for the orthorhombic phase γ -LiAlH₄. Both the valence band maximum and the conduction band minimum are located at the Γ point which causes a direct band gap of about 3.82 eV implying a semiconducting behavior at high temperature. The band gap of this compound was found in previous work [13, 14] to be larger than 4eV at low pressure. However, at high pressure, the band structure changes and the band gap decreases. The valence band is represented by a single band located between -6.7 eV and E_F . The latter occurs at around 0.025 eV.

b. γ -Li₃AlH₆ (Fd $\bar{3}$)

The calculated band structures in Fig.3 show that there is an energy overlap at E_F between valence and conduction bands for the cubic phase γ -Li₃AlH₆, excluding therefore the possibility of an energy gap and conferring a metallic character to this phase. However, the valence band can be divided into two energy bands: above -5.8 eV up to E_F , and the interval $[-10.5$ eV , -6.6 eV]. E_F occurs here at around 0.24 eV.

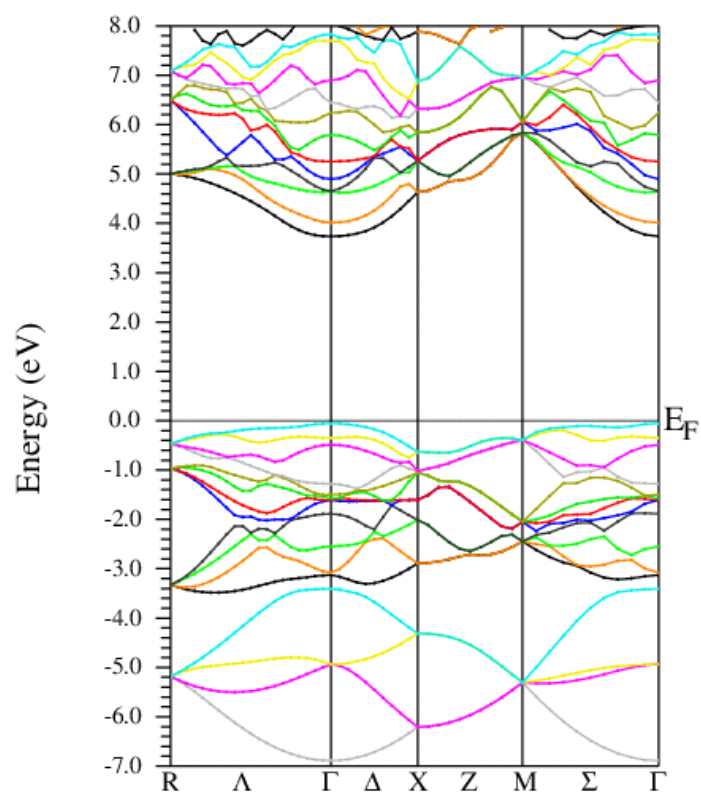


Figure 2. Band structures of γ -LiAlH₄

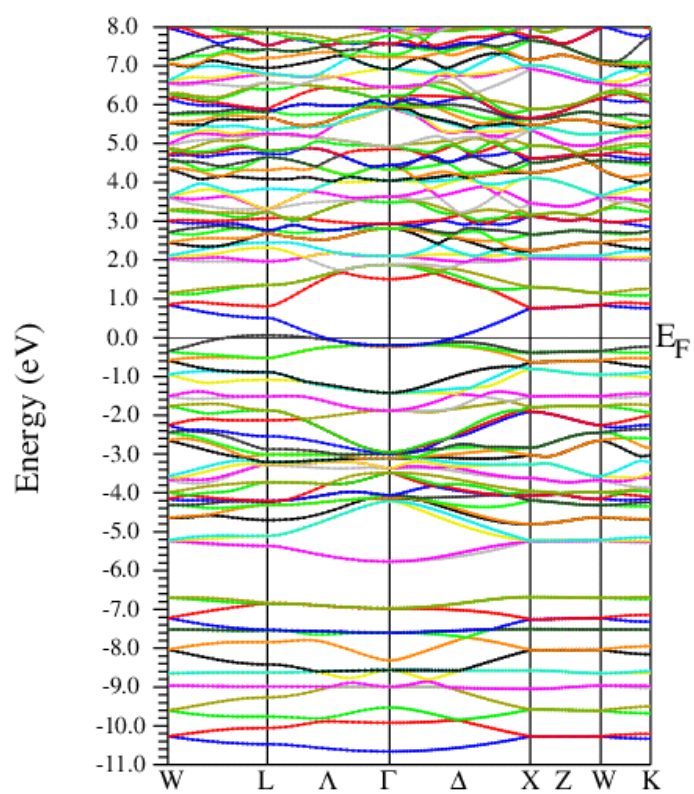


Figure 3. Band structures of γ -Li₃AlH₆.

3.2.2 Total and partial densities of states

a. γ -LiAlH₄ (Pnma)

The total densities and partial densities of states are illustrated as Fig.4 a (total for compound), b (partial for s and p orbitals in Li), c (partial for s, p, and d orbitals in Al), and d (partial for s orbital in H).

The valence band is formed as a single block as noted in the band structure discussion between -6.7 eV and E_F . Just below E_F , we observe a high interaction of H s states with Al p and d states and a somehow lower interaction with Li states. For deep states in the lower part of the valence band, we notice a high value for Al s states which indicates a positively charged aluminium in the complex hydrides. The energy gap is also confirmed between E_F and 3.82 eV. The electronic structure of the LiBH₄ hydride has shown an energy gap of 6.8 eV [27].

b. γ -Li₃AlH₆ ($Fd\bar{3}$)

The total densities and partial densities of states are illustrated as Fig.5 a (total for compound), b (partial for s and p orbitals in Li), c (partial for s, p, and d orbitals in Al), and d (partial for s orbital in H).

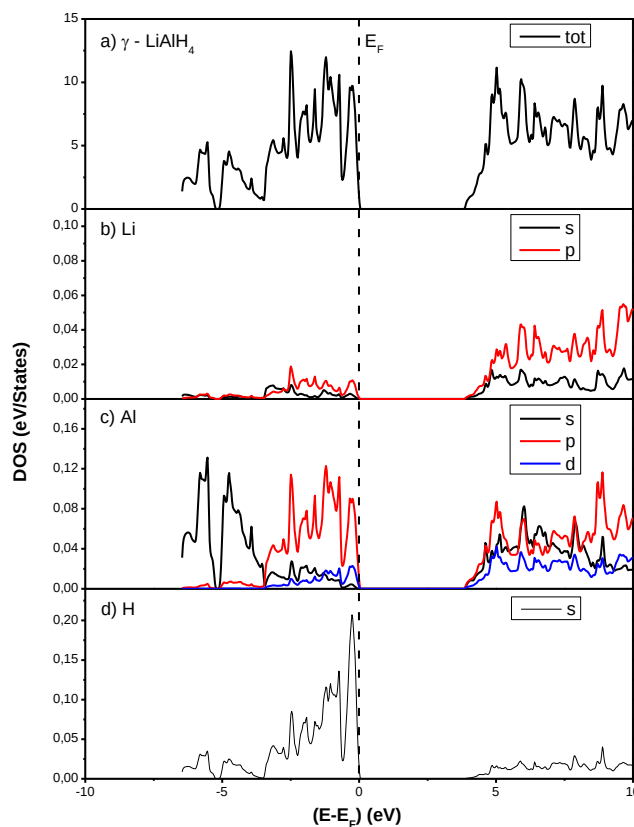


Figure 4. Total (a) and partial densities of states for Li (b), Al (c) and H (d) atoms in γ -LiAlH₄.

The valence band is formed as a double block as noted in the band structure discussion: the interval [-10.5 eV , - 6.6 eV] and the range between – 5.8 eV and E_F . As noted in γ -LiAlH₄ just below E_F , we also observe in this compound a high interaction between H s states and Al p and d states with a lower interaction with Li states. For deep states in the lower part of the valence band, we notice a high interaction between s states from all atoms.

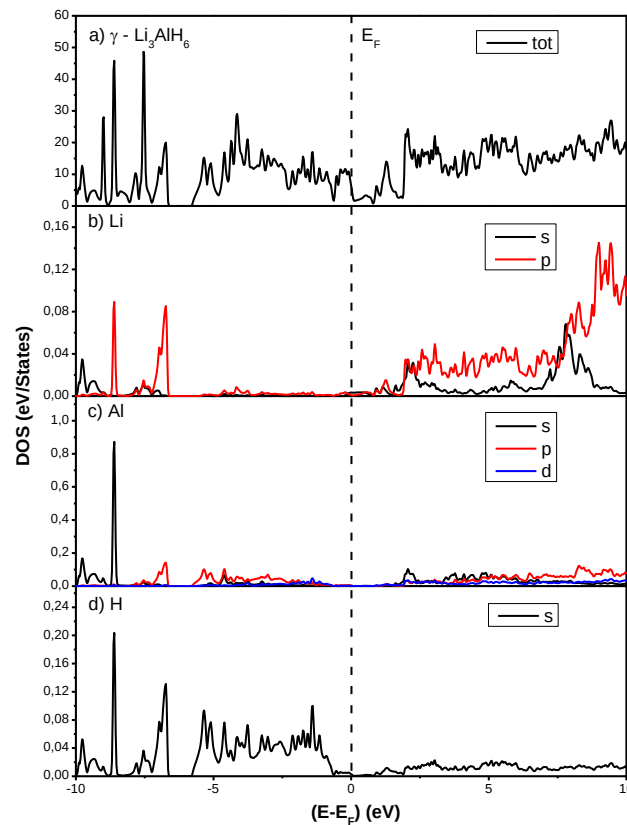


Figure 5. Total (a) and partial densities of states for Li (b), Al (c) and H (d) atoms in γ -Li₃AlH₆.

3.3 Optical properties

In a dynamic electrical field of pulse ω , the dielectric function $\tilde{\epsilon}(\omega)$ of a material can be written as a complex quantity $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where the real part ϵ_1 correlates with the local polarizability and the imaginary part ϵ_2 connects to the absorption of energy in the material. Optical characterization in a solid requires a determination of its complex refractive index [28, 29], $\tilde{n}(\omega) = n(\omega) + ik(\omega)$, where n is the usual refractive index and k is the extinction coefficient. Both complex quantities are connect by the relation $\tilde{\epsilon} = \tilde{n}^2$ which, when expanded, leads to $\epsilon_1 + i\epsilon_2 = (n^2 - k^2) + 2ink$. Conversely, n and k may be expressed as:

$$n(\omega) = \frac{1}{2}\{[\epsilon_1^2(\omega) + \epsilon_2^2(\omega)]^{1/2} + \epsilon_1(\omega)\} \text{ and } k(\omega) = \frac{1}{2}\{[\epsilon_1^2(\omega) + \epsilon_2^2(\omega)]^{1/2} - \epsilon_1(\omega)\}$$

In addition, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are connected through the Kramers-Kronig relations [29]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \text{ and } \varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega',$$

where P is the principal part of the Cauchy integration.

The reflectivity $R(\omega)$ is defined as the fraction of electromagnetic radiation energy that is reflected on a solid. It is given by the formula [30]:

$$R(\omega) = \left| \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1} \right|^2 = \frac{(n - 1)^2 + k^2}{(n + 1)^2 - k^2}$$

where $\tilde{n}(\omega)$, n and k have the same above-mentioned meanings.

The absorption coefficient α which represents the fraction of electromagnetic radiation energy that is absorbed by a solid is defined by [30]:

$$\alpha = \frac{4\pi k}{\lambda} = \frac{\varepsilon_2 \omega}{cn}$$

where λ is the radiation wavelength, c is the celerity of light and the other variables have their usual meaning.

When electrons move in a solid, they are scattered inelastically according to the energy-loss function $L(\omega)$ defined by $Im[-\frac{1}{\varepsilon(q, \omega)}]$, $\hbar q$ and $\hbar \omega$ being the momentum transfer and the energy loss of the inelastic process respectively, which determines the inelastic scattering probability events, the energy-loss distribution and the scattering angle distribution in a sample [31].

These optical properties are calculated in the energy domain 1 – 40 eV corresponding to near IR, visible and UV electromagnetic radiations.

3.3.1 Dielectric constant

The optical properties of crystals are essentially determined by the complex dielectric function $\tilde{\varepsilon}(\omega)$, whose real part characterizes the linear response of the material to an electromagnetic radiation whereas the imaginary part accounts for the optical absorption in the crystal.

a. Imaginary part of ε

The imaginary parts $\varepsilon_2(\omega)$ of the dielectric function are displayed in Fig. 6a and Fig. 7a, for γ -LiAlH₄ and γ -Li₃AlH₆ respectively. For the former compound, ε_2 increases from zero starting at about 3.5 eV towards a peak at around 6 eV for both the x and z directions, then returns slowly to zero at around 23 eV (Fig. 6a). This peak corresponds to the maximum of energy absorption in this material. For the latter compound, ε_2 increases from zero starting at about 0.5 eV towards a first peak at ca. 1 eV, then keeps on rising to the highest peak at ca. 3 eV before stabilizing up to ca. 5.5 eV where another peak is visible, and then falls gradually to zero (Fig. 7a). There is no difference at all between the curves for x and z axes, since γ -Li₃AlH₆ has a cubic structure.

b. Real part of ε

The real parts $\varepsilon_1(\omega)$ of the dielectric function are displayed in Fig. 6b and Fig. 7b, for γ -LiAlH₄ and γ -Li₃AlH₆ respectively. For the former compound, ε_1 starts increasing from a constant value to a peak at around 5 eV for both x and z axes and then decreases to a minimum at circa 8 eV before rising again towards a stable value (Fig 6b). The inflection point occurs at around 6 eV, which corresponds to the peak in absorption for ε_2 . For the latter compound, ε_1 shows a double peak at 1 and 3 eV which decreases to a minimum at ca. 8.5 eV before growing again towards a stable value (Fig. 7b). The inflection point is less clear-cut this time and corresponds roughly to 4 eV. There is no difference in any respect between the curves for x and z axes as this compound has cubic symmetry, unlike the orthorhombic one where one can discern distinctly the two curves.

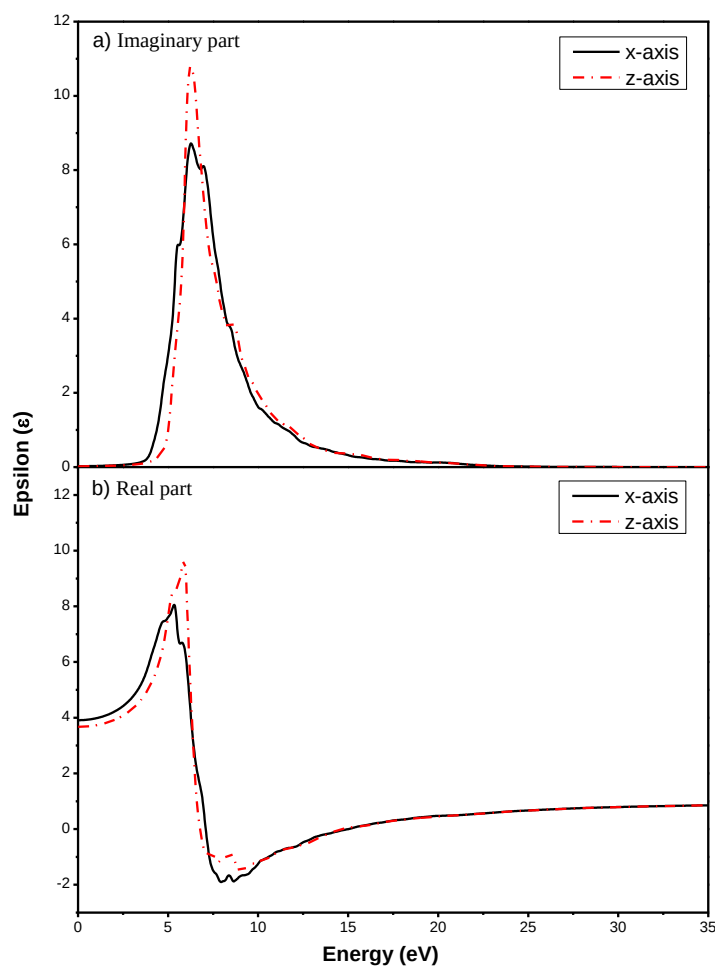


Figure 6. Imaginary part (a) and real part (b) of the dielectric function for γ -LiAlH₄.

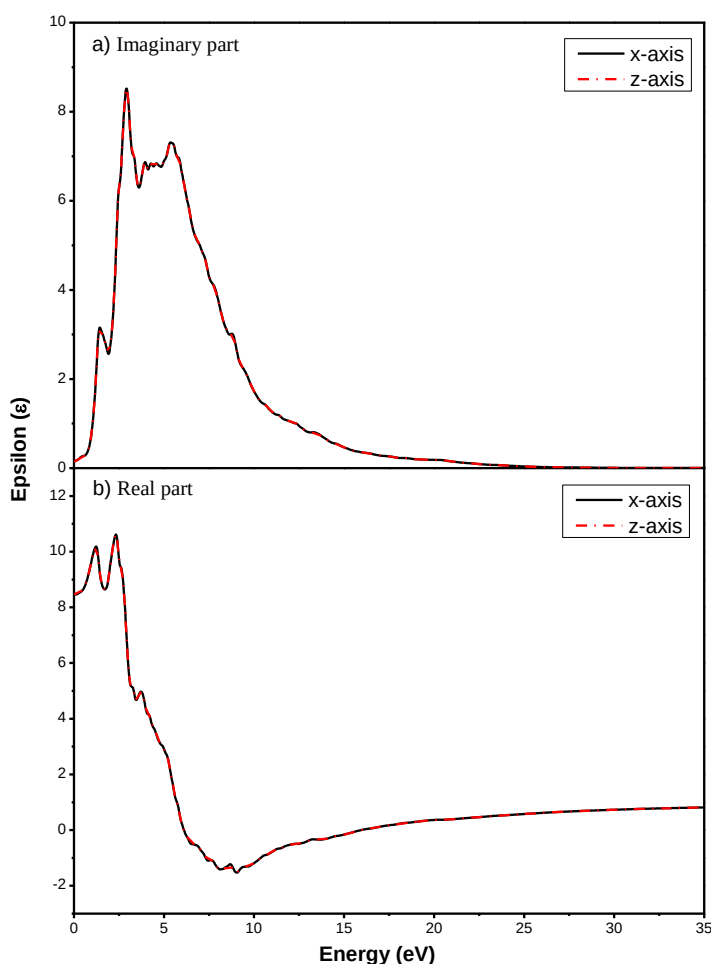


Figure 7. Imaginary part (c) and real part (d) of the dielectric function for γ - Li_3AlH_6 .

3.3.2 Refractive index

We now consider another frequency-dependent linear optical constant which is the refractive index $n(\omega)$. This index describes the behavior of an electromagnetic wave in a medium. The spectra are displayed in Fig. 8.

The values at the beginning of the curve start at around 2 for γ - LiAlH_4 in both x and z directions, then increase towards peak values at 6 eV (~ 3.3 on the z-axis, and ~ 3.0 on the x-axis) before decreasing to a shallow minimum at lower than ~ 0.5 at 14 eV for both x and z axes. For higher energies, both indexes rise gradually toward a value of unity as shown in Fig. 5a. We note a slight anisotropy between the x and z directions.

For cubic γ - Li_3AlH_6 , the values at the beginning of the curve start at around 2.9 and increase towards two peaks values (~ 3.25) at 1.5 eV and 2.5 eV, then decrease to a shallow minimum of ~ 0.5 at 15 eV before rising slowly toward unity as shown in Fig. 5b. We note here no difference between the x and z directions for symmetry reasons.

To our knowledge, no experimental or theoretical data are available for comparison to the present results.

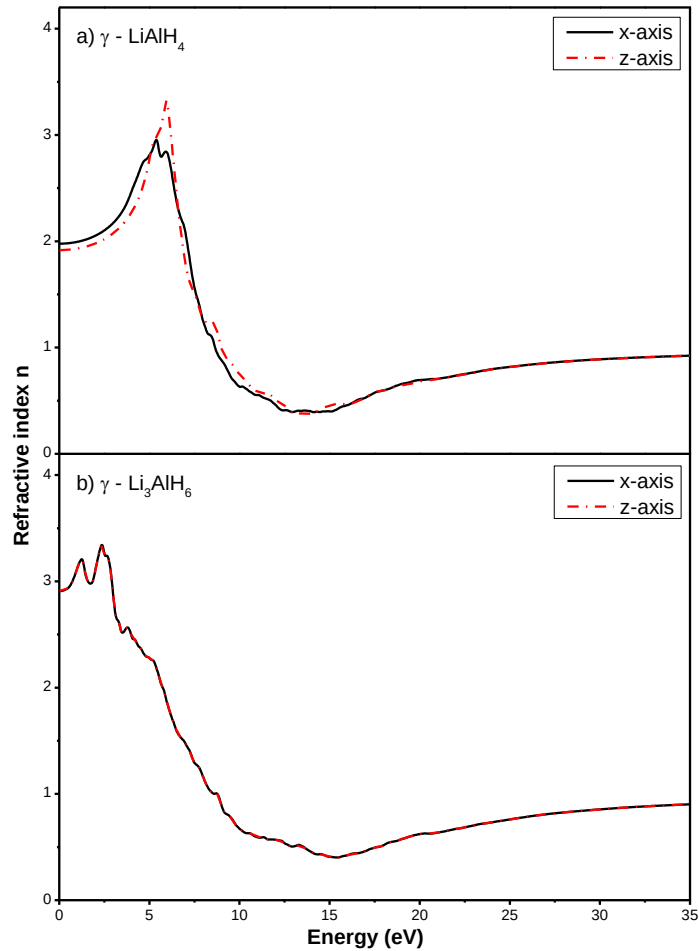


Figure 8. Refractive index $n(\omega)$, for (a) γ -LiAlH₄ and (b) γ -Li₃AlH₆

3.3.3 Reflectivity

Another interesting optical property that we consider in this study is the reflectivity $R(\omega)$. The results of this optical parameter are shown in **Fig. 9** for γ -LiAlH₄ (a) and γ -Li₃AlH₆ (b).

Starting at around 10%, the curve of reflectivity for γ -LiAlH₄ grows for both x and z axes to a wide swinging peak at ~40% between 6 and 13 eV before decreasing toward practically zero value at 25 eV for both directions. For γ -Li₃AlH₆, the curve of reflectivity starts at a value of ~24% and grows swingingly up to ~40% at 9.5 eV, then decreases likewise to ~30% at 15 eV before falling rapidly to almost zero at ~30 eV.

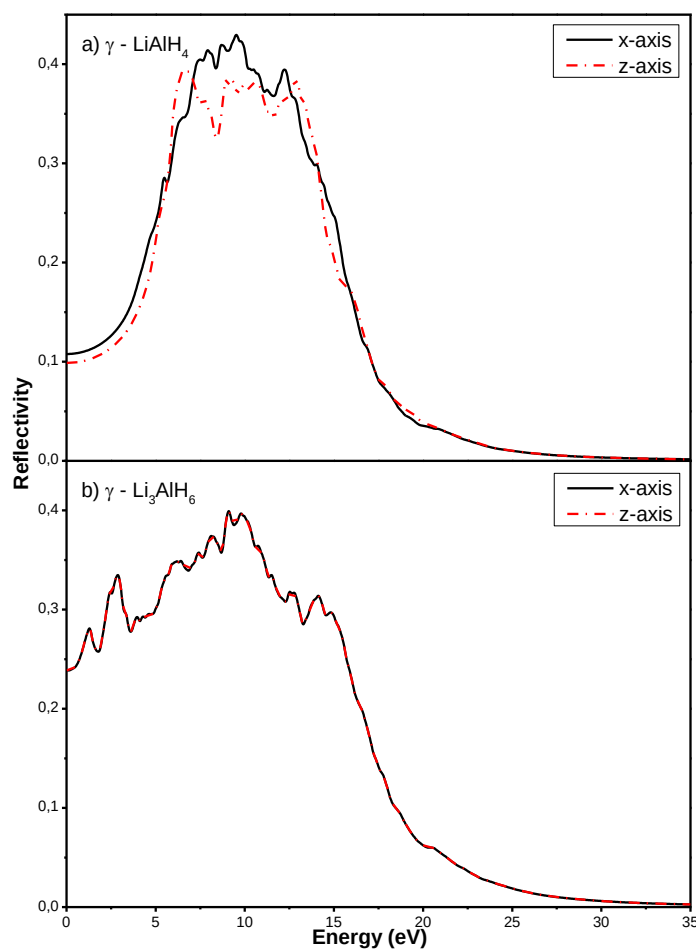


Figure 9. Reflectivity $R(\omega)$ for (a) γ -LiAlH₄ and (b) γ -Li₃AlH₆.

3.3.4. Absorption coefficient

Fig. 10 shows the absorption coefficient for γ -LiAlH₄ (a) and γ -Li₃AlH₆ (b). In γ -LiAlH₄, this coefficient has a threshold at ~ 4 eV above which it grows sharply to $1,52 \times 10^6 \text{ cm}^{-1}$ at an energy of ~ 8 eV for the x-axis. For the z-axis, despite having nearly the same shape, the coefficient exhibits two peaks at $\sim 1,45 \times 10^6 \text{ cm}^{-1}$ for ~ 7 and ~ 9 eV. For both directions, the coefficient falls then rapidly and almost vanishes at ~ 26 eV. In cubic γ -Li₃AlH₆, the absorption coefficient has a threshold at ~ 1 eV above which it grows sharply to $1,39 \times 10^6 \text{ cm}^{-1}$ at an energy of ~ 9 eV (for both identical axes). It then falls rapidly and almost vanishes at ~ 28 eV.

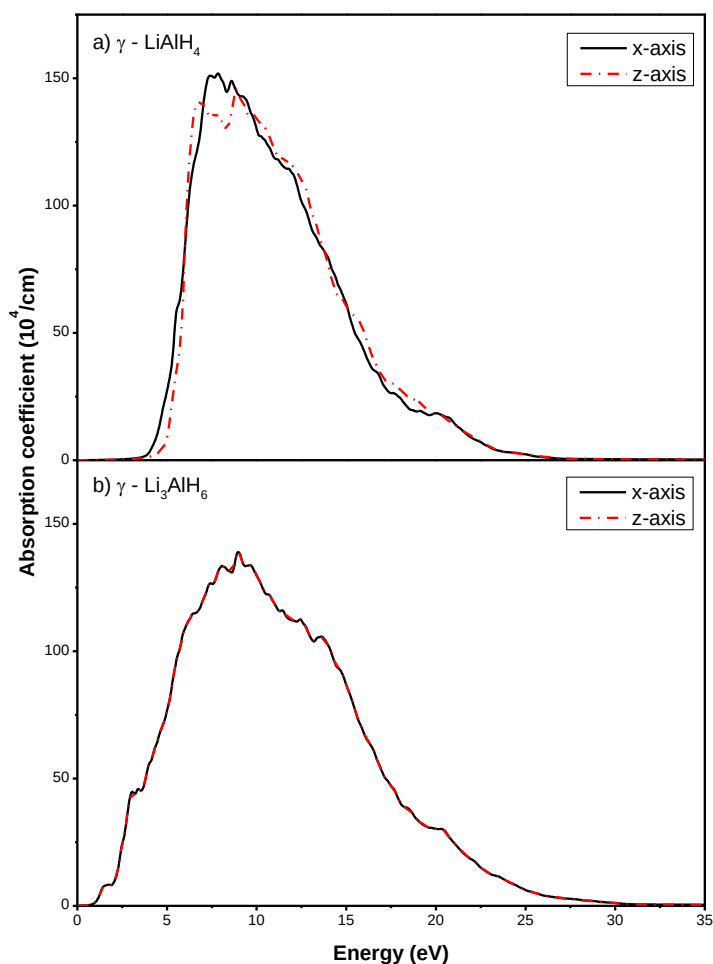


Figure 10. Absorption coefficient $I(\omega)$ for (a) γ -LiAlH₄ and (b) γ -Li₃AlH₆

3.3.5 Energy loss function

The curves of energy loss exposed in Fig. 11a show non zero values in the energy region situated between nearly 5 and 23 eV for γ -LiAlH₄, with a maximum value at an energy of for the x-axis and at an energy of ~ 17 eV for the z-axis, even though both peaks are centered at the same position of ~ 15.5 eV. Energy loss is nil outside this energy range.

The curves of energy loss drawn on Fig. 11b show non zero values in the energy region situated between nearly 1 and 26 eV for γ -Li₃AlH₆, with a maximum value at an energy of ~ 17 eV for both x- and z-axes due to cubic symmetry. Energy loss is zero outside this energy range.

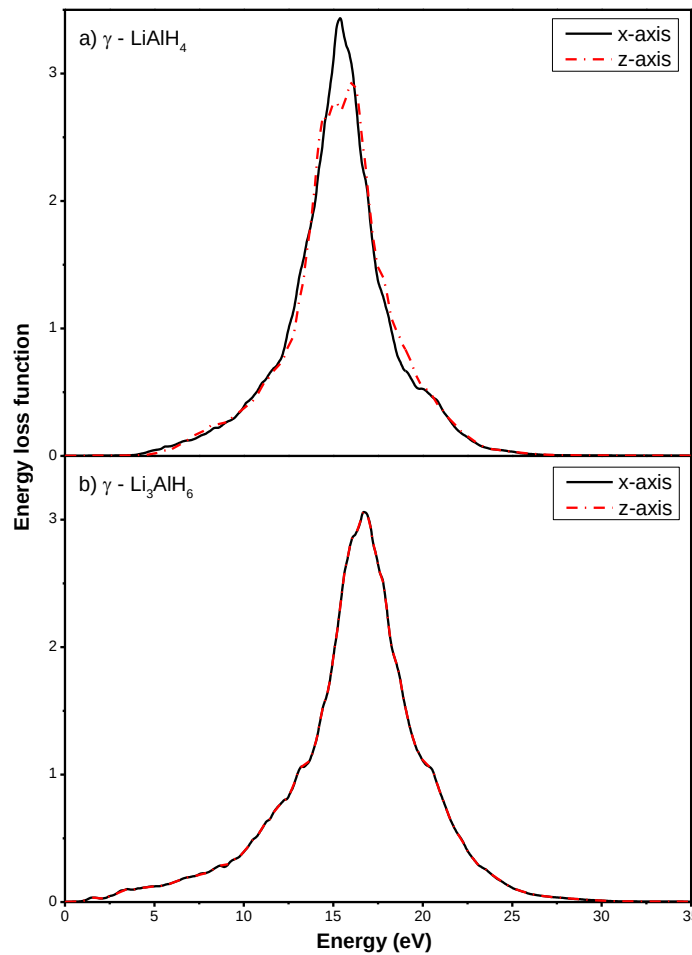
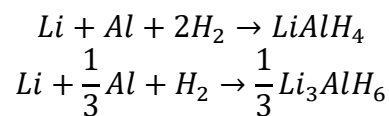


Figure 11. Energy-loss function for (a) γ -LiAlH₄ and (b) γ -Li₃AlH₆.

3.4 Electrochemical investigation

Alanes merit particular consideration due to their higher reversibility and higher hydrogen densities, hinting to a high reversible lithium ion capacity [32-34]. Lithium has the highest tendency to lose electrons as it has only one electron in its outer shell. When lithium is part of the γ -LiAlH₄ and γ -Li₃AlH₆ hydrides, it is very essential to study its reversibility in those systems using the following equations:



Formation energies, using the above equations, are calculated for 1 mol of lithium, respectively, as follows:

$$\begin{aligned} E_f(\text{LiAlH}_4) &= E_{\text{tot}}(\text{LiAlH}_4) - E_{\text{tot}}(\text{Li}) - E_{\text{tot}}(\text{Al}) - 2E_{\text{tot}}(\text{H}_2) \\ E_f(\text{Li}_3\text{AlH}_6) &= \frac{1}{3}E_{\text{tot}}(\text{Li}_3\text{AlH}_6) - E_{\text{tot}}(\text{Li}) - \frac{1}{3}E_{\text{tot}}(\text{Al}) - E_{\text{tot}}(\text{H}_2) \end{aligned}$$

The calculated formation energies are -68.82 kJ/mol Li for γ -LiAlH₄ and -53.02 kJ/mol Li for γ -Li₃AlH₆. The latter is less stable than the former. Therefore, the γ -Li₃AlH₆ hydride, as an anode in

lithium ion cells, is more Li reversible than the γ -LiAlH₄. Yang has synthesized a high performance Li₃AlH₆ anode via a solid-state ion exchange reaction between LiBH₄ electrolyte and Na₃AlH₆, but he has not mentioned which phase of Li₃AlH₆ it is [11].

4. CONCLUSION

The present calculations use the full-potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) method with the generalized gradient approximation (GGA). The structural properties were calculated at the equilibrium volume values and utilized to compute electronic properties. The band structure for the orthorhombic phase γ -LiAlH₄ displays a direct band gap of about 3.82 eV, whereas the cubic phase γ -Li₃AlH₆ exhibits no such gap. The valence band of the latter is split in two separate regions. Our calculations show that the results for both compounds agree well with previous theoretical and experimental data.

The dielectric functions are calculated and presented. Based on the band structures, we have ascribed the peaks in the imaginary part and found that transitions occurring between the highest valence bands and the lowest conduction bands are responsible for most of the optical absorption. Higher photon energy involves bands near the Fermi level. The frequency-dependent linear optical constants are essentially determined by the complex dielectric function $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, the anisotropic refractive index $n(\omega)$, and the reflectivity $R(\omega)$. The latter grows at different rates along the x- and y-axes for γ -LiAlH₄ and the energy range 4.66 – 14.35 eV displays characteristic peaks, the major one of about 68% being at 10.5 eV on the y-axis. For γ -Li₃AlH₆, starting at ca. 10% for the x-axis, the reflectivity spectra show a larger region characterized by a strong amplitude, the maximum of about 70% being located at 8.97 eV. For the absorption coefficient $I(\omega)$ in γ -LiAlH₄, a strong peak is observed at ~8 eV along both axes and, for γ -Li₃AlH₆, the peak is highest at ~9 eV. The energy-loss function $L(\omega)$ has its peak position at 15.5 eV and 17 eV for γ -LiAlH₄ and γ -Li₃AlH₆, respectively. The γ -Li₃AlH₆ hydride, as an anode in lithium ion cells, is more Li reversible than the γ -LiAlH₄.

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