Electronic properties of $SrAl_2H_2$ for hydrogen storage

K. Khodja[1,*] and Y. Bouhadda[1,**]
[1]Unité de Recherche Appliquée en Energies Renouvelables, URAER, Centre de Développement des Energies Renouvelables, CDER, 47133, Ghardaïa, Algeria
Email: *khodja_kh@yahoo.fr, **bouhadda@yahoo.fr

Abstract-*In this paper we report the $SrAl_2H_2$ electronic structure which is a zintl phase hydride in frame of the density functional theory (DFT) using the plane wave and pseudopotential method. We discuss the chemical bond nature using total and partial density of states (DOS) and also we calculated the enthalpy formation of the $SrAl_2H_2$, the phonon frequencies and the thermodynamic functions for hydrogen storage.*

Keywords: *Hydrogen Storage, Zintl Phase, Metal Hydride, Electronic Properties, Density Functional Theory.*

Introduction:

Many metals and intermetallic compounds exhibit the ability to absorb and react with hydrogen. Recently aluminum-derived hydrides have been considered as an alternative method for hydrogen storage, because they offer the improved energy density.

Hydrogen materials with Al–H bond such as $SrAl_2H_2$ have received more attention those last years for their high capacity of storage [1, 2].

Gingl et al. [3] discovered that $SrAl_2H_2$ is a Zintl-type hydride. This compound is synthesized by exposing the intermetallic $SrAl_2$ to hydrogen gas under 50bar and rising the reaction temperature slowly from 100 to 200°C [3]. It's crystallizes with trigonal structure in $P\bar{3}m1$ space group (see Figure 1-a).

Alkali metal aluminum hydride can absorb and desorb large amount of hydrogen reversibly at moderate conditions.

In order to optimize the hydrogen storage in $SrAl_2H_2$ compound several experimental and computational works have been realized. Gingl et al. [3] have studied the hydrogenation of $SrAl_2$ by X-ray powder diffraction and found that the reaction proceeds in three steps. Orgaz et al. [5] investigated the electronic structure of $SrAl_2H_2$, Ca_3SnH_2, and Ca_5Sn_3H by means of the full-potential linearized augmented-plane-wave method. They found the $SrAl_2H_2$ and Ca_5Sn_3H hydrides are metallic and Ca_3SnH_2 is a small-gap semiconductor. The bonding characteristics study of SrAlSiH, $SrAl_2H_2$, $SrGa_2H_2$ and $BaGa_2H_2$ using DFT calculations were done by Subedi et al. [6]. Their results indicate that in $SrAl_2H_2$ the Al layers are nominally neutral i.e not polyanionic.

In this study, all the computations have been done using the ABINIT code [7] based on pseudopotentials and plane waves in density functional theory (DFT) [8]. Fritz–Haber–Institute GGA pseudopotentials [9] are used to represent atomic cores. The enthalpy formation is calculated using LDA approximation of Troullier and Martins [10].The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 40 hartree and a 6 × 6 ×6 grid for k-point was used.

The aim of this work is to contribute to the investigation of the zintl phase hydride $SrAl_2H_2$ by calculating and analyzing the electronic properties and enthalpies formation of this compound.

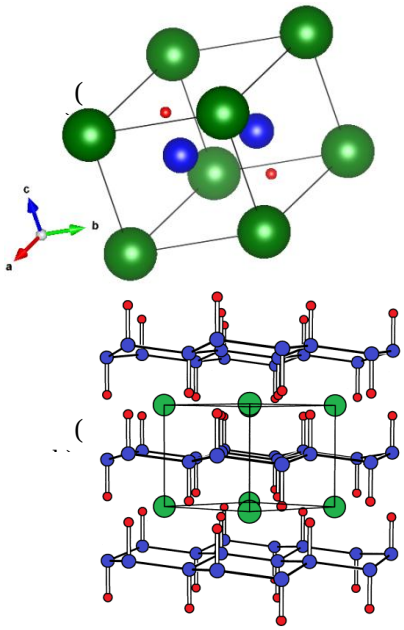


Figure 1: $SrAl_2H_2$ structure (green: Sr, blue: Al, red: H), (a) our work, (b) taken from ref [3]

Results and discussions

Crystal structure

The crystal structure of $SrAl_2H_2$ is known and occurs in a trigonal space group $P\bar{3}m1$ (164) with Sr (0, 0, 0), Al (1/3, 2/3, 0.4608) and H (1/3, 2/3, 0.0964) and has a cell parameters of a=4.5283(Å), c=4.7215(Å) which are experimentally determined [3]. The relaxed structure obtained in this study is in good agreement with the reported structure from the experiments [3] (a=4.5949(Å) and c=4.7909(Å), Al (1/3 2/3 0.4570), H (1/3 2/3 0.0849)). Also the lattice constants of Sr and Al which have a fcc structure are taken from reference [11].

Al atoms are arranged as a slightly puckered graphitic layer. Additionally each Al atom is coordinated to one hydrogen atom. In $SrAl_2$ the puckered Al hexagonal layers are connected by a long Al-Al interlayer bonds which are cut in $SrAl_2H_2$ and terminated by hydrogen atoms (see Figure 1-b).

In Table I, we reported the bonding distances of each element that composes the $SrAl_2H_2$ compound.

Bondings	Distance (Å)
Sr-Al	3.4396
Sr-H	2.6838
Al-H	1.7826
Al-Al	2.6846
H-H	4.7809

Table 1: Bonding distance in $SrAl_2H_2$

The formation energy (enthalpy formation)

We have take into account two reactions related to the formation of the zintl phase hydride $SrAl_2H_2$:

$Sr + 2Al + H_2 \rightarrow SrAl_2H_2$ (1)[a]

$SrAl_2 + H_2 \rightarrow SrAl_2H_2$ (2)[b]

To calculate the formation heat of the reaction (1) we subtracted the total energies of the pure elements Sr, Al and the hydrogen molecule from their hydride $SrAl_2H_2$.

Table 2 contains the total energy and the formation enthalpy computed of $SrAl_2H_2$ for two different reactions. The total energy of the hydrogen molecule is -31.4020 (eV) and has been also calculated. The heat formation of the second reaction is much less than the first one, making the reaction (2) more favorable for the formation of $SrAl_2H_2$ compound.

Elements	Total Energy (eV)	Enthalpy Formation (kJ/mol)
Sr	-576.4821	-
Al	-64.0722	-
H_2	-30.8229	-
$SrAl_2$	-712.3662	
$SrAl_2H_2$	-743.6903	795.1257[a] 48.3584[b]

Table 2: Calculated heat of formation of $SrAl_2H_2$

Electronic structure

The total and the partial densities of state for $SrAl_2H_2$ are plotted in "Fig. 2" and "Fig. 3" which are similar to that obtained previously by Orgaz and Aburto [5], Subedi and Singh [6]. The electronic structure is metallic without the energy gap. We can also say that $SrAl_2H_2$ is weakly metallic because the DOS reach a value of 0.0016 (states/eV/cell) at the Fermi level (-0.3129 eV).

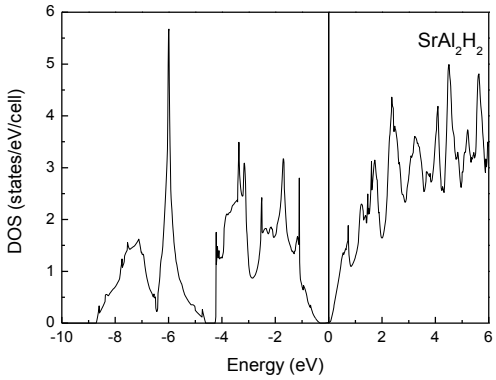


Figure 2: The total density of state of $SrAl_2H_2$

In Figure 2 at the bottom of energy scale, we can see two peaks; the first concerns the H-s/Al-s bonding interaction. This is followed by a second peak mainly produced by the H-s states, where a non-negligible and small Al-s,p orbital contribution is present. This can be seen in the PDOS plots of Figure 3. The second part of the DOS plot is well separated from the first. Two main contributions appear in increasing order of energy. First, there is a complex H-s/Al-s orbital interaction including small Sr-d and Al-p contributions. This is completed by the Al-p states up to the Fermi energy. The PDOS of Sr has a very small contribution to the valance band from the region -10 (eV) to 0.

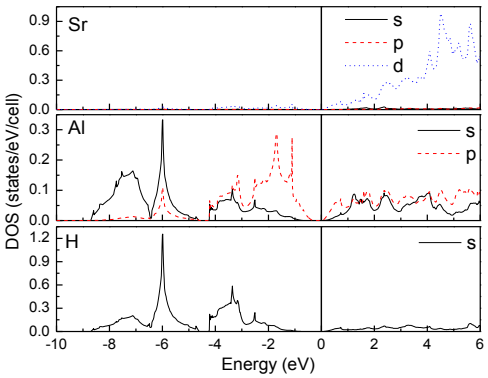


Figure 3: Partial density of state for $SrAl_2H_2$

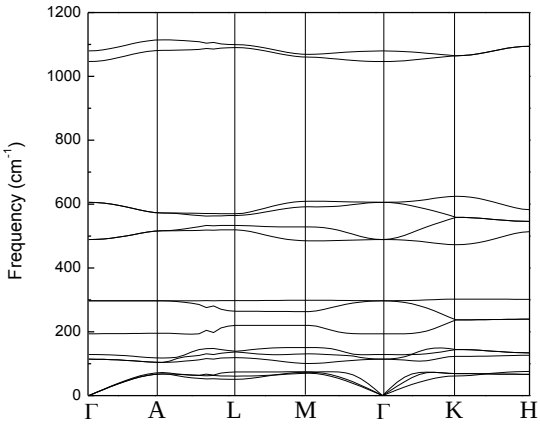


Figure 4: Calculated phonon dispersion curves along symmetry lines for $SrAl_2H_2$

The dynamical Properties

Phonon frequencies were subsequently obtained using the linear-response method, which avoids the use of supercells and allows the calculations of the dynamical matrix at arbitrary q vectors. These were later employed to obtain by interpolation, the phonon frequencies at arbitrary points in reciprocal space and the phonon-dispersion relations. The phonon densities of state (DOS) could be obtained from the phonon-dispersion curves.

The phonon dispersion curves for $SrAl_2H_2$ along several high-symmetry lines are plotted in "Fig. 4". These results agree qualitatively with phonon DOS of $SrAl_2H_2$ reported by Subedi et al. [6] using linear response as implemented in the QUANTUM-ESPRESSO package [6], and by Lee et al. [12] using direct method with supercells and plane-wave basis set in the VASP code [12].

Firstly, it can be noticed the presence of four separate bands due to a large mass difference between H atoms and (Sr, Al) atoms. Secondly, the $SrAl_2H_2$ is dynamically stable since throughout the Brillouin zone all phonon frequencies are positive. The phonon frequencies are in the range of 0-1080 cm^{-1}.

It is noticed also the existence of frequency gap between optical and acoustical modes due to the mass difference between Sr and Al atoms. The frequency-gap between the acoustic and optical branches depends on the mass difference.

Thermal properties

Thermodynamic functions of $SrAl_2H_2$, could be determined by the whole phonon spectrum. In the present study, the phonon contribution to the Helmholtz free energy F, the internal energy E, the entropy S and the constant-volume specific heat C*v*, at temperature T, are calculated using the harmonic approximation [13]:

$$F = k_B T \int_0^{\omega_{\max}} \ln(2\sinh(\frac{\hbar\omega}{2k_B T}))g(\omega)d\omega \quad (1)$$

$$E = \frac{\hbar}{2}\int_0^{\omega_{\max}} \omega\coth(\frac{\hbar\omega}{2k_B T})g(\omega)d\omega \quad (2)$$

$$S = k_B \int_0^{\omega_{\max}} \left[\frac{\hbar\omega}{2k_B T}\coth(\frac{\hbar\omega}{2k_B T}) - \ln(2\sinh\frac{\hbar\omega}{2k_B T}\right]g(\omega)d\omega \quad (3)$$

$$C_v = k_B \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{2k_B T}\right)^2 \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_B T}\right)g(\omega)d\omega \quad (4)$$

Where:

k_B is the Boltzman constant. $\omega_{\max}$ is the largest phonon frequency.

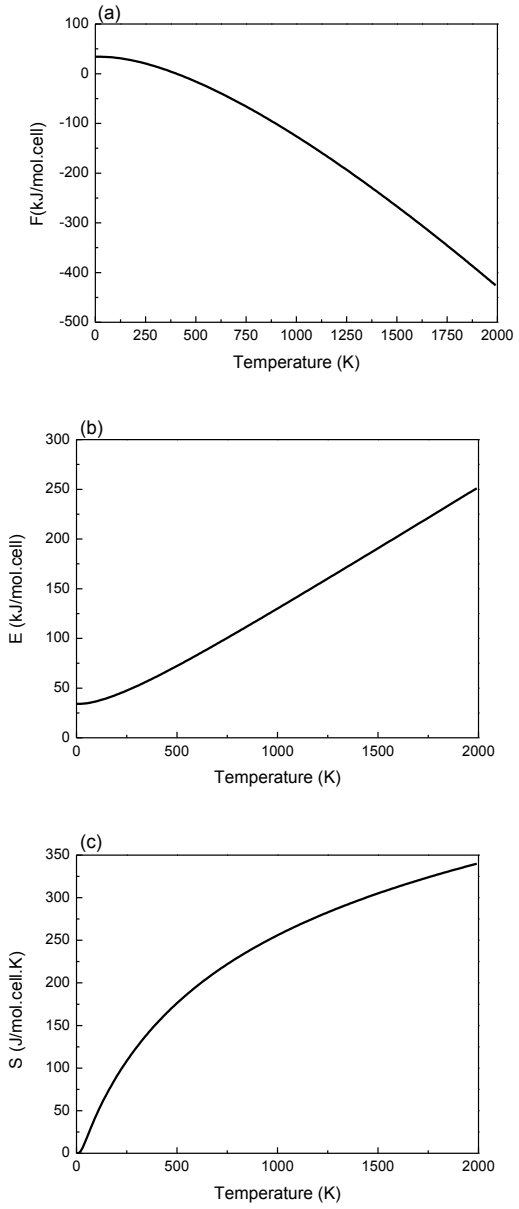
$g(\omega)$ is the normalized phonon density of states with $\int_0^{\omega_{\max}} g(\omega)d\omega = 1$.

The obtained results are shown in "Fig. 5". When temperature increases; the calculated free energy F for $SrAl_2H_2$ decreases gradually. However, the calculated E and S increase continually. F and E at zero temperature represent the zero-point motion [11] and the calculated value is 34.127 kJ/mol.

The calculated C_v exhibits the expected T^3 power-law behavior C_v at lower temperatures, for higher temperatures reaches a classic limit of 123.365 J/mol.cell.K, in good agreement with

the classic law of Dulong-Petit at higher temperatures.

Unfortunately, no experimental values of C_v for $SrAl_2H_2$ are found. Our calculated values can be seen as a prediction for future investigations.



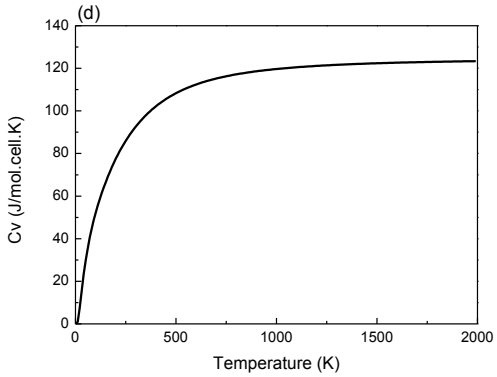


Figure 5: The calculated phonon contribution to the Helmholtz free energy F (a), the internal energy E (b), the entropy S (c) and the constant-volume specific heat C_v (d)

Conclusion

In this work we report the electronic structure calculations for $SrAl_2H_2$ compound using the ABINIT code. The electronic structure is obtained from GGA, generalized gradient approximation. Formation energy for $SrAl_2H_2$ is calculated for two different possible reaction pathways. This allowed us to know that is better to synthesize our compound from the precursor material $SrAl_2$ than from each element that composes the zintl phase hydride. Also from the plot of the DOS, we noted that $SrAl_2H_2$ has no gap which means that our compound is a metallic and the valence band is dominated by hydrogen atoms. The phonon frequencies and phonon density of states at the Brillouin zone have been obtained using the density functional perturbation theory. No experimental values of the thermodynamic functions for $SrAl_2H_2$ compound have been reported in the literature; thereby the calculated values could be used for future studies.

References:

[1] B. Bogdanovic, R. A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys. Compd, Vol. 302, pp. 36-58, 2000.

[2] K. J. Gross, G. Sandrock, G. J. Thomas, J. Alloys. Compd, Vol. 330, pp. 691-695, 2002.

[3] F. Gingl, T. Vogt, E. Akiba, "Trigonal $SrAl_2H_2$: the first Zintl phase hydride", J. Alloys. Compd, vol. 306, pp. 127-132, 2000.

[4] B. Bogdanovic and M. Schwickardi, J. Alloys. Compd, 253–254: 1–9,1997.

[5] E. Orgaz and A. Aburto, "Bonding Properties of the New Zintl-Phase Hydrides", Int. J. Quantum. Chem, vol. 101, no. 6, pp. 783–792, 2005.

[6] A. Subedi and D. J. Singh, "Bonding in Zintl phase hydrides: Density functional calculations for SrAlSiH, $SrAl_2H_2$, $SrGa_2H_2$, and $BaGa_2H_2$", Phy. Rev. B, vol. 78, pp. 1-7 (045106), 2008.

[7] X. Gonze, J.M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Gohsez, J.Y. Raty, D.C. Allan, " First-principles computation of material properties: the ABINIT software project", Comput. Mater. Sci, Vol. 25, no. 3, pp. 478-492, 2002.
[8] W. Kohn, L.J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects", Phys. Rev, Vol. 140, no. 4A, pp. A1133-A1138, 1965.
[9] M. Fuchs, M. Scheffle, Comput. Phys. Comm. 119 (1999) 67
[10] N. Troullier, J. L. Martins, "Efficient pseudopotentials for plane-wave calculations", Phys. Rev. B, Vol. 43, No. 3, Jan. 1991, pp. 1993-2006.
[11] C. Kittel, Introduction to Solid State Physics, John Wiley & sons Inc., USA: 2005.
[12] M. H. Lee, O. F. Sankey, T. Bjorling, D. Moser, D. Noreus, S. F. Parker, and U. Häussermann, Inorg. Chem. 46, 6987, 2007.
[13] C. Lee, X. Gonze, Phys. Rev. B 51, 8610, 1995.