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Electronic properties of Zintl phase hydride for hydrogen storage

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Abstract - *In this paper we report the $SrAl_2H_2$ electronic properties which is a Zintl phase hydride in frame of the Density Functional Theory 'DFT' using the plane wave and pseudo potential method. We discuss the chemical bond nature using total and partial density of states 'DOS and PDOS', also we calculated the bonding distance of hydride compound and its precursor SrAl2 and the enthalpy formation of the $SrAl_2H_2$ for hydrogen storage.*

Résumé - *Dans ce travail, nous avons étudié les propriétés électroniques du $SrAl_2H_2$ qui est un composé hydride de phase Zintl dans le cadre de la Théorie de la Fonctionnelle de la Densité (DFT) en utilisant la méthode des ondes planes et du pseudo potentiel. Grâce à la densité d'état totale et partielle 'DOS et PDOS', nous avons pu discuter la nature des liaisons chimiques. Nous avons aussi calculé les distances des liaisons du composé hydride et de son prédécesseur le $SrAl_2$ et son enthalpie de formation pour une application dans le domaine du stockage de l'hydrogène.*

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

1. INTRODUCTION

Aluminum hydrides have been a strong candidate for hydrogen storage. These compounds have satisfactory hydrogen content for storage but complications with kinetics and reversibility have made them slow to reach practical storage applications.

When hydrogen is absorbed in a metal hydride, the bond between the atoms in the H_2 molecule is broken as electrons from the metal lattice is filled into the anti bonding orbitals of the H_2 molecule and the H atoms are intercalated into the interstitial sites between the metal atoms.

The bond between the hydrogen and the metal atoms should be too strong to make it possible for hydrogen to be stored and released at temperatures and pressures close to ambient.

$SrAl_2H_2$ which is a Zintl phase compound was synthesized by hydrogenating of its precursor $SrAl_2$ at about 463 K under pressure of 50 bars [1]. Increasing the hydrogenation temperature to 513 K, $SrAl_2H_2$ further absorbs hydrogen to form Sr_2AlH_7 and Al.

In order to optimize the hydrogen storage in $SrAl_2H_2$ compound many experimental and computational works have been realized. Gingl *et al.* [1] have studied the hydrogenation of $SrAl_2$ by X-ray powder diffraction and found that the reaction proceeds in three steps. $SrAl_2H_2$ is formed in the first step starting at about 190 °C and as the temperature is raised; the compound is further hydrogenated to a second hydride phase in different structure with higher hydrogen content.

Orgaz *et al.* [2] 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. Lee *et al.* [3, 4] have investigated the vibrational properties of $SrAl_2H_2$ and SrAlSiH by means of inelastic neutron scattering 'INS' and first-principles calculations.

The results showed that SrAlSiH is characterized by very weakly dispersed Al-H modes with well-resolved overtones, while $SrAl_2H_2$ yields a solid-state dispersed phonon spectrum. 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.* [5]. Their results indicate that in $SrAl_2H_2$ the Al layers are nominally neutral, i.e not polyanionic.

The Zintl phase alloy $SrAl_2$ can absorb hydrogen to form $SrAl_2H_2$ or Sr_2AlH_7, the hydrogenation kinetics is quite slow especially for the latter one. Zhu *et al.* [6, 7] studied experimentally the structural and hydrogenation properties of the Zintl phase alloy $SrAl_2$.

Zhang *et al.* [8] synthesized the Sr_2AlH_7 hydride by ball milling of a Sr_2Al alloy under hydrogen but it was followed by further hydrogenation of different types of samples.

The aim of our work is to investigate the electronic properties of $SrAl_2H_2$ and its precursor $SrAl_2$ by calculating the heat formation and the bonding distances and also discussing the chemical bond nature using total and partial density of states 'DOS' of each compound.

2. METHODOLOGY

In this study, all the computations have been done using the Abinit code [9] based on pseudo potentials and plane waves in density functional theory 'DFT' [10]. We have used the local density approximation 'LDA' of Troullier *et al.* [11] to approximate the exchange-correlation energy, where the Sr (3d, 4p, 5s), Al (3s, 3p) and H (1s) orbitals are treated as valence states.

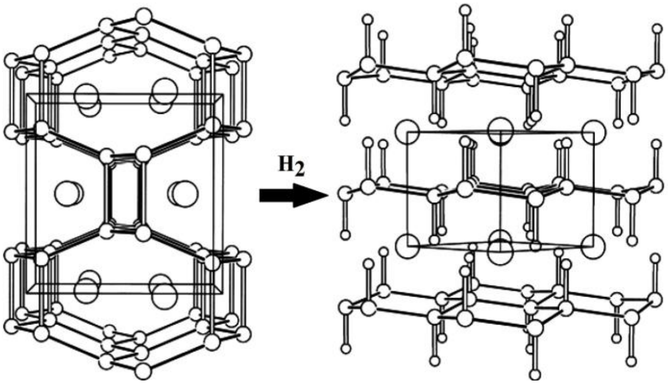

Fig. 1: Crystal structures of $SrAl_2$ (left) and $SrAl_2H_2$ (right), big, medium and small circles denote Sr, Al, and H atoms, respectively [1]

The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 40 Hartree. Integrals over the Brillouin zone were approximated by sums of 6×6×6 mesh of special k-point.

3. RESULTS AND DISCUSSIONS

3.1 Crystal structure

The crystal structure of $SrAl_2H_2$ is known and occurs in a trigonal space group $P\bar{3}m1$ (164). 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 (Fig. 1).

The relaxed structural parameters agreed very well with the experimentally and computationally determined ones (**Table 1**).

Table 1: Calculated relaxed structural parameters for $SrAl_2H_2$ compared with computational and experimental parameters

$SrAl_2H_2$	**Our work**	**Compt**			**Exptl [2]**
a (A°)	4.6868	4.5267 [4]	4.5280 [6]	4.5289 [12]	4.5283
c (A°)	4.8867	4.7195 [4]	4.7220 [6]	4.7248 [12]	4.7215
Al (1/3, 2/3, z)	0.4642	0.4613 [4]	0.4608 [6]	0.4614 [12]	0.4589
H (1/3, 2/3, z)	0.0952	0.0978 [4]	0.0964 [6]	0.0988 [12]	0.0976

In **Table 2**, we reported the bonding distances of each element that composes the $SrAl_2H_2$ compound and its precursor. As already mentioned in Gingl *et al.* [1] work, our Al-Al bond length of $SrAl_2H_2$ (2.72 A°) is considerably shorter than the ones in $SrAl_2$ (2.84 A°) and the distances between Sr and Al are slightly longer ($SrAl_2$: 3.42 A°, $SrAl_2H_2$: 3.53 A°).

Table 2: Bonding distances

Bond (A°)	**Our work**		**Exptl [2]**	
	$SRAl_2H_2$	$SrAl_2$	$SRAl_2H_2$	$SrAl_2$
Sr-Al	3.53096	3.42357	3.654	3.59
Sr-H	2.74562	-	2.653	-
Al-H	1.80319	-	1.706	-
Al-Al	2.72845	2.84744	2.641	2.79

3.2 The formation energy (enthalpy formation)

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

$$Sr + 2Al + H_2 \rightarrow SrAl_2H_2 \tag{1}$$

$$SrAl_2 + H_2 \rightarrow SrAl_2H_2 \tag{2}$$

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 $SrAl_2H_3$, and we have done the same with the second one.

$$\Delta H\,(SrAl_2H_2) = \Delta E\,(SrAl_2H_2) - \Delta E\,(Sr) - 2\Delta E\,(Al) - \Delta E\,(H_2) \qquad (3)$$

Table 3 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 -30.8229 eV and has been also calculated. We noted that 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.

Table 3: Calculated heat of formation of $SrAl_2H_2$

Elément	**Total energy (eV)**	**Enthalpie formation (kJ/mol)**
Sr	-576.4821	-
Al	-64.0722	-
H_2	-30.8229	-
$SRAl_2$	-712.5062	-
$SrAl_2H_2$	-743.7879	804.4945 44.2674

3.3 Electronic structure

In this section the lattice parameters were calculated and reported in **Table 1**. 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 *et al.* [2], Subedi *et al.* [5]. The electronic structure is metallic without the energy gap. This is in agreement with the computational and experimental work of Lee *et al*. [3]. We can also say that $SrAl_2H_2$ is weakly metallic because the DOS reach a value of 0.0354 (states/eV/cell) at the Fermi level [2].

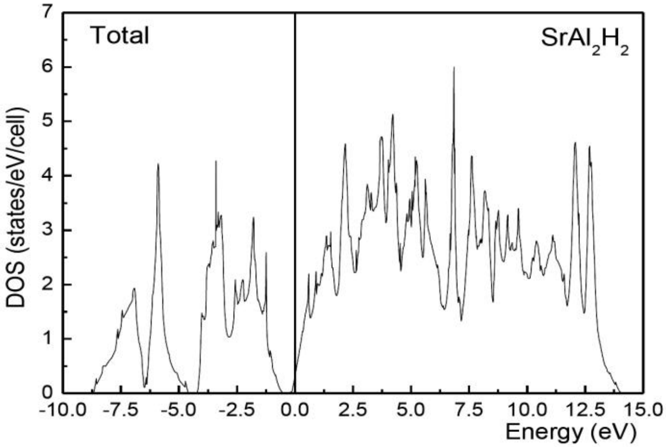

Fig. 2: The total density of state of $SrAl_2H_2$

In Fig. 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 Fig. 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 valence band from the region -10 (eV) to 0.

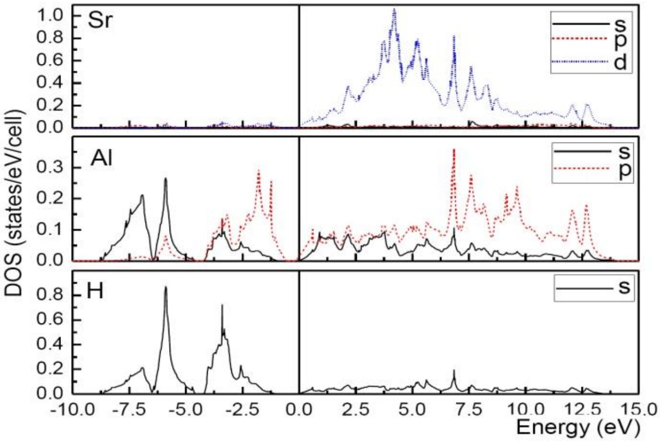

Fig. 3: Partial density of state for $SrAl_2H_2$

4. CONCLUSION

In this work we report the electronic structure calculations for the ternary hydride $SrAl_2H_2$ using the ABINIT code. The electronic structure is obtained from LDA total-energy minimizations. 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 its precursor $SrAl_2$ 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.

NOMENCLATURE

Sr: Strontium	Al: Aluminum
H: Hydrogen	a , b : Cell parameters
ΔH : Enthalpy formation	A° : Interatomic distance unit
DOS : Total density of charge	PDOS : Partial density of charge
eV : Energy unit	state/eV/cell : Density of state unit

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