A COMPARATIVE STUDY OF THE ELECTRONIC PROPERTIES OF PEROVSKITE HYDRIDES OF TYPE ABH_3

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DECLARATION

I do hereby declare that the project work incorporated in the thesis entitled ”A COMPARATIVE STUDY OF THE ELECTRONIC PROPERTIES OF PEROVSKITE HYDRIDES OF TYPE ABH_3” is a work carried out by us in the Department of Physics, NIT Rourkela, under the supervision and guidance of Biplab Ganguli.

Date: Shiv Kumar Sahoo

DEPARTMENT OF PHYSICS AND ASTRONOMY

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CERTIFICATE

This is to certify that the project thesis entitled," A COMPARATIVE STUDY OF THE ELECTRONIC PROPERTIES OF PEROVSKITE HYDRIDES OF TYPE ABH_3" submitted by Shiv Kumar Sahoo, INTEGRATED M.Sc. student of Department of Physics and Astronomy, National Institute of Technology, Rourkela in partial fulfillment of the requirements for the award of degree of M.Sc. in Physics has been carried out by him under my supervision and guidance. The results incorporated in the thesis have been reproduced by TB-LMTO code.

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DATE Shiv Kumar Sahoo

ABSTRACT

The electronic properties of some Perovskite hydrides; $LiMgH_3, KMgH_{3,} LiCaH_3$ are studied using the Tight Binding Approximation included in the TB-LMTO program. The band structures and density of states are calculated. From the density of states calculation we found out the band gap. Also from the Fermi energy level we interpreted whether the compound has metallic behavior or not. Finally,a comparative study of their electronic properties is carried out.

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1. INTRODUCTION

Materials with high hydrogen content are of great importance. They can really solve the problem of storing hydrogen which can act as a great substitute to carbon related fuels. The hydrides formed by the elements of gr I-III can be used to store hydrogen because of their light weight [1]. Having a very simple cubic structure as well as light weight the perovskites like $CsCaH_3$, $RbCaH_3$, $KMgH_3$, $BaLiH_3$, are widely studied[2,5].

Light mass of hydrogen influences the electronic properties of metal hydrides. There is very strong electron phonon interaction especially if the hydrides show metallic behaviour[6]. In the compound ABH_3 if we change A or B or both then the density of states is also going to change. A comparative study of the electronic properties is done by changing both A and B.

COMPUTATIONAL METHODS

We applied first principle computational technique which is based on the density functional theory. This density functional theory is applied to tight binding linear muffin tin Hamiltonian. This is included in the TB-LMTO-ASA program [7]. TB stands for tight binding method. LMTO stands for linear muffin tin orbital. ASA for atomic spheres approximation. In this a muffin tin potential is defined as

$$U(r) = V(|r - R|), \quad when|r - R| < r_0 \text{(Core or atomic region)}$$

$$= V(r_0) = 0, \quad when|r - R| > r_0 \text{ (the interstitial region)}$$

Where r_0 is less than half the nearest neighbor distance.

Previously the muffin tin orbitals were used for first principle calculation of band structure. The minimal but long ranged base of muffin tin orbitals was successfully transformed into a tight binding base [8]. The bands in a muffin tin potential is calculated by the green function method of KKR (KKR method).

Ordinary Schrodinger equation is written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(r)\right)\Psi_k(r) = \varepsilon(k)\Psi_k(r)$$

It is also equivalent to write the Schrodinger equation as

$\Psi_k(r) = \int dr'\, G_{e(k)}(r - r')U(r')\Psi_k(r')$ where U(r') is the muffin tin potential.

This is possible as G satisfies

$$\left(\varepsilon + \frac{\hbar^2 \nabla^2}{2m}\right) G(r - r') = \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}')$$

The band structures and density of states of $LiMgH_3$, $KMgH_{3,}$ $LiCaH_3$ was calculated using the TB-LMTO program. The development of the program has been managed by Ole Krogh Andersen of Max Planck Insti-tut fu'r Festkorperforschung, Stuttgart, Germany; the first version was constructed mostly by Mark van Schilfgaarde during 1987-88. This software is a free software for scientific and/ or educational purposes. This program was written using the powerful FORTRAN language within ANSI-77 standards. The energy gaps found by using the program were compared with available experimental/theoretical data.

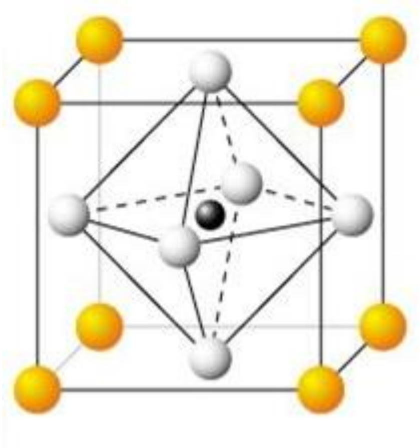
3. LITERATURE SURVEY

3.1 PEROVSKITE STRUCTURE

Perovskite family has the structure as that of $CaTiO_3$. The ideal crystal structure of ABX_3 consists of an octahedral formed by one B atom present in the interstitial position and X atoms present at face centered positions with A atoms taking the position of corners of the cube . most of the perovskites do not have the ideal structure but have distorted shapes . Because of their ability to accommodate almost all the elements of the periodic table has led to great interest in these compoundsss [9].

Crystal structure of perovskite-

A large oxide ion in combination with a small radii metal ion forms a closed pack crystal structure with the metal ion present in the centre surrounded by oxygen atoms.. In these crystal structures the metal ions remain in interstitial position with the oxygen atom taking the face centered positions.. The chemical formula can be written as ABX3 and the crystal structure is called perovskite. X is often oxygen but also other larger ions can take part to form perovskites.

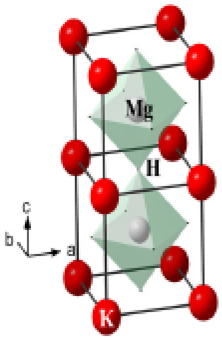


In the above figure , for the general formula ABX_3 , the X atoms lie at the face centered position of the cube. Since it is shared by 2 cells so the contribution of six X atoms to one cell is 3. The B atoms lies at the centre of the cube. The A atoms are located in the corner position. It is shared by 8 cells. So the contribution of eight A atoms to one cell is 1. So the formula for a perovskite is ABX_3.

3.2 $KMgH_3$

In recent years complex hydrides of group I-III have become more interesting. These are

interesting because of their potential use as hydrogen storage materials because of their light weight. A lot of research is being carried upon hydrides that functionalize at low temperatures. Perovskite hydrides are of great impotance because of their relatively simple cubic structure. Magnesium based perovskites are more interesting because of light weight and low cost production.

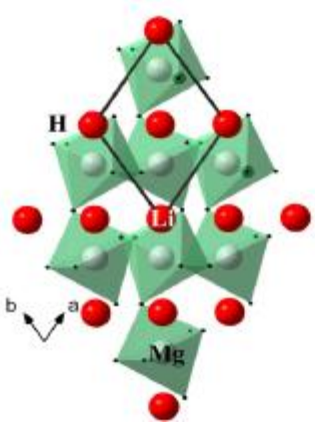


Crystal structure of $KMgH_3$

structural information of hydrides are limited due to complexities involved in deriving hydrogen positions[10]. However, most of these materials are not we ll-described and thermodynamic data are absent[11]. For Mg-based Perovskite hydride $KMgH_3$, we don't have any experimental or theoretical data to predict the exact stable state. The perovskite- type $KMgH_3$ crystals possess the space group Pm-3m. The structural properties of different states of $KMgH_3$are the following: first, the structure unstable- $KMgH_3$(US1) with atomic position K (0, 0, 0),Mg (1/2, 1/2, 1/2), and H (0, 1/2, 1/2) given; secondly, the unstable- $KMgH_3$ (US2) with atomic position K (0, 0, 0),Mg (1/2, 1/2, 1/2), and H (1/2, 0, 0),; and thirdly, the stable- $KMgH_3$ (Stable) with atomic position Mg (0, 0, 0), K (1/2, 1/2, 1/2),and H (1/2, 0, 0)

3.3 $LiMgH_3$

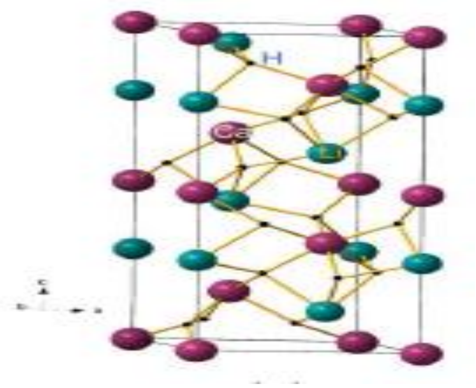
Similar to $KMgH_3$ there is great interest in hydrides containing lithium instead of potassium. Most of the previous work was done on studying the electronic properties of $LiBeH_3$. It was finally concluded that $LiBeH_3$ is an insulator. Focus has now shifted to $LiMgH_3$.



Crystal structure of $LiMgH_3$

Structure of $LiMgH_3$ is rhombohedral. Its space group is R3c. Its lattice constant is a = 4.958 A and c= 13.337 A. Position of Li: (0,0,0.2887). Position of Mg (0,0,0) . Position of H(.0376,.3626,.5637).

3.4 $LiCaH_3$



Structure of $LiCaH_3$

Among the MCaH3 phases, in LiCaH3 and NaCaH3 phases are the prime candidates to be used as hydrogen storage device as their hydrogen storing ability is more. The rest of the considered phases have relatively low wt.% of H content. Due to wide scale application in electronics industry we need to find the structural phase stability of the perovskites. Experimentally it is found that for the RbCaH3 and CsCaH3 phases, CaTiO3-type atomic arrangement has the lowest energy than the other considered structure types[13].

So the space group of $LiCaH_3$ is pm-3m with lattice constant 4.07 A[6] . The atomic positions are Li: (0,0,0). Position of Ca(0.5,0.5,0.5). Position of H(0,0.5,0.5).

4 Results and Discussion

4.1 $KMgH_3$

The electronic band structure of perovskite hydride $KMgH_3$ in its three phases was found.

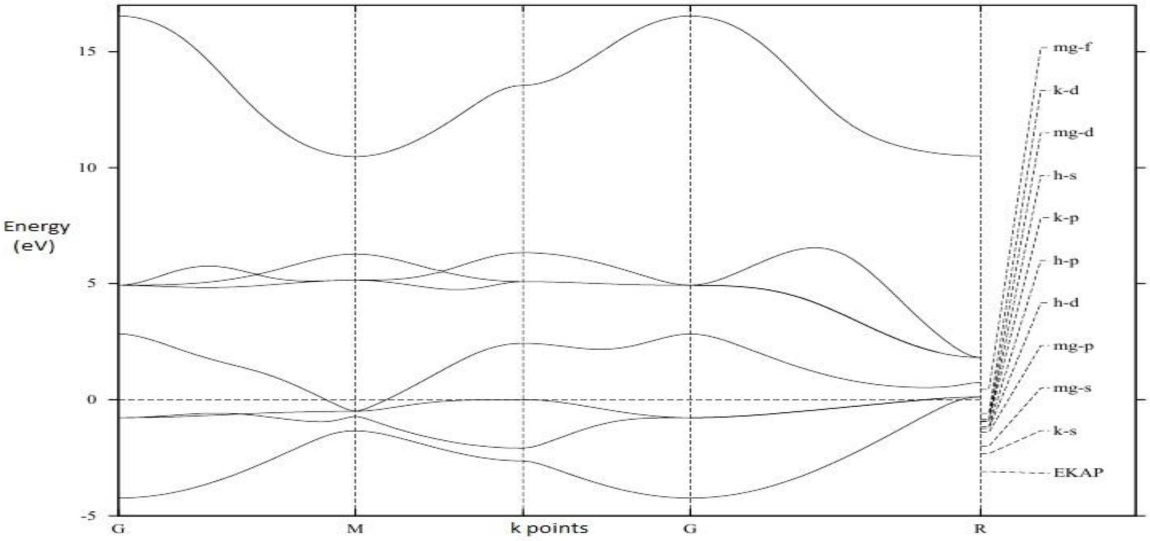


Fig 1. Electronic band structure of $KMgH_3$ unstable (US2) state.

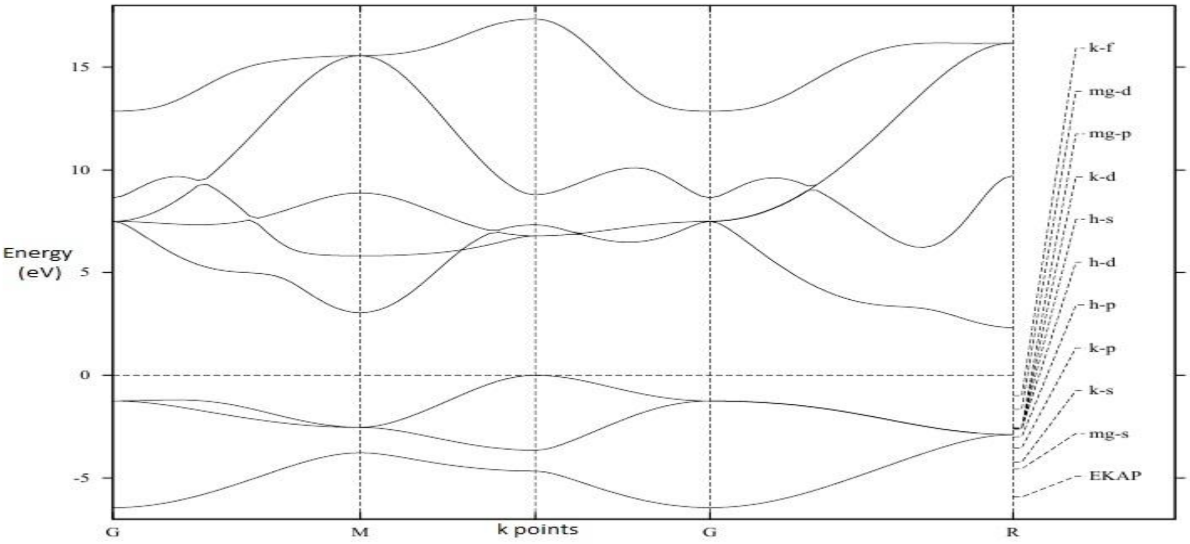


Fig2. Electronic band structure of $KMgH_3$ unstable(US1) state

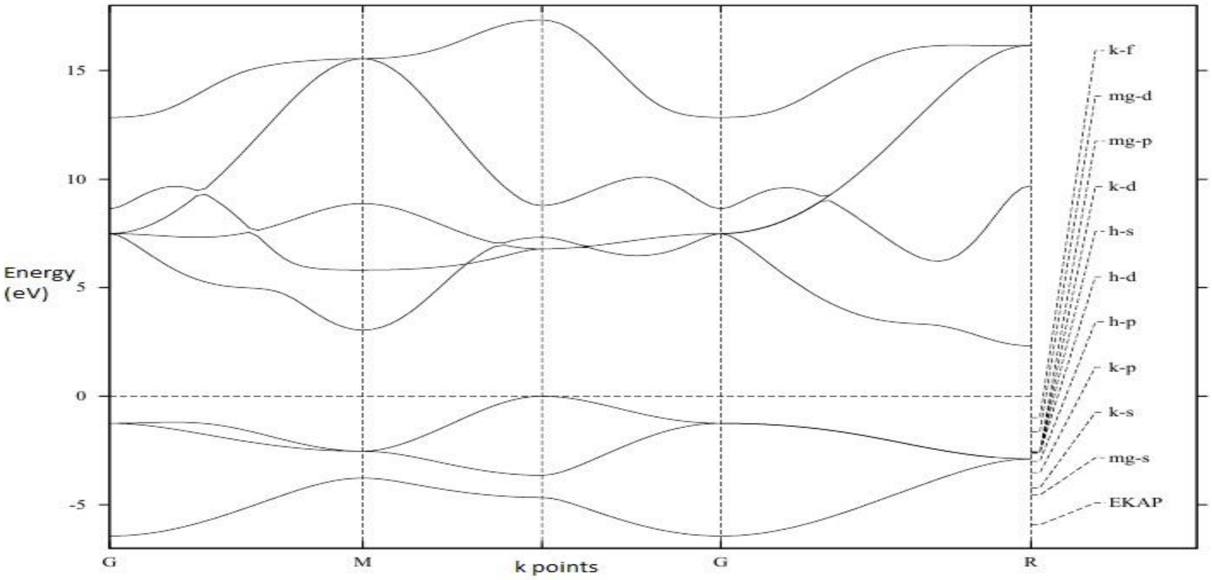


Fig 3. Electronic band structure of $KMgH_3$ stable state.

The band structures of US(1) phase and stable phase was found to be very similar. One more important conclusion from these band structures was found to that: the unstable state US(2) has no energy gap i.e it behaves like a metal. Whereas, US(1) and stable state was found to have energy gap. So they are not insulator. To find whether they would behave like semiconductors or insulators, the density of states were then calculated:

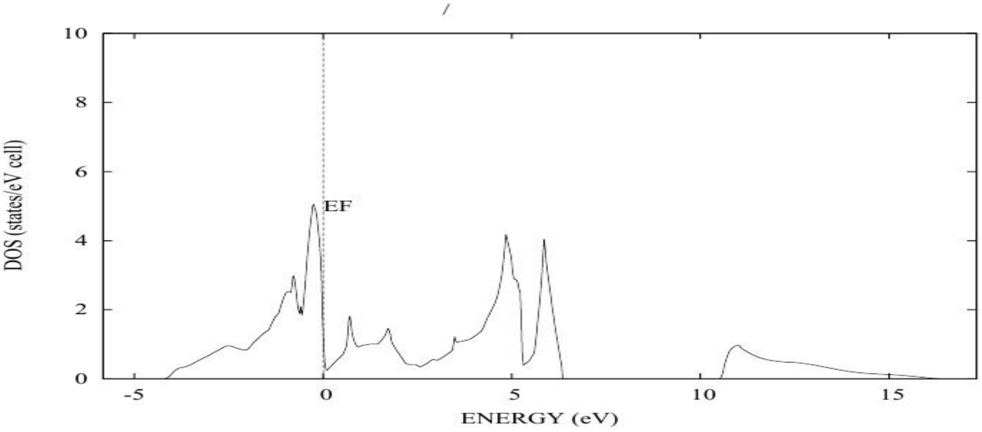


Fig 4. The density of states of $KMgH_3$ US(2) state.

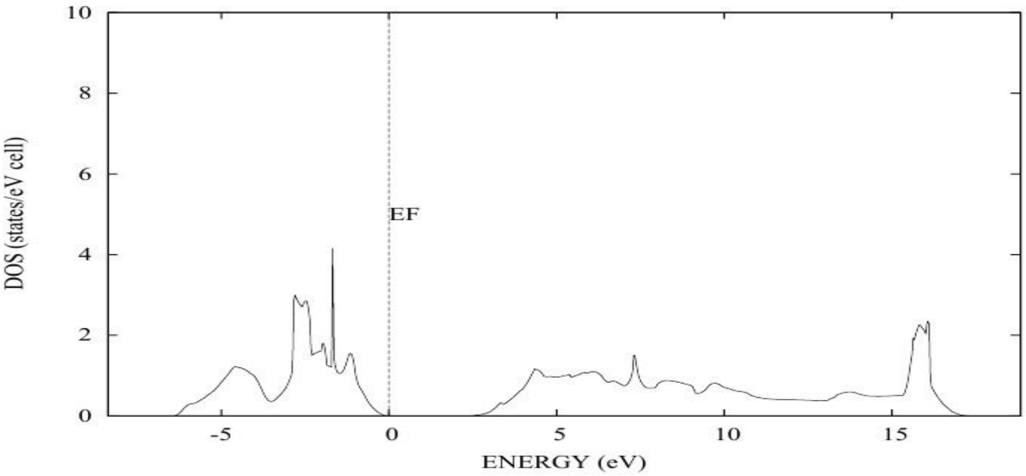


Fig 5. Density of states of $KMgH_3$ US(1) state.

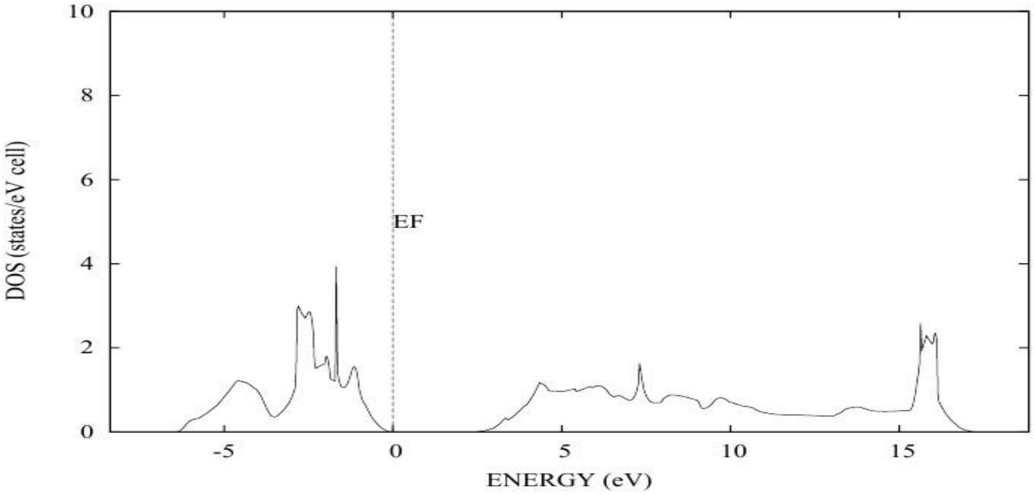


Fig 6. Density of states of $KMgH_3$ stable state

From the above findings we are now confirmed that near the Fermi level the there is no energy gap in US(2) state i.e it shows metallic behavior. The energy gap in both US(1) and US(2) states are nearly same; near about 2.5 eV. Similar work was carried out by Ali H. Reshak et.al and they found the energy gap to be 2.53e V. The US(1) state and the stable state show semiconductor behavior[12].

By changing the hydrogen position from (0.5,0.5,0) in US(1) state to (0.5,0,0) in stable state the electronic properties remained the same. We don't see any marked difference. So we can describe the $KMgH_3$ perovskite by only the stable state. The energy gap of 2.5 eV is generally bit high for a semiconductor. So $KMgH_3$ is not like a traditional semiconductor. To have a better understanding of the contribution of hydrogen , magnesium and potassium PDOS(partial density of states) can be calculated. Ali H. Reshak et.al[12] have found, by calculating PDOS, that the contribution to the valence band was maximum by s-state of hydrogen, with very less contribution from potassium and magnesium. Whereas maximum contribution to conduction band was from d – state of potassium. They have also found out that the energy states of magnesium in valence bands are non-degenerate where as they are degenerate in case of conduction band.

4.2 $LiMgH_3$

The electronic band structure of $LiMgH_3$ was calculated.

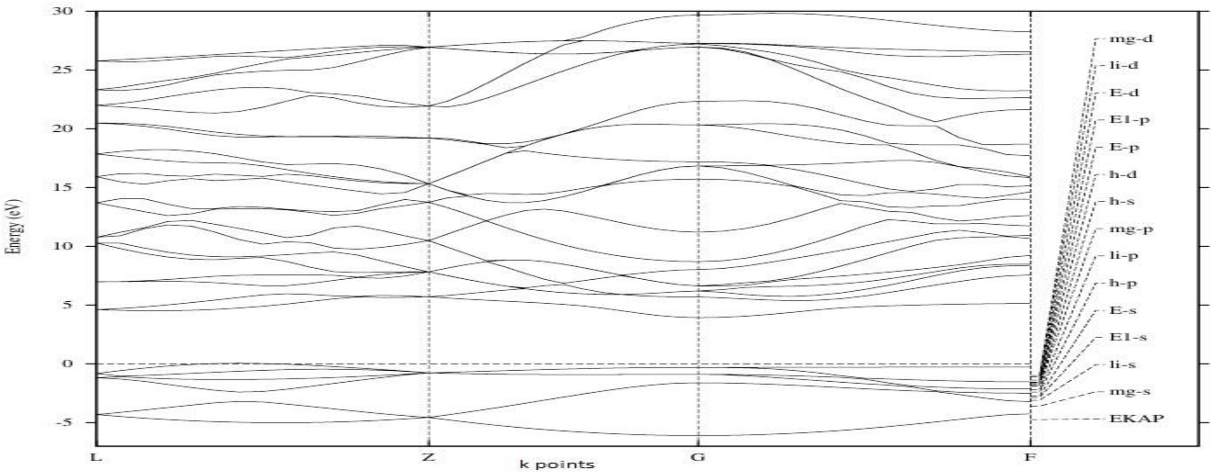
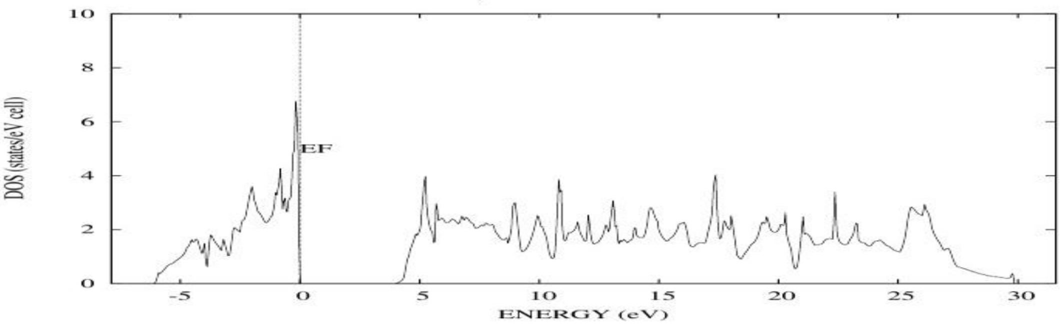


Fig 7. Electronic band structure of $LiMgH_3$

Density of states of $LiMgH_3$ was also calculated to find the energy gap.



We find that there is band gap between the valence band and the conduction band from the band structure calculation. From the density of states calculation we find that the energy gap comes around 4 e V. Here also we find that the fermi energy line is in the valence band. This confirms non metallic behaviour.

P. Vajeeston et.al.[14] have reported that the energy gap of $LiMgH_3$ is 3.98 e V. This indicates that $LiMgH_3$ is an insulator. We can explain the insulating behviour by considering this:

One valence electron of Lithium will fill the partially filled s- orbital of one hydrogen. The other two partially filled orbitals of hydrogen will be filled by two valence electrons of magnesium. Since the valence electrons are completely filled , it acts as an insulator.

4.3 $LiCaH_3$

The electronic band structure of $LiCaH_3$ was calculated.

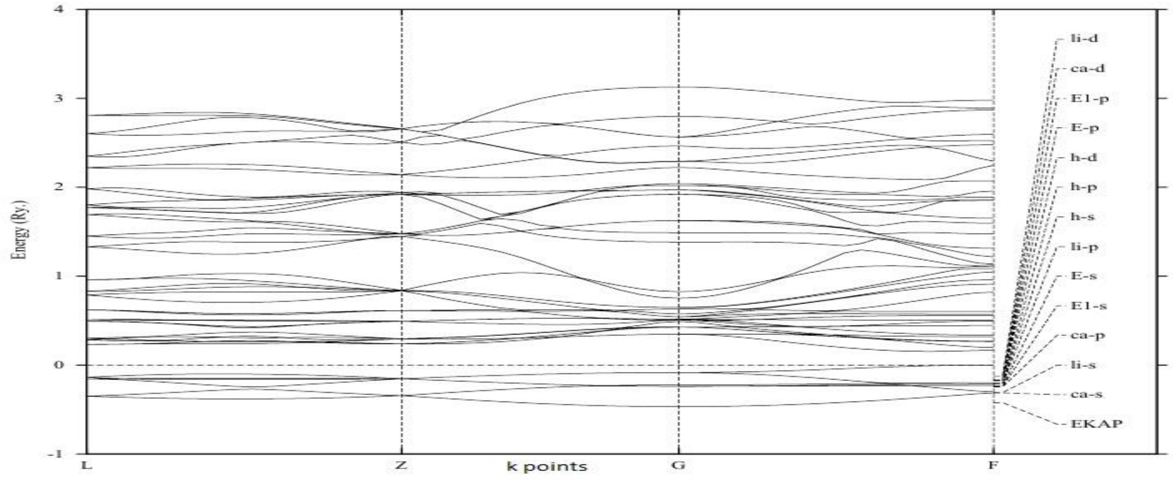
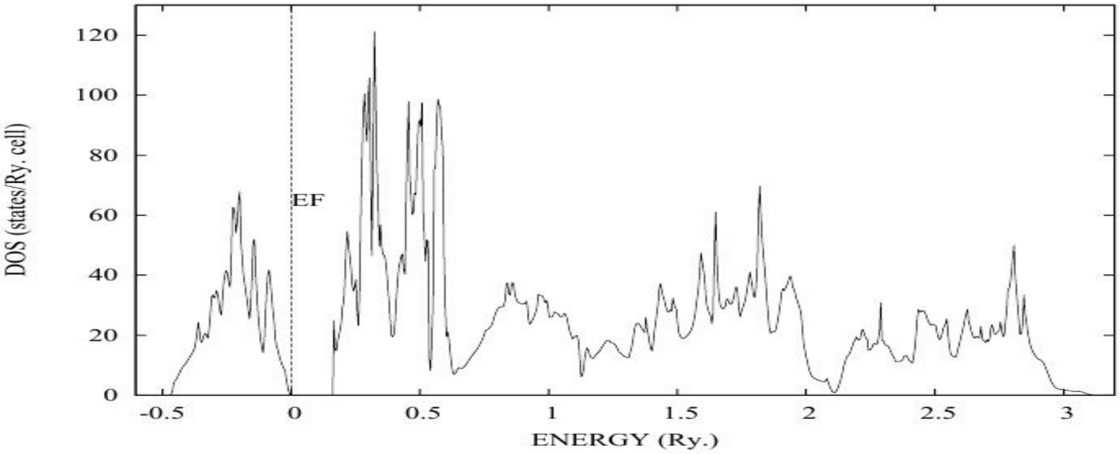


Fig 9. Electronic band structure of $LiCaH_3$

The density of states was calculated and found to be:



The density of states calculation shows clearly that $LiCaH_3$ is not a metal but insulator. The fermi energy line is in the valence band. This also confirms the non metallic behaviour. We can use similar reasoning as we gave in case of $LiMgH_3$ to infer why it shows insulating behaviour.

4.4 COMPARASION

PEROVSKITE HYDRIDE	BAND GAP ENERGY(eV)	OTHER THEORETICAL RESULT
$KMgH_3$	2.5	2.53[12]
$LiMgH_3$	4	3.98[15]
$LiCaH_3$	2.72	3.5[6]

Comparing all the data that were found using the TB-LMTO-ASA program and all the available data, we can say that our result is in good confirmation with those of other similar work. Of all the compounds that we used , in their stable state, none is a metal. To good degree of accuracy we can say (from most of the work done in this area) that most of the Perovskite hydrides show non- metallic behavior.

5 Conclusion –

The electronic properties of $KMgH_3$, $LiMgH_3$ and $LiCaH_3$ were by the tight binding linear muffin tin orbital method included in the TB-LMTO-ASA program. The band structure and density of states were calculated for all the three compounds. The band structure calculation showed that the US(2) state of $KMgH_3$ is metallic where as US(1) state and stable state are semiconductor in nature. The stable state had an energy gap of 2.5e V.

$LiMgH_3$ and $LiCaH_3$ were found to be insulators. $LiMgH_3$ is found to be less conducting than $LiCaH_3$. Their energy gaps were found to be 4.0 e V and 2.72 e V respectively.

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