

STUDY ON THE HYDROGEN COMPLEXES OF DILUTE MAGNETIC SEMICONDUCTORS

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ABSTRACT

Atomic hydrogen is known to spread across semiconductor lattices, where it forms complexes with impurities and binds to them in a way that may result in a complete cancellation of the impurity's effects.

Using first-principles DFT-LSD and LDA+U theoretical methods, the structural, vibrational, electronic, and magnetic properties of complexes formed by H in the $Mn_xGa_{1-x}As$ ($x=0.03$) dilute magnetic semiconductor have been investigated in the current paper. These properties include: structural, vibrational, electronic, and magnetic.

The findings provide an explanation for previous experimental discoveries that point to a passivation by hydrogen of the electrical and magnetic characteristics of manganese in gallium arsenide. In addition, it was shown that the correlation of electrons has a significant impact on the characteristics of H-Mn complexes.

Keywords: *Hydrogen Complexes, semiconductors*

1. INTRODUCTION

Hydrogen is the element that occurs in the greatest abundance throughout all of space. Hydrogen has a wide range of applications; it can be used as a fuel for transportation and heating; it can be used as a means of storing and transporting renewable energy; it can be used as a raw material in industrial processes; and it can also be used as the fuel in fuel cells, which produce electricity with a high level of efficiency directly on board a moving vehicle. The emergence of fuel-cell technology presents significant business potential for automakers. This is due to the fact that, in contrast to completely electric vehicles, hydrogen fuel-cell automobiles are able to generate their own source of power. At the moment, a hydrogen electric car that is being sold commercially is capable of travelling a distance of more than 500 kilometres on a single tank.

This is a distance that is comparable to the range that an average gasoline car can reach on a full tank and is a distance that is larger than the range that an average electric car can reach on a single full charge. However, while the amount of time necessary to refuel a hydrogen-powered electric car in a dedicated service station has already begun to approach the typical amount of time spent to refuel a gasoline-powered car, the amount of time necessary to recharge the battery of a battery-powered electric vehicle may require more than thirty minutes.

Significantly, the hydrogen fuel-cell technology may even be more crucial for automotive makers, especially those that make trucks. In point of fact, the weight of the lithium-ion batteries that are used in electric passenger cars has not been a major concern; however, it has been a prohibitive factor in the truck industry, where there is currently an agreement that hydrogen-powered electric powertrains would be the only option for environmentally friendly trucks of the future.

In recent years, there has been a significant increase in the amount of focus placed on the exploration of how electron spin may be used in microelectronics. It is widely agreed that dilute magnetic semiconductors, also known as DMS, which combine magnetic ordering with the features of semiconductors, are one of the most important components of such devices.

In the DMS, a metal species (such as Mn) will produce itinerant holes in addition to locally concentrated magnetic moments. It is believed that the holes operate as a mediator for the exchange interactions that take place between the magnetic moments, making these moments and holes absolutely necessary for the DMS to exhibit ferromagnetic activity.

Experiments were carried out not too long ago to study how the presence of atomic hydrogen in a $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ ($x=0.037-0.051$) DMS changed its properties. Infrared observations of hydrogenated (deuterated) $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ indicate local vibrational modes that are indicative of complexes produced by hydrogen with group II acceptors in GaAs.

These modes are designated as As-H (As-D). Magnetization tests reveal that as-grown $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ films have a ferromagnetic character, but following hydrogenation, these same films take on a paramagnetic quality. In addition, studies of electronic transport suggest that the density of the free holes is dramatically decreased as a result of the hydrogenation process. The influence that hydrogen typically has on the characteristics of IV and III-V semiconductors are what sparked interest in the properties of hydrogenated DMS in the first place.

Atomic hydrogen is capable of diffusing across the lattice of a semiconductor and occupying a variety of interstitial locations, depending on whether it is acting as a donor or an acceptor. In particular, it exhibits the characteristics of a donor in p-type materials and vice versa for n-type materials.

Therefore, H acts as an amphoteric impurity that may compensate both acceptors and donors in chemical reactions. In addition, hydrogen has the ability to attach to impurities, which results in the formation of complexes that drastically alter the impurity's chemical characteristics. Because of this, it is possible that the electronic levels caused by the impurity in the energy gap would vanish, which will result in the complete neutralisation or passivation of the impurity's electronic effects. Because of this, the effects of H are of relevance in the context of technical applications as well.

The preceding considerations and experimental findings served as the impetus for the present study, which investigated the structural, vibrational, electronic, and magnetic properties of complexes formed by H in the $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ ($x=0.03$) DMS by employing first-principles DFT-LSD and LDA+U theoretical methods. Specifically, the study focused on complexes formed by H in the $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ ($x=0.03$) DMS.

According to the findings, hydrogen bonds to the As atom that is most closely located to the Mn atom, which causes it to form a stable complex known as As-H(-Mn). At this particular complex, the hydrogen atom is found in a position that is quite near to the bond's centre between As-manganese and which corresponds to a different geometry than that which is predicted by the IR measurements. The computed magnetization of the Mn atom in the complex and the anticipated As-H vibrational frequency both correspond quite well with the results of the experiment. In addition, an analysis of the defect level caused by the Mn atom in the energy gap indicates that such a level is eliminated from the gap when the As-H(-Mn) complex is created. This conclusion was reached as a result of the finding that the formation of the As-H(-Mn) complex.

Because of this, the theory proposes that the Mn acceptor is fully passivated by hydrogen rather than being compensated for, which is in keeping with the observed development of the electronic and magnetic characteristics of MnGaAs following hydrogenation. Concerning the electron correlation effects, this investigation also yielded some very interesting findings. It has been shown that the electron correlation does, in fact, have important impacts on the characteristics of the H complexes, which need to be taken into consideration in order to arrive at a model that is in excellent agreement with the experiment.

2. OBJECTIVE OF THE STUDY

The major objective of this paper is to find out the complexes in dilute magnetic semiconductors of Hydrogen

3. MATERIALS AND METHODS

The characteristics of the X-H complexes in MnGaAs, with X denoting either manganese or arsenic, have been explored using local density functional techniques in a supercell approach. The total energies have been computed by the use of ultrasoft pseudopotentials, plane-wave basis sets, the special-points approach for k-space integration, and the PBE gradient corrected exchange-correlation functional.

In the specifics, a Monkhorst-Pack mesh with (4,4,4) k-points, a 64-atom supercell, and cutoffs of 25 Ry were used. We have also used the LDA+U formalism, which was implemented with a plane-wave basis set, in order to circumvent the inadequate DFT description of the electron correlation and to take into account the strong localization of the d levels of Mn. This was done in order to keep the strong localization of the d levels of Mn in mind. All of the geometry optimizations have been completed by completely relaxing the locations of every atom inside a supercell and reducing the amount of atomic force that they exert on one another.

The values of the vibrational frequencies have been computed here by adjusting a H displacement to a harmonic potential of the second degree. The transition energies $\epsilon^{n/n+1}$ have been computed using the approach described in the reference, and more information on the theoretical methodology is provided in the same reference. The PWscf code was used throughout each and every one of the computations.

4. RESULTS AND DISCUSSIONS

The H complexes that were researched may be seen in Figure 1, which is attached to this article. In further detail, the structures of two H complexes are shown in Figures 1(a) and 1(b), respectively, where the hydrogen atoms are situated at a bondcentered (bc) and an antibonding (ab) site, respectively. In the earlier example, the hydrogen atom is located rather near to the core of an as-manganese connection and forms a covalent bond with the manganese atom. The name given to this kind of complex is going to be a bc-Mn complex.

In the second complex, the hydrogen atom is bound to the manganese atom and is situated along the axis of the manganese-aspartate bond on the manganese atom's side. In the following, we shall refer to this compound as an ab-Mn complex. In a similar manner, the complexes in which H is linked to the As atom of an As-Mn or an As-Ga bond will be referred to as, for example, bc-As(Mn) and, correspondingly, bc-

As(Ga). It is possible for H complexes to have bent geometries, such as in the case of the bc-As(Mn) complex, in addition to the linear structures depicted in Figure 1.

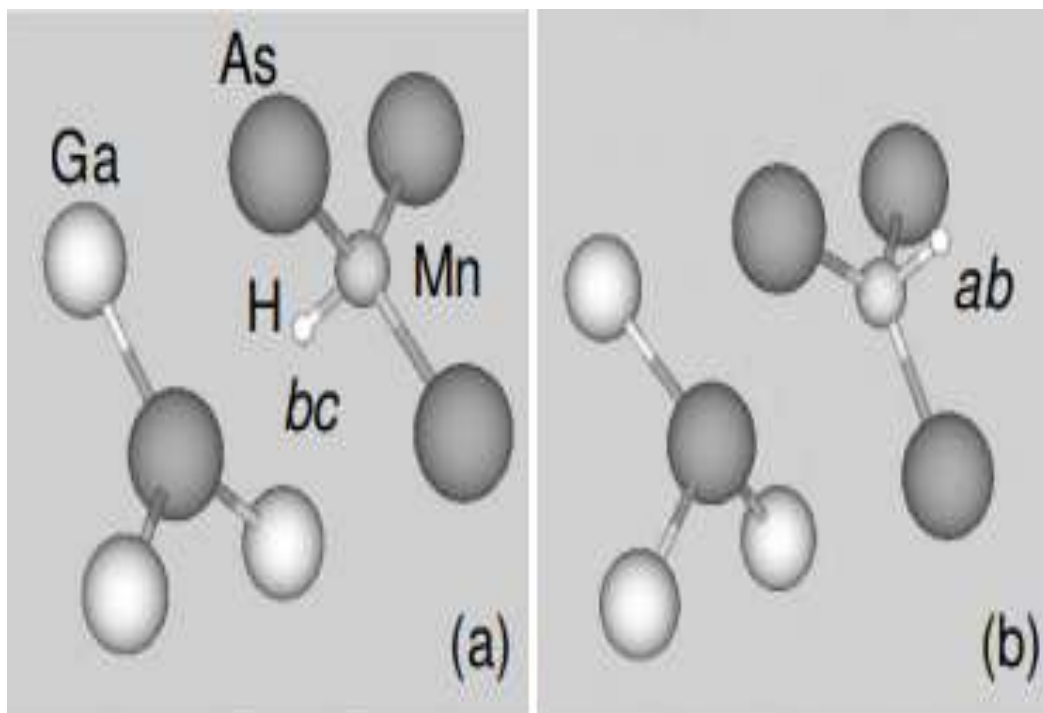


Fig 1 Atomic configurations of two hydrogen complexes in Mn_xGa_{1-x} (a) bc-Mn complex, (b) ab-Mn complex, bc and ab indicate a bond centred and an antibonding site of H, respectively.

In this study, the structure of several (As)-H-Mn complexes was analysed by placing a hydrogen atom at a variety of interstitial locations and then attempting to minimise the atomic forces exerted by the atoms included inside the supercell. In Table I, the specifics of the geometry discovered for the most intriguing hydrogen complexes are shown with the relative total energies of each complex. The abMn complex is the one with the greatest degree of stability.

Along with the corresponding values of the total magnetization and transition states, the stretching frequencies that were determined for the H-As and H-Mn bonds of the complexes listed in Table I are provided in Table II. Calculations based on LSD have been used to arrive at each and every one of these outcomes.

The numbers that are reported in Tables I and II demonstrate that the results that were attained for the most stable complex (ab-Mn) do not coincide with the findings that were obtained via experimentation. In particular, the theoretical conclusions do not accord with a vibrational frequency that was found to be 2143 cm^{-1} and a total magnetization that was observed to be $5\text{ }\mu\text{B}$ (see Table 2).

On the other hand, the energies of the H complexes that may be consistent with the experiment, such as the linear bc-As(Mn), are much greater than those of the ab-Mn complex. In terms of the electronic properties, the transition state 0/1 (Mn) that was calculated for the Mn atom that was substituting for the Ga atom in GaMnAs was found to be in good agreement with the experimental findings. These findings located the Mn acceptor level approximately 100 meV above the top of the GaAs valence band.

Table 1: The atomic distances and total energy values (ΔE values) of a variety of hydrogen complexes in MnGaAs, as determined via LSD calculations.

The absolute value of the total energy is determined in relation to the energy of the most stable complex, which is set at zero. A linear geometry is shown by the notation X=Mn,Ga LIN (atoms in the complex located on a same axis).

complex	ΔE (eV)	As-H (Å)	X-H (Å)	As-X (Å)	config.
abMn	0.00	4.05	1.60	2.45	LIN.
bcAs(Mn)	0.33	1.62	1.75	2.75	BENT
bcAs(Mn)	0.53	1.56	1.82	3.29	LIN.
abAs(Mn)	0.59	1.58	3.85	2.50	BENT
bcAs(Ga)	0.66	1.55	1.83	3.38	LIN.
abAs(Ga)	1.02	1.54	4.63	3.09	LIN.

Table 2: : Stretching frequencies of X-H bonds (X=As, Mn), total magnetization (μ_{tot}) and transition states evaluated by LSD calculations for different H complexes. lin. stands for a linear geometry (atoms in the complex located on a same axis)

complex	ν_s (cm^{-1})	μ_{tot} (μ_B)	$\epsilon^{0/-1}$ (meV)
abMn	1761	3.00	120
<i>bent</i> bcAs(Mn)	1671	5.00	
<i>lin.</i> bcAs(Mn)	2119	5.00	
abAs(Mn)	1926	5.00	
bcAs(Ga)	2179	5.00	
abAs(Ga)	2162	5.00	
Mn(Ga)		4.00	150

The value of $\epsilon^{0/-1}$ (ab-Mn) that was computed for that complex is just marginally greater than the value of 0/1 (Mn). This would suggest that the acceptor level that was generated by Mn in the energy gap is not erased by the creation of the ab-Mn complex, which would equate to a H compensation rather than a H passivation of Mn. We have also researched the characteristics of di-hydrogen complexes (which are not mentioned here), and the results of those investigations do not demonstrate a sufficient agreement with the findings of the experiments.

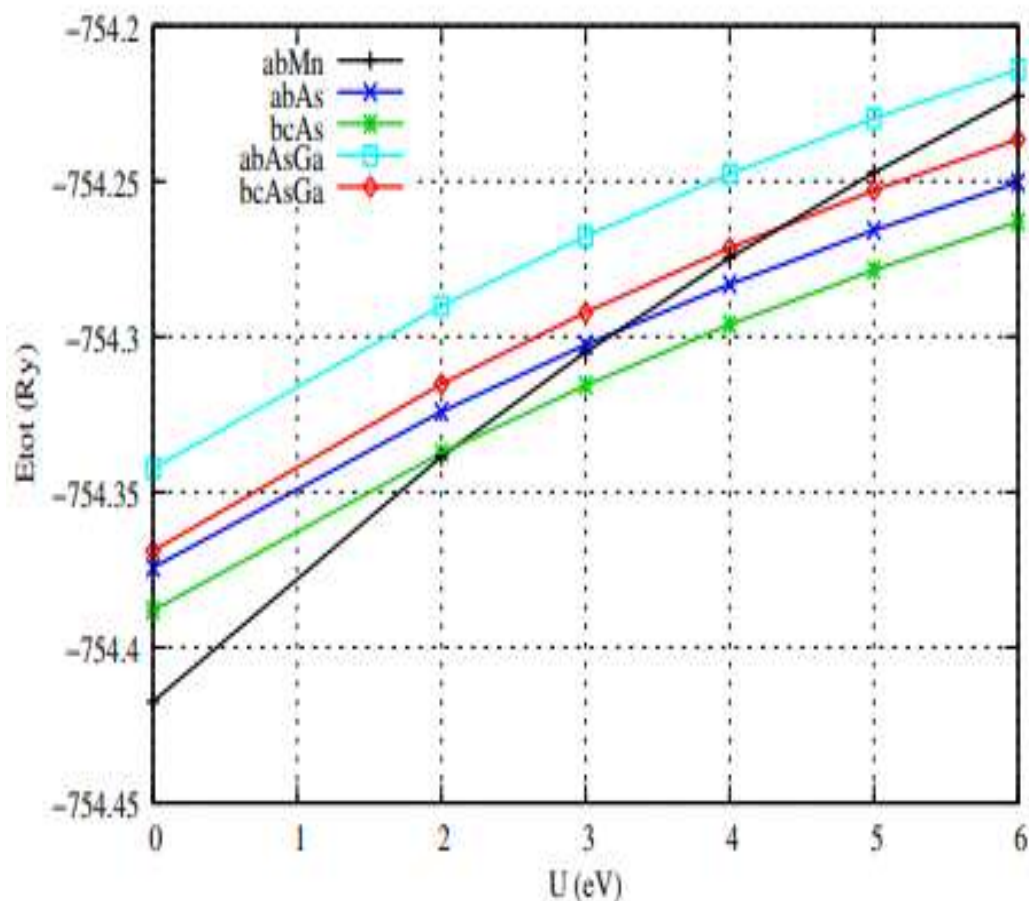


Fig 2 Different hydrogen complexes total energies are calculated with diverse values of U by using LDA+U methods.

Table 3: Stretching frequencies of the X-H pairs (X=As, Mn), total magnetization (μ_{tot}) and transition states evaluated by taking into account correlation effects (LDA+U) for different H complexes. lin. stands for a linear geometry (atoms in the complex located on a same axis).

complex	V_s (cm^{-1})	μ_{tot} (μ_B)	$\epsilon^{+1/0}$ (meV)	$\epsilon^{0/-1}$ (meV)
<i>bent</i> bcAs(Mn)	2030	5.00	-80	
<i>lin.</i> bcAs(Mn)	2133	5.00		
abAs(Mn)	1842	5.00		
abMn	1551	3.00		260
bcAs(Ga)	2109	5.00	-20	
abAs(Ga)	2012	5.00		
Mn(Ga)		4.00		280

A difference of around 4 eV from the value that was measured experimentally, which was approximately 2.5 eV below the top of the GaAs valence band. On the other hand, calculations using LDA+U, which take into account correlation effects, reduce the number of Mn d orbitals found in the valence band by bringing them to a position that is consistent with the experiment. This results in a lower value. Based on the factors presented above, it seems that the LSD treatments provide an inadequate description of the atomic-like nature of the Mn d orbitals.

Therefore, according to the LSD description, the d orbitals may play an excessive role in the creation of the H-Mn bond, which would result in the ab-Mn complex being overstabilized. As a result, we have expanded our research into the characteristics of H complexes by carrying out LDA+U calculations. These calculations were carried out in order to take into consideration the correlation effects. Figure 2 depicts the change in the total energy of the most significant hydrogen complexes as a function of the value of U at various points in time.

We have shown that when U is set to 4 eV, there is a significant shift in the relative stability of the H complexes, with the bc-As(Mn) complex emerging as the most stable of the bunch. It is important to note that the value U=4eV is also the minimum value of U that may lead to a position of the Mn d orbitals in the valence band that is consistent with the experiment. This fact is important to keep in mind. The values of the stretching frequencies of the H-As and H-Mn bonds, as well as the total magnetization and the transition

states, have been determined for a variety of H complexes using the LDA+U technique with a U value of 4 eV.

These values are shown in Table III. The bent and linear configurations have energies that are quite close to one another ($\Delta E=0.02$ eV), and the stable complex, bc-As, exhibits both of them. The vibrational frequency and the total magnetization that were determined by the experiment are consistent with both configurations. In addition, a complete H passivation of Mn is suggested by a comparison of the value of $\epsilon^{+1/0}$ (bc-As) with the value of $\epsilon^{0/-1}$ (Mn), both of which were computed using LDA+U. This finding is in agreement with the experiment.

5. CONCLUSION

Using first-principles DFT-LSD and LDA+U theoretical methods, the structural, vibrational, electronic, and magnetic properties of complexes formed by H in the $Mn_xGa_{1-x}As$ ($x=0.03$) dilute magnetic semiconductor have been investigated in the current paper. These properties include: structural, vibrational, electronic, and magnetic properties. The acquired findings may be used to account for new experimental evidence about the impact of hydrogen on the electrical and magnetic characteristics of the MnGaAs DMS material.

The current findings demonstrate, in addition, that correlation effects have important influences on the characteristics of H complexes. Last but not least, they propose a complete hydrogen passivation rather than a correction for the manganese impurity.

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