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Theory of Hydrogen Complexes in $Mn_xGa_{1-x}As$ Dilute Magnetic Semiconductors

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Atomic hydrogen diffuses in semiconductor lattices and binds to impurities by forming complexes that can lead to a full neutralization of the impurity effects. In the present paper, 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 by using first-principles DFT-LSD and LDA+U theoretical methods. The results account for recent experimental findings showing a H passivation of the electronic and magnetic properties of Mn in GaAs. Moreover, they show that electron correlation has crucial effects on the properties of H-Mn complexes.

Keywords: Hydrogen Complexes in $Mn_xGa_{1-x}As$; Dilute magnetic semiconductor; LDA+U

I. INTRODUCTION

The use of electron spin for microelectronics applications has been under intense investigation in recent years.[1] Dilute magnetic semiconductors (DMS), which combine magnetic ordering with the properties of semiconductors are generally considered key ingredients of such devices. In the DMS, a metal species (e.g., Mn) yields both localized magnetic moments and itinerant holes. These moments and holes are crucial for a ferromagnetic behavior of the DMS, as the holes are thought to mediate the exchange interactions between the magnetic moments.[2] Recently, the effects of the introduction of atomic hydrogen in a $Mn_xGa_{1-x}As$ (x=0.037-0.051) DMS have been investigated experimentally. Infrared measurements of hydrogenated (deuterated) $Mn_xGa_{1-x}As$ show As-H (As-D) local vibrational modes characteristic of the complexes formed by hydrogen with group II acceptors in GaAs.[3, 4] Magnetization measurements show that as-grown $Mn_xGa_{1-x}As$ films are ferromagnetic whereas they are found to be paramagnetic after hydrogenation.[5] Moreover, electronic transport measurements indicate that the density of the free holes is significantly reduced by hydrogenation. The interest for the properties of hydrogenated DMS is motivated by the effects H generally has on the properties of IV and III-V semiconductors.[6] Atomic hydrogen can diffuse in the lattice of a semiconductor occupying different interstitial sites where it has a donor or an acceptor character. In particular, it has a donor character in *p*-type materials and viceversa. H behaves therefore as an amphoteric impurity which can compensate both acceptors and donors.[7] Moreover, H can bind to an impurity by forming complexes which significantly change its chemical properties. This may cause the disappearance of the electronic levels induced by the impurity in the energy gap, thus leading to a full neutralization or passivation of its electronic effects. The effects of H are therefore of interest also for technological applications. The above considerations and experimental results have motivated the present study, where the structural, vibrational, electronic and magnetic properties of complexes formed by H in the $Mn_xGa_{1-x}As$ (x=0.03) DMS have been investigated by using first-principles DFT-LSD and LDA+U theoretical methods. The results show that H forms a stable As-H(-Mn) complex where it binds to an As atom nearest neighboring the Mn atom. In this complex, H is located close to the center of the As-Mn bond, which corresponds to a different geometry from that suggested by the IR measurements.[3] The estimated As-H vibrational frequency and the calculated magnetization of the Mn atom in the complex agree well with the experiment. Moreover, an investigation of the defect level induced by the Mn atom in the energy gap shows that such a level is removed from the gap when the As-H(-Mn) complex is formed. Thus, the theory suggests a full passivation of the Mn acceptor by H rather than compensation, in agreement with the observed evolution of the electronic and magnetic properties of MnGaAs upon hydrogenation. A further significant result achieved here concerns the electron correlation effects. It is shown indeed that electron correlation has *crucial effects* on the properties of the H complexes that have to be taken into account in order to achieve a good agreement with the experiment.

II. METHODS

The properties of the *X*-H (*X*=Mn,As) complexes in MnGaAs have been investigated by local density functional methods in a supercell approach. Total energies have been calculated by using ultrasoft pseudopotentials,[8] plane-wave basis sets, the special-points technique for **k**-space integration, and the PBE [9] gradient corrected exchange-correlation functional. In detail, a 64-atom supercell, the (4,4,4) **k**-point Monkhorst-Pack mesh, and cutoffs of 25 Ry have been used. In order to keep into account the strong localization of the *d* levels of Mn and to circumvent the poor DFT description of the electron correlation, we have also used the LDA+U formalism, as implemented with a plane-wave basis set[11]. All the geometry optimizations have been performed by fully relaxing the positions of all of the atoms of a supercell by minimizing the atomic forces. Vibrational frequency values have been calculated here by fitting a H displacement to a harmonic 2nd-degree potential. Transition energies $\varepsilon^{n/n+1}$ have been estimated as in Ref. [12], further details on the theoretical methods are given in the same reference. All calculations

have been performed using the PWscf code[10]

III. RESULTS AND DISCUSSION

Figure 1 exemplifies the H complexes investigated in the present work. In detail, Figs. 1(a) and 1(b) show the structure of two H complexes where the H atom is located at a bond-centered (bc) and at an antibonding (ab) site, respectively. In the former complex, H is close to the center of an As-Mn bond and binds to the Mn atom. Such a complex will be referred to as a bc-Mn complex. In the latter complex, H is located along the axis of the As-Mn bond on the side of Mn and binds to this atom. This complex will be referred to as an ab-Mn complex. Similarly, the complexes where H is bonded to the As atom of an As-Mn or an As-Ga bond will be referred to as, e.g., bc-As(Mn) and bc-As(Ga), respectively. In addition to the linear structures shown in Fig. 1, H complexes may have bent geometries as in the case of the bc-As(Mn) complex.

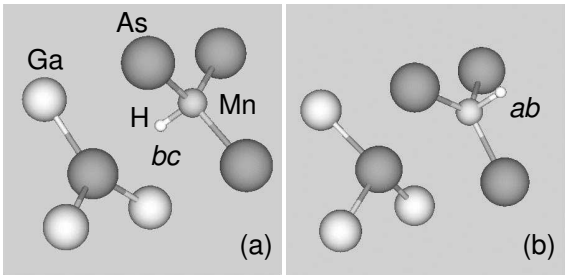

FIG. 1. Atomic configurations of two hydrogen complexes in $Mn_xGa_{1-x}As$: (a) bc-Mn complex, (b) ab-Mn complex. *bc* and *ab* indicate a bond centered and an antibonding site of H, respectively.

The structure of different (As)-H-Mn complexes has been investigated here by locating a H atom at different interstitial sites and by minimizing the atomic forces of the atoms in the supercell. Details of the geometry found for the most interesting hydrogen complexes are given in Table I together with the relative total energies. The most stable complex is the ab-Mn one. The stretching frequencies calculated for the H-As and H-Mn bonds of the complexes in Table I are reported in Table II together with the corresponding values of the total magnetization and transition states. All of these results have been achieved by performing LSD calculations. The values given in Tables I and II show that the results achieved for the most stable complex (ab-Mn) do not agree with the experimental findings. In particular, the theoretical results do not agree with a measured vibrational frequency of 2143 cm^{-1} and a total magnetization of 5 μ_B,[3, 5] see Table II. On the other hand, the H complexes that could agree with the experiment, e.g., the linear bc-As(Mn), are much higher in energy than the ab-Mn one. For what concerns the electronic properties, the transition state $\varepsilon^{0/-1}$(Mn) calculated for the Mn substituting the Ga atom in GaMnAs is in a good agreement with the experimental findings locating the Mn acceptor level about 100 meV above the top of the GaAs valence band.[13] The

TABLE I: Atomic distances and total energy values (ΔE values) of different hydrogen complexes in MnGaAs evaluated by LSD calculations. Total energy values are relative to the energy of the most stable complex that is taken equal to zero. *X*=Mn,Ga. *LIN.* indicates a linear geometry (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 II: 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)	$\varepsilon^{0/-1}$ (meV)
abMn	1761	3.00	120
bent bcAs(Mn)	1671	5.00	
lin. 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

$\varepsilon^{0/-1}$(ab-Mn) calculated for that complex is slightly higher than the $\varepsilon^{0/-1}$(Mn) value. This would indicate that the acceptor level induced by Mn in the energy gap is not removed by the formation of the ab-Mn complex, thus corresponding to a H compensation instead of H passivation of Mn. We have also investigated the properties of di-hydrogen complexes (not reported here), which also do not show a satisfactory agreement with the experimental findings.

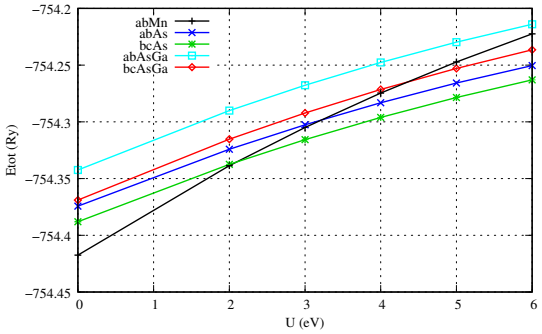

FIG. 2. Total energies of different hydrogen complexes calculated with different values of U by using LDA+U methods.

In the ab-Mn complex, a H atom directly bonded to Mn leads to a five-fold coordinated Mn atom. The stability of such a complex configuration suggests that *d* orbitals of Mn are involved in the H-Mn bond. Previous theoretical studies have shown that LSD calculations locate the Mn *d* orbitals at

TABLE III: 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	ν_s (cm^{-1})	μ_{tot} (μ_B)	$\varepsilon^{+1/0}$ (meV)	$\varepsilon^{0/-1}$ (meV)
bent bcAs(Mn)	2030	5.00	-80	
lin. 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

about 2.5 eV below the top of the GaAs valence band at variance with the value of 4 eV experimentally found.[14] On the other hand, LDA+U calculations, which take into account correlation effects, lower the Mn *d* orbitals in the valence band by leading them to a location in agreement with the experiment. The above considerations suggest that the Mn *d* orbitals have an atomic-like character poorly described by the LSD treatments. Thus, in the LSD description, the *d* orbitals could be too much involved in the formation of the H-Mn bond and overstabilize the ab-Mn complex. We have further investigated, therefore, the properties of H complexes by performing LDA+U calculations in order to take into account the correlation effects. Figure 2 shows the evolution of the total energy of the most important hydrogen complexes for different values of U. We observe that for U=4eV the relative stability of the H complexes dramatically changes, the bc-As(Mn) complex becoming the stable one. It has to be noted that the value U=4eV also represents the smallest value of U leading to a location of the Mn *d* orbitals in the valence band in agreement with the experiment. Table III reports the value of the stretching frequencies of the H-As and H-Mn bonds, of the total magnetization and of the transition states calculated for different H complexes by using the LDA+U method with U=4eV. The stable complex, the bc-As one, presents a bent and a linear configurations very close in energy (ΔE=0.02 eV). Both configurations agree with the vibrational frequency and total magnetization given by the experiment. Moreover, a comparison of the $\varepsilon^{+1/0}$(bc-As) value with the $\varepsilon^{0/-1}$(Mn) value, both calculated with LDA+U, suggests a full H passivation of Mn, which also agrees with the experiment.

IV. CONCLUSIONS

In the present paper, 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 by using first-principles DFT-LSD and LDA+U theoretical methods. The achieved results account for recent experimental data concerning the effects of H on the electronic and magnetic properties of the MnGaAs DMS. Present results also show that correlation effects have *crucial effects* on the properties of H complexes. Finally, they suggest a full H passivation rather than a compensation of the Mn impurity.

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