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Ab initio predictions of the stability and structural properties of zincblende (III,TM)V magnetic semiconductor alloys

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ABSTRACT

First-principles calculations and statistical methods were combined to study electronic, magnetic, thermodynamic and structural properties of zincblende (III,Mn)V and (III,Cr)V magnetic semiconductor alloys, including both nitride and arsenide alloys. From phase diagrams it was observed that nitride alloys are much less stable than arsenide ones, although the former ones have more localized *d*-states at the Fermi level. It was observed that all alloys present an anisotropic behavior, with the strongest magnetic interaction in the ⟨110⟩ direction. The relationship between the structural properties of these alloys and their electronic and magnetic characteristics (i.e., their half-metallicity) was investigated.

1. Introduction

Over the past decades, considerable research activities have been directed towards the development of functional diluted magnetic semiconductors (DMS), formed by alloying transition metal (TM) atoms in conventional semiconductors, due to their potential application on spintronics [1,2]. The great advantage of DMS is to allow an interplay between magnetic and electronic properties, being structurally compatible with most semiconductors epitaxially grown, which also make them potential materials for integration of photonic, electronic, and magnetic devices on a single chip. Some outstanding functionalities have already been demonstrated as the control of magnetism by means of electric fields [3,4], the Coulomb Blockade regime, the current-induced domain displacement without the assistance of a magnetic field. Besides, several devices have also been proposed, such as non-volatile memories, spin-transistors, spin light-emitting diodes and spin-lasers. Among many possible choices for magnetic semiconductors, those based on III-V elements have drawn much attention since the 1990s, being (Ga,Mn)As the DMS most studied [1,4–15].

One of the main concerns in the study of DMS is the increase of TM concentration in the semiconductor matrix, which can be directly related to the increase of Curie temperature. Since pioneering works [5], a great effort has been made in this direction, and it is already possible to grow GaMnAs samples with ~20% of Mn using non-equilibrium techniques such as low-temperature molecular-beam epitaxy (LT-MBE) and post-growth treatment techniques as annealing in order to decrease the amount of defects [4,6]. For these high TM compositions, one can no longer say that the material is diluted, but the correct term should be magnetic semiconductor (MS) alloy.

However, despite the many investigations, many questions about their properties still persist, e.g., the origin and control of ferromagnetism is one of the most controversial research topic in materials science and condensed-matter physics [16]. One important issue, which has been pointed as the cause of the origin of ferromagnetism in some MS is the limited solubility of TM impurities in some hosts, which can result in nanoclusters of magnetic cations [16]. Moreover, the control on the distribution of magnetic ions into a semiconducting host is crucial for the functionality of magnetically doped semiconductors [17]. In this sense the construction of phase diagrams provides an effective tool to analyze if the MSs are fully miscible, or not, i.e., in which cases and conditions there are indications for a miscibility gap and the

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formation of these nanoclusters. Another interesting point is the unusual behavior of lattice parameters with the composition. The lattice parameters of ordinary semiconductor alloys usually obey Vegard's law, but different behaviors have been observed in DMS alloys such as arsenide and nitride based ones [18]. It was predicted a direct correlation between the magnetic moment and the anion-TM bond length which shows that the lattice parameter has two distinct behaviors, depending on whether the alloy is half-metallic or not [12]. So, the understanding of the electronic, magnetic, thermodynamical, structural properties, as well as, their correlation is required for the understanding of the physical phenomena and, consequently, applications of MS.

The purpose of this paper is to study electronic, thermodynamic, structural and magnetic properties of (III,TM)V magnetic semiconductor alloys. We make a comparison of these properties for GaMnAs, GaCrAs, GaMnN, GaCrN, AlMnN, and AlCrN grown in the zincblende (ZB) structure. Thereby, we can assess the influence of the cation (Ga or Al), anion (As or N) and TM atom (Mn or Cr) on the properties of MS alloys. Initially, in Section 2, we briefly address the method employed, which combines ab initio calculations and a statistical approach. Then, in Section 3, we show the results of our calculations and discuss the main similarities and differences among the alloys studied. In Section 3.1, we present phase diagrams for all the alloys and analyze their stability. In Section 3.2, we focus on the electronic properties of all these alloys, calculating a spin resolved density of states (DOS) for a 3.125% molar fraction of TM atom: with this, we are able to make a comparison, using the same method, between a distinct set of alloys, evaluating the influence of the cation, anion and TM atom. In Section 3.2 we also obtain the dependence of the exchange energy with the crystal direction and the distance between two TM atoms. Finally, in Section 4, we summarize the work.

2. Methodology

In order to study the alloys mentioned before, we use ZB supercells with different sizes, depending on the property analyzed, namely:

(i) *Phase diagrams* : In order to build the phase diagrams and analyze the stability of the alloys, antiferromagnetic (AFM) states are as important as ferromagnetic (FM) states [19]. As the number of configurations increases exponentially with the cell size, we use cells with 8 atoms (4 cations and 4 anions), for which all FM and AFM states are calculated, resulting in a total of 9 configurations not related by symmetry.

(ii) *Electronic properties* : Aiming to compare DOS and exchange interactions for small compositions of TM atoms, without employing any statistics, we use 64-atoms supercells in these calculations.

(iii) *Structural properties* : To determine the influence of magnetization on lattice parameters and bond lengths, we force TM to be ferromagnetically aligned, using cells with 16 atoms (implying 16 configurations not related by symmetry) [12].

In almost all calculations, the lattice parameter of the supercell is optimized by total energy minimization. Exchange interaction calculations are the exceptions, where the lattice parameter was kept constant for all configurations, since we intend to establish the behavior of the energy difference between FM and AFM states varying the distances between TM atoms.

In energy calculations, we employ density functional theory (DFT) [20] with the generalized gradient approximation (GGA) as proposed by Perdew and Wang [21] for exchange–correlation potential. Kohn–Sham equations are solved in the projector augmented wave method (PAW) [22] as implemented through 'Vienna ab initio simulation package' (VASP) [23]. We use an energy cutoff parameter of $E_{cut} = 400$ eV and a $7 \times 7 \times 7$, $5 \times 5 \times 5$, and $3 \times 3 \times 3$ Γ-centered k-point mesh in the Monkhorst–Pack scheme for supercells with, respectively, 8, 16, and 64 atoms. The density of states was performed by considering a $11 \times 11 \times 11$ Γ-centered k-point mesh. The total energy convergence for all electronic steps was set at 10^{-8} eV. All atomic coordinates were relaxed until the Hellmann–Feynman forces were small in proportion to the convergence in energy, using the criterion that the energy difference between two successive changes of atomic positions was lower than 10^{-7} eV.

Thermodynamic properties are addressed using a statistical method known as generalized quasichemical approximation (GQCA) [24]. This method, which has been widely employed in the study of several alloys [19,25–28], represents an alloy as an ensemble of individual clusters statistically and energetically independent of surrounding atomic configuration. Each cluster is realized by a supercell with a certain number of atoms (the same for all clusters). For (III,TM)V MS alloys, since the alloying mechanism occurs only at the cation sublattice (the anions are mere spectators and do not account for the composition of the alloy), N alludes to the number of cations in each cluster. In principle, there are 2^N different clusters, nonetheless, some of these 2^N are energetically equivalent, and it is possible to group all the 2^N configurations into a total of J classes of equivalent clusters, each class having g_j equivalent clusters (g_j is the degeneracy of the class). Here, we adapted the method in order to take into account the different magnetic states, such as AFM and FM, by considering the total energy ε_j for each atomic configuration as the weighted average between the different magnetic states. Certainly, all the g_j, when summed over, must fulfill:

$$\sum_{j=1}^{J} g_j = 2^N \tag{1}$$

Of course, all the probabilities must satisfy

$$\sum_{j=1}^{J} x_j = 1, \tag{2}$$

and the total composition should be expressed by

$$x = \sum_{j=1}^{J} \frac{x_j n_j}{N}, \tag{3}$$

n_j being the number of TM atoms of the jth cluster. Until this moment, we have not given the full conditions to determine $x_j(x, T)$. To achieve this, we must consider the mixing free energy of the alloy:

$$\Delta F(x, T) = \Delta U(x, T) - T\Delta S(x, T), \tag{4}$$

where $\Delta U(x, T)$ and $\Delta S(x, T)$ represent mixing internal energy and mixing entropy, respectively. If we consider that the alloy is composed by the overlap of a total of M clusters, then the number Ω of microstates is

$$\Omega = \frac{M!}{(x_1 M)!\ldots(x_J M)!}(g_1)^{x_1 M}\ldots(g_j)^{x_j M} \tag{5}$$

This permits us to calculate the mixing entropy as $\Delta S = k_B \ln \Omega$, where k_B is the Boltzmann constant. On the other hand, the mixing internal energy is