First-principle Calculation of GaAs Electronic Structure by Doping with Mn and P

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Abstract. The geometry structure of Mn, P doped 64-atom supercell of GaAs (Ga\textsubscript{1-x}Mn\textsubscript{x}As\textsubscript{1-y}P\textsubscript{y}) was optimized and studied by the self-consistent full-potential linearized augmented plane wave method (FP_LAPW) based on the density functional theory (DFT). Cell parameters of both doped and undoped were calculated theoretically. Band structure, binding energies, partial density of states, mulliken charges, and electron density different of doped GaAs crystals were calculated and analyzed in detail. The results revealed that the both doped compounds are true half-metallic ferromagnets and the near distance doped one is a stable ground state.

1. Introduction

The interplay between the charge carriers in a semiconductor and the electron spins of a ferromagnetic metal doped into the semiconductor can be utilized for many magneto/spin-electronic devices. The desirable features for the successful application of a semiconductor spintronics material are that it should show ferromagnetism or half-metal ferromagnets with a reasonably high $T_C$, and a sizable concentration of magnetic sites. Interest in the family of carrier induced dilute magnetic semiconductors (DMS) started with the discovery of ferromagnetism in ~5% Mn-doped InAs and GaAs with a Curie point of 110 K\textsuperscript{[1]} and the study of ferromagnetism in (Ga, Mn)As and a theoretical prediction that Mn-doped GaN could be ferromagnetic(FM)at or above room temperature\textsuperscript{[2]}, have led to intensive research on transition metal elements doped (III, V) DMSs \textsuperscript{[3-18]}. Among the various DMS materials, Mn-doped GaAs is particularly interesting because GaAs is a direct wide energy band gap semiconductor with high thermal, chemical, and mechanical stability. In addition, Mn-doped GaAs is one of the few materials where magnetism above room temperature has been reported and is extensively studied. Half-metallic ferromagnetism, especially dilute magnetic semiconductors \textsuperscript{[19,20]}, have attracted more and more attentions since its first discovery by De Groot et al. in 1983 \textsuperscript{[21]}. Recently, there is considerable controversy in the reported results. The nature and origin of the magnetic coupling in this material continue to be hotly debated issues. The mechanism for the observed magnetic behaviour is complex and appears to depend on a number of factors.

The first attempt to explain carrier-controlled ferromagnetism in Mn-doped III-V semiconductors was made by Dietl \textit{et al.}\textsuperscript{[2]} who used the double-exchange Zener model\textsuperscript{[8]} of ferromagnetism and

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predicted how the incorporation of Mn ions induces ferromagnetic behaviour via hole-mediated exchange interaction (Ruderman-Kittel-Kasuya-Yosida type). Litvinov and Dugaev[9] subsequently proposed the indirect exchange interaction caused by virtual electron excitations from magnetic impurity acceptor levels to the valence band. Ab initio calculations [10–13] have also been carried out to understand the underlying mechanism of carrier-induced ferromagnetism in transition-metal (TM) doped III-V and II-VI semiconductors. Schilfgaarde and Mryasov[10] have performed a thorough investigation of the anomalous magnetic interactions in doped DMS systems and they had performed linearized muffin-tin orbital calculations on a zinc-blend structured supercell, in order to investigate the exchange interactions between 3d magnetic dopants (Cr, Mn, and Fe) in different III-V semiconductors (GaAs, GaN, and AlN). They had observed that doping caused deviations in the magnetic exchange interaction from what is predicted by simple models due to the formation of deep levels and concluded that short-range interaction between the dopant atoms could cause a clustering of these atoms. More recently, Ohno and co-workers has enabled its practical growth with stoichiometric amounts of Mn,Ga$_{1-x}$As alloys, are inherently compatible with existing GaAs technology, resulting in the practical realization of device structures combining ferromagnetic and nonmagnetic layers.

In this paper, we present a detailed study of the electronic and magnetic properties of Mn, P-doped GaAs(Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$) supercell and the wurtzite structure to demonstrate the effect of the compounds. We calculated using the WIEN2K package [22], a full potential linearized augment plane wave method within the density functional theory. The generalized gradient approximation (GGA) [23] proposed in 1996 by Perdew, Burke and Emzerhof is used for the exchange-correlation potential and the relativistic effect is taken into account in the scalar approximation, but the spin–orbit coupling is neglected because it does not destroy the half-metallicity. The radii $R_{mt}$ of the muffin tins are chosen to be as large as possible according to the approximate ionic radii but not overlapped and $R_{mt}K_{max}$ are all taken to be 9.0. The self-consistency is better than $10^{-4}$ e/a.u. for charge density, and the stability is better than $10^{-5}$ Ry for the total energy per formula unit. Our \textit{ab initio} investigations yield the electronic structure, energetics, and magnetism of Mn and P-doped GaAs in a c1uster as well as in a bulk crystalline environment. In Sec. II we outline our computational results and discussed.

2. Results and discussion

The study presented in this work is based on Ga$_{1-x}$Mn$_x$As$_{1-y}$P$_y$ materials. The crystalline structure used by the host semiconductor is a 64-atom cubic cell Ga$_{32}$As$_{32}$. In this cell one Ga atom has been substituted by one Mn atom and one As atom has been substituted by one P atom. Atoms of Mn and P were located as far as possible in Far Crystalline (FC) and in the Near Crystalline (NC) two atoms were located as immediate neighbors, which were shown in Fig.1. In this structure the atomic environment of the transition-metal atoms has a tetrahedral symmetry considering their immediate neighbors and the calculated bond lengths for Mn substituting the Ga site and P substituting As site are listed in Table 1. where they are compared with the ideal bond length in the pure GaAs. Substitution of Mn on the Ga site creates a longer bond in FC than in NC. Ignore the influence of atom P, the As atoms can be broken down into two groups: those directly bonded to the Mn atoms (As1) and those which are not (As2). Using the \textit{ab initio} method described above, we have carried out an extensive analysis of the electronic structure, energetics and magnetism prosperities of FC and NC. We find both the doped compounds structures to be energetically stable, with the NC spin order structure lower in energy 0.002eV per supercell than FC which indicates that the NC structure is more stable. The reason due to bond strength of Mn-P in NC is smaller than that of Mn-As bond strength which is shown in Table 1.

Table 1. Calculated bond lengths for Mn substituting the Ga site and P substituting As site in the supercells of FC and NC

| Bond length for FC(Å) | Bond length for NC(Å) |
|-----------------------|-----------------------|
| Mn-As Ideal 2.303    | P-Ga Ideal 2.303     |
| Mn-As Ideal 2.292    | P-Ga Ideal 2.301     |
| Mn-As Ideal 2.448    | P-Ga Ideal 2.448     |
| Mn-As Ideal 2.225    | P-Ga Ideal 2.448     |
From the FC structure, we find a global magnetic moment of 3.99409 \(\mu_B\) per-supercell. As expected, the Mn dopant atom is found to be the main contributor to the magnetic moment of the structure, having a localized magnetic moment of 3.76882 \(\mu_B\) per atom and in the NC structure the magnetic moment of Mn is bigger by 0.01214 \(\mu_B\). The As neighbors of Ga together make a much smaller contribution of about 0.002 \(\mu_B\), while the Mn second neighbors of As together contribute about 0.0008 \(\mu_B\) to the magnetic moment, which due to the conjugation effect of the spin delocalization between manganese ions and arsenic atoms. Note that this nonintegral value of magnetic moment is due to the use of atomic sphere approximation in our self-consistent calculation.

**Figure 1.** Cell of GaAs(a), Far Crystalline (b) and the Near Crystalline (c). the red and blue balls stand for Mn and P atoms, respectively

**Figure 2.** Cell of GaAs(a), Far Crystalline (b) and the Near Crystalline (c). the red and blue balls stand for Mn and P atoms, respectively
The main characteristic near the Fermi energy is the determination of the magnetic properties. The density of states (DOS) of the two Ga\(_{1-x}\)Mn\(_x\)As\(_{1-y}\)P\(_y\) (x=y=3.125%) compounds is illustrated in Fig.2 and Fig.3. The horizontal axis is energy relative to the Fermi energy (\(E_F\)). The host valence band consists of two parts. One is the low-lying Ga-3d band which appears at approximately 1.2 Ry below \(E_F\) as a peak whose width is 0.35 Ry. The other is the broad As-2p band which distributes from ~4.0 Ry to ~0.2 Ry. Between the valence band and the conduction band, which consists of Ga-4s states, there are impurity-3d bands. These impurity bands show large exchange splitting. Because the exchange splitting is larger than the crystal field splitting, as shown in figure 3, the TM is in the high-spin states. The half-metallic DOS means that the DOS is metallic for up-spin states and insulating for down-spin states, or vice versa. This kind of asymmetry in the DOS at \(E_F\) is shown in the other III–VI-based DMSs, and it is proposed that these III–VI compound-based DMSs are useful to realize spintronic devices such as a spin-injection device and a spin-polarized FET and so on. Also as Fig.3 shows, a half-metallic behaviour in the sense that the Fermi level state density is finite for the spin-up and zero for the spin-down, which is different with the ferromagnetic behaviour of Mn-doped GaAs[24]. This half-metallicity is due to the Mn-3d states hybridize well with the As-2p states, and the P-2p states. Due to this hybridization with the Mn-3d states, holes are itinerant with keeping their d-character, therefore the kinetic energy is lowered so efficiently that the ferromagnetic state is stabilized by the double-exchange mechanism. As shown in figure 2, the impurity bands appeared between the valence band and the conduction band of the host GaAs. The introduction of Mn, therefore, changes the semiconducting nature of GaAs. The result are similar to the obtained previously for Cr-doped GaN [24], where it was suggested that the half-metallicity is due to Cr-3d hybridizing with the N-2p state. In Fig.2(b), it is also significance that the Mn-d band of DOS is strongly spin split into three-peaked structure. The peaks for the Mn-d band spin-up just above the valence band edge, which is in tune with what Mayasov[24] have mentioned in their paper. This implies that Mn acts as a provider in the doped-structure.

![Figure 2.](image)

**Figure 2.** Density-of-states cover for: (a) Mn\(_{0.063}\)Ga\(_{0.937}\)As, (b) Mn\(_{0.0375}\)Ga\(_{0.9625}\)P\(_{0.0375}\)As\(_{0.9625}\) for near distance, and (c) Mn\(_{0.0375}\)Ga\(_{0.9625}\)P\(_{0.0375}\)As\(_{0.9625}\) for far distance

### 3. Conclusions

We have studied the structural, electronic, and magnetic properties of Mn and P doped GaAs with far and near distance through first-principles calculations. The result suggest that the two compounds are likely to order half-metallicity, leading to a dilute magnetically order semiconductor. The two compounds of Ga\(_{1-x}\)Mn\(_x\)As\(_{1-y}\)P\(_y\) with a realistic Mn and P content of x=y=0.3125% are all found to possess a magnetic moment of about 4.0\(\mu_B\) per-supercell and the Mn dopant atom is found to be the main contributor to the magnetic moment of the structure. But in the NC structure the magnetic moment of Mn is a smaller bigger than FC which due to the spin delocalization. Also, we found both the doped compounds structures to be energetically stable, with the NC spin order structure lower in energy 0.002eV per supercell than FC which indicates that the NC structure is more stable.
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