Trends in ferromagnetism in Mn-doped dilute III-V alloys from a density functional perspective

Roby Cherian and Priya Mahadevan
Department of Material Sciences and Advanced Materials Research Unit, S.N. Bose National Centre for Basic Sciences, JD-Block, Sector III, Salt Lake, Kolkata 700098, India

Clas Persson
Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden
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Mn doping in dilute III-V alloys has been examined as a route to enhance ferromagnetic stability. Strong valence-band bowing is expected at the dilute limit, implying a strong modification of the ferromagnetic stability upon alloying with even an increase in some cases. Using first-principles electronic structure calculations we show that while codoping with a group V anion enhances the ferromagnetic stability in some cases when the effects of relaxation of the lattice are not considered, strong impurity scattering in the relaxed structure result in a reduction in the ferromagnetic stability.

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I. INTRODUCTION

Dilute magnetic semiconductors have been intensively studied in recent times with the intention of replacing conventional electronic devices with those based on these materials.[1] No real devices have been realized so far and the interest in this field has been based on concept devices. An essential aspect of dilute magnetic semiconductors-based devices is the manipulation of the spin of the electron which one would like to do at room temperature. Hence the search is on for a room-temperature ferromagnet. One material that has been intensively studied for this purpose is Mn-doped GaAs.[2] The ferromagnetic (FM) Curie temperature (T_c) is still far from desirable reaching a maximum of 250 K in specially designed superlattices.[3] Alternate materials such as transition-metal atoms doped in II-VI semiconductors,[4] perovskite oxides,[5] other oxides,[6] III-V semiconductors, and chalcopyrites[7] have been synthesized and studied and the search is on for the most suitable material. In this work we confine our attention to Mn doping in III-V semiconductors. Theoretical calculations predict a higher ferromagnetic stabilization energy for Mn in GaN than in GaAs.[8] However, the main conclusion from experiments is that the effective interaction between the Mn atoms is antiferromagnetic (AFM) (Ref. 9) or could be weakly ferromagnetic.[10] Strong ferromagnetism has been observed though the origin seems to be in the presence of ferromagnetic clusters of Mn present at large doping concentrations.[11]

In this work we examine an alternate strategy to obtaining high Curie temperatures by considering dilute alloys of III-V semiconductors. Strong valence-band bowing is expected in the dilute limit in some cases, and we want to use that to modify the ferromagnetic stability. These ideas are not new to the current work and have been proposed earlier in the literature.[12] However there is no detailed theoretical work which has examined the electronic structure, modified interaction strengths, and the consequent implications on the T_c. The basic idea that one aims to exploit here is to use semiconductors with band edges energetically closer to the Mn $3d$ levels. This increases the hydridization between the host anion p states and the Mn d states. This however results in a deep acceptor level in the band gap. Thus the ferromagnetism-mediating holes are more localized. A system that has been proposed as a strong candidate is a dilute alloy of GaAs with GaP. The hope is that the itinerancy of the carriers is retained while the p-d exchange is enhanced because of the shorter Mn-anion bond lengths. LDA+U/coherent potential approximation based calculations[13] have looked at 25%, 50%, and 75% alloys of GaAs and GaP and found a modest increase in T_c. Experiments[14,15] have looked at the dilute limit of $Ga_{1-x}Mn_xAs_{1-y}P_y$ and $Ga_{1-x}Mn_xAs_{1-y}N_y$ with $y \sim 0.01-0.04$. There is a strong decrease in T_c with increasing y even at this dilute limit. As the dilute limit has not been studied theoretically we examine whether the experimental trends may be captured within our calculations and if not, then the cause is due to extraneous factors not included in the present approach. We are able to capture the reduction in T_c in GaAs alloyed with GaN as well as the case of GaAs alloyed with GaP.

II. METHODOLOGY

In order to address these issues we have considered 216 atom supercells of GaAs, GaP, and GaN. One Mn was placed at the origin while the second was placed at the fourth fcc neighbor position as earlier work has shown that the ferromagnetic stability is strongest for Mn atoms at these positions.[16] We consider dilute III-V alloys as the host semiconductor into which Mn is doped. In order to form the dilute III-V alloys a group-V anion impurity is codoped at different distances on the line perpendicular to the line joining the two Mn sites. For GaAs alloyed with GaP we included higher dopant concentrations also. The optimized lattice constants for the GaAs, GaP, and GaN are 5.72, 5.49, and 4.52 Å, respectively. The lattice constant of the supercell is set according to Vegard's law for the III-V alloy. Full optimization of the internal positions is carried out within the first-principles electronic structure calculations using a plane-wave pseudopotential implementation of the density-functional theory.[17] A plane-wave cutoff of 400 eV was used

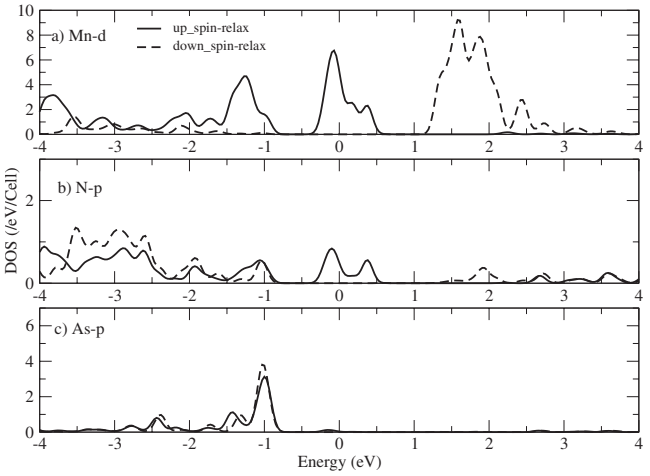

FIG. 1. (a) The up (solid line) and down (dashed line) spin projected density of states for Mn d, (b) N p, which is the nearest neighbor of the Mn, and (c) for the As p calculated for (Ga,Mn)N codoped with As. The zero of energy corresponds to the Fermi energy. The structure considered here corresponds to the relaxed FM configuration.

for the basis set. The electronic structure was solved considering the generalized gradient approximation[18] for the exchange at gamma point alone using projected augmented wave (PAW) potentials.[19]

III. RESULTS AND DISCUSSION

We first consider the case of As doped into GaN. GaN we know has a large band offset with GaAs with the former having a deeper valence-band maximum. Mn when doped into GaN has been shown to introduce states into the band gap with significant Mn character. However, in contrast, Mn when doped into GaAs is found to introduce states with weak Mn character in the band gap. Although in both cases the formal oxidation state of the Mn is 3+, in the former case the configuration is d^4 while in the latter case is $\{d^5+\text{hole}\}$.[20] Since at this dilute limit, alloys show significant band bowing effects, we investigate Mn doping in this limit to probe modifications in the ferromagnetic stability. In Fig. 1 we have plotted the Mn d partial density of states. The N p partial density of states of a N atom which is nearest neighbor of the Mn as well the As p partial density of states has been shown. The valence-band maximum seems to comprise of primarily As p states with some N p admixture. However there is hardly any As p character at the Fermi level. We can understand this effect within a simple model that was proposed earlier to explain the electronic structure of transition-metal (TM) impurities in semiconductors.[20] The dominant interaction seems to be between the transition-metal impurity and its nearest neighbors. Atoms farther away from the TM impurity interact to a much lesser extent.

The next question we ask was how the ferromagnetic stability is modified. Should the presence of the As impurity affect the ferromagnetic stability? As the As levels are between the Mn d and the N p levels one would expect a modification in the ferromagnetic stability, possibly a value between the two end limits of Mn in GaN and GaAs. In this dilute alloy limit the valence-band maximum is intermediate between that for GaAs and GaN. The ferromagnetic stability as well as the corresponding mean-field estimate of T_c is given in Table I for various distances of the As impurity from either Mn atom. In the absence of As impurity, the ferromagnetic stability is ~84 meV and at the other limit of Mn in GaAs it is ~164 meV. This drastically drops to ~21 meV in the presence of an As impurity at 3.76 Å. As the As impurity is moved farther away the ferromagnetic stability is partly regained though it still remains less than the value in the absence of As impurity. This is contrary to our expectations and indicates that one must consider other factors such as alloy scattering in addition to the modified energy denominator for the interaction.

TABLE I. Effect on the ferromagnetic stability and Curie temperature by As codoping in (Ga,Mn)N host. The distance of the As atom from either Mn atoms in both the ferromagnetic and AFM relaxed configuration is also given.

Distance (Å)		Ferromagnetic stability (meV)	T_c (K)
FM	AFM	$(E_{FM}-E_{AFM})$	
		−83.8	324.2
3.72	3.71	−20.6	79.6
5.89	5.86	−50.0	193.4
6.71	6.69	−50.0	193.4
8.11	8.10	−34.8	134.6

Examining the opposite limit of GaAs into which the N is doped we find a similar trend in the ferromagnetic stabilization energy. In GaAs, Mn doping gives rise to a ferromagnetic stabilization energy of 164 meV (Table II). This drastically drops to 100 meV (Table II) for a N impurity introduced at 4.73 Å. Ferromagnetic stability corresponding to the unalloyed limit is partially regained for the N atoms farther away from Mn as shown in Table II.

Recent experimental work[14] on dilute magnetic semiconductors have focused on transition-metal impurities in dilute alloys with an aim of understanding the mechanism of the

TABLE II. Effect on the ferromagnetic stability and Curie temperature by N codoping in (Ga,Mn)As host. The distance of the N atom from either Mn atoms in both the FM and AFM relaxed configuration is also given.

Distance (Å)		Ferromagnetic stability (meV)	T_c (K)
FM	AFM	$(E_{FM}-E_{AFM})$	
		−163.8	633.6
4.73	4.75	−100.1	387.2
7.41	7.42	−154.3	596.9
8.44	8.44	−161.7	625.5
10.18	10.19	−147.5	570.6

TABLE III. Effect on the ferromagnetic stability and Curie temperature by P codoping in (Ga,Mn)As host. The distance of the P atom from either Mn atoms in both the FM and AFM relaxed configuration is also given.

Distance (Å)		Ferromagnetic stability (meV)	T_c (K)
FM	AFM	$(E_{FM}-E_{AFM})$	
		−163.8	633.6
4.73	4.75	−154.3	596.9
7.42	7.44	−162.1	627.0
8.45	8.45	−169.1	654.1
10.21	10.21	−172.7	668.0

ferromagnetism better. If the hole introduced by Mn doping is a valence-band hole the belief is that it should be weakly perturbed by alloying effects at the dilute limit. However a hole which resides in an impurity band is expected to be strongly affected by alloying effects. We artificially tune the hole introduced by the Mn doping with a introduction of U on the Mn d states in $(Ga,Mn)As_{0.99}N_{0.01}$. With a U of 4 eV on the Mn d states, the hole moves toward a valence-band hole. Hence, alloy scattering effects are expected to be weaker. Indeed our calculated ferromagnetic stability results reflect this. The FM stability changes by about 64 meV in the absence of U to 15 meV in the presence of U. Stone *et al.*[14] examined P doping in GaMnAs and found an insulator to metal transition as a function of doping. Usually high effective mass have to be assumed for the carriers to explain the experimental observations. This reinforces the idea of the carriers residing in an impurity band.

While Mn in GaN has usually been accepted as a system in which the hole introduced by Mn doping resides in an impurity band, the case of Mn in GaAs is heavily debated with supporters on both sides. In order to quantify our observations further we examined Mn doping in dilute alloys formed by P introduction in GaAs. If our earlier results of the N doping in GaAs established the validity of the impurity band model, then we should see strong effects on the ferromagnetic stability here also. The results as a function of the impurity distance are given in Table III. The perturbation seems to be very weak and consequently the variations in the ferromagnetic stabilization energy from the unperturbed case are small. Hence modifications of ferromagnetic stability in alloyed systems are not proof enough for the impurity band picture. The deviation between our results and experimental results of $GaMnAs_{1-y}P_y$ could be due to various reasons. One cause could be that the impurity potential is stronger. This is engineered by the clustering of the impurity atoms. Indeed when we introduced two P impurities, such that each P atom is the nearest neighbor to one of the Mn atom and also these P atoms connect the Mn atoms via a Ga atom, we found a reduction in the ferromagnetic stability from 164 meV in the unalloyed limit to 110 meV. Thus impurity scattering is responsible for the reduction in ferromagnetic stability.

Closer analysis revealed that there are two parts which need to be considered when an impurity atom is introduced.

TABLE IV. Effects of relaxation on the stability in the case of (Ga, Mn)As host codoped with N.

	Energy (eV)		Ferromagnetic stability (meV)	T_c (K)
	E_{FM}	E_{AFM}	$(E_{FM}-E_{AFM})$	
Unrelaxed	−907.192	−906.989	−203.2	786.0
Relaxed	−909.264	909.164	−100.1	387.2

The first part is that associated with the modified electronic interaction strengths of the impurity with the host and the second with the strain in the host lattice. Indeed we cannot decouple the two effects completely but the effects of these perturbations may be discussed within calculations performed under some constraints.

In Table IV we consider the case of N codoped into GaAs at a distance of 4.73 Å. The ferromagnetic stability is evaluated in the unrelaxed case where the calculation is performed assuming that N merely replaces an As atom. This calculation would capture the effects of modified interaction strengths as a result of N doping. Ferromagnetic stability of the Mn pairs is increased from 164 meV in the absence of N impurity to 203 meV. Examining the density of states corresponding to the unrelaxed limit, we find that N p states are energetically closer to the Mn d states and hence the increased interaction between the two could explain the increased ferromagnetic stability. This is reflected in the inset of Fig. 2(c) which shows the N p character near Fermi energy. Ga-N bonds are much smaller than the Ga-As bonds. Allowing the atoms to optimize their internal positions by total-energy minimization We find that the Ga-N bonds are

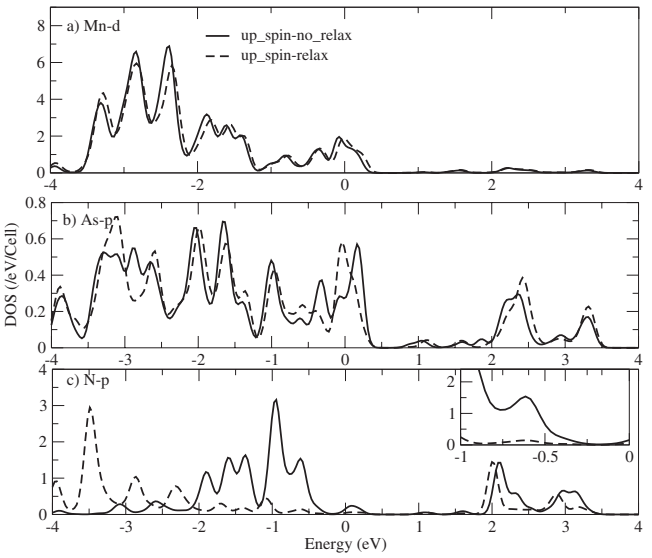

FIG. 2. (a) The spin-up-projected density of states for Mn d, (b) As p, which is the nearest neighbor of the Mn, and (c) for the N p calculated for (Ga,Mn)As codoped with N. Inset of (c) shows a magnified view of the N p density of states near the Fermi energy region. The solid lines correspond to the unrelaxed structure while the dashed lines correspond to the relaxed structure. The zero of energy corresponds to the Fermi energy.

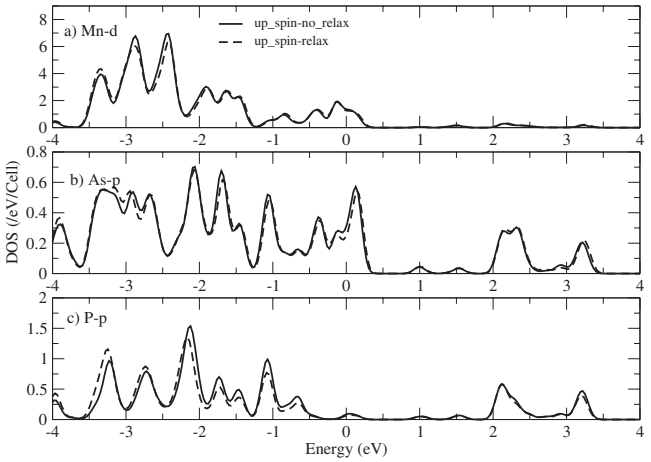

FIG. 3. (a) The spin-up-projected density of states for Mn *d*, (b) As *p*, which is the nearest neighbor of the Mn, and (c) for the P *p* calculated for (Ga,Mn)As codoped with P. The solid lines correspond to the unrelaxed structure while the dashed lines correspond to the relaxed structure. The zero of energy corresponds to the Fermi energy.

~2.08 Å long while the Ga-As bonds close to the N atom are 2.53 Å long. Those far away from the N impurity are 2.48 Å long. Examining the ferromagnetic stability in such a configuration, we find that it is drastically reduced to 100 meV. Examining the density of states (Fig. 2) we find that there is hardly any change in the As *p* density of states plotted for the nearest-neighbor As atom as well as the Mn *d* partial density of states with and without relaxation. N *p* density of states show significant changes with relaxation with the N *p* states moving from −1 to −3.5 eV below the Fermi level. In the inset of Fig. 2(c) we magnify the near Fermi energy region of the N *p* density of states and see that there is significant N *p* character at the Fermi energy in the unrelaxed case which is reduced upon relaxation. Since movement of N *p* levels should imply reduced interaction with Mn, the main effect of ferromagnetic stability reduction has to be the lattice strain. Considering the case of P in GaAs doped with Mn (Fig. 3), we find that the effects of relaxation are very weak as a result of which ferromagnetic stability is hardly affected (Table III). Thus we are able to elucidate the microscopic origin of the reduction in T_c when we alloy III-V semiconductors with another group V anion. Although our calculations provide us with qualitative trends, an exact numerical expression for the T_c as a function of concentration in the dilute limit is difficult. This is because the ferromagnetic stability is a strong function of the disorder position as well as of concentration. Strong disorder potentials caused by clustering of the alloying atoms results in a stronger decrease in T_c than when one has a random distribution.

IV. CONCLUSION

We have examined Mn doping in the dilute alloy limit, where strong valence-band bowing is observed, as a possible route to enhance the ferromagnetic transition temperature. This has been quantified in our calculation as the ferromagnetic stabilization energy for a pair of Mn atoms occupying lattice sites for which ferromagnetic stability has been observed to be strong. Contrary to expectations of enhanced ferromagnetic stability on alloying we find a reduction in the case of $Ga_{1-x}Mn_xAs_{1-y}N_y$ and $Ga_{1-x}Mn_xAs_{1-y}P_y$ where $y \sim 0.01$. Mn doping in $Ga_{1-x}Mn_xAs_{1-y}P_y$ shows very small changes in the ferromagnetic stability for 1% anion doping but for larger percentage of doping shows a reduction in T_c. The origin of reduced ferromagnetic stability is traced to the strong strain effects that accompany the introduction of the anion impurity. This strongly scatters the electron and therefore modifies the ferromagnetic stability.

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