

Influence of the local As antisite distribution on ferromagnetism in (Ga,Mn)As

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The effect of the inclusion of As antisites in the diluted magnetic semiconductor (Ga,Mn)As is studied within the density functional theory in the local spin density approximation. In the case of the homogeneous distribution of Mn ions, we find that the ferromagnetism is weakened by the presence of the antisites. This is due to the compensation of the free holes which mediate the long-range ferromagnetic order. In contrast, when two Mn ions are coupled through only one As ion, the ferromagnetic and antiferromagnetic states are comparable in energy. In this case, the magnetic ground state depends on: (i) the position of the As antisites relative to the Mn, and (ii) the As antisite concentration. We explain our results using a model of competing antiferromagnetic super exchange and ferromagnetic double exchange via localized Zener carriers. © 2001 American Institute of Physics. [DOI: 10.1063/1.1375834]

In the past ten years, the study of diluted magnetic semiconductors (DMS) has been strongly revitalized since the discovery of ferromagnetic order in $\text{In}_{1-x}\text{Mn}_x\text{As}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$.^{1,2} The potential utility of room temperature ferromagnetism in a semiconductor based system is enormous. On one hand, DMS could replace the existing metallic magnetic elements in storage media.³ On the other hand, DMS can be used as spin injectors into semiconductors.^{4,5} This is a critical step in the physical realization of quantum computation based on the spin degree of freedom in a solid state device.⁶ In fact, although it has been shown that spin can be coherently transported over several micrometers in GaAs,⁷ its injection from metallic magnetic contacts has been largely unsuccessful.⁸ Injection from DMS is however possible^{4,5} and (Ga,Mn)As–GaAs–(Al,Ga)As is the most promising material system to date for the injection, storage, and manipulation of spins in semiconductors.

Although there is general agreement on the carrier (hole-) mediated origin of the ferromagnetism in (Ga,Mn)As, the detailed mechanism is still debated. The Zener model in the mean field approximation⁹ provides a good starting point. However, its prediction of the Curie temperature as a function of Mn and hole concentration largely overestimates the actual value if a dynamic description of the Mn spins is considered.¹⁰ Moreover, recent density functional theory (DFT) results¹¹ show that the p - d coupling in (Ga,Mn)As is very strong and the mean field approximation cannot be completely justified.

All the models agree on the following important points: (i) Mn^{2+} ions substitute the Ga^{3+} cations in the zincblende lattice providing local $S=5/2$ spins, and (ii) there are free holes in the system although the actual concentration is much smaller than the density of the Mn ions.^{1,2} This latter point suggests that some mechanism of compensation must be taking place, most likely the presence of intrinsic donor defects such as As antisites (As_{Ga}). In the aforementioned models,

the compensation mechanism is implicitly incorporated in the mean field description of the GaAs valence band, since the hole concentration is a free parameter. As a result, the local effects of magnetic and chemical disorder are neglected.

In this letter, we consider explicitly the effects of the inclusion of As_{Ga} in (Ga,Mn)As, and study how the chemical environment modifies the magnetic interaction between the Mn ions. We perform DFT calculations within the local spin density approximation (LSDA), and investigate the dependence of the magnetic coupling between the Mn ions on: (i) Mn concentration, (ii) As_{Ga} concentration, and (iii) relative positions of the Mn ions and the As_{Ga} defects. The main result of our analysis is that, for a uniform distribution of Mn ions, As_{Ga} antisites significantly weaken the ferromagnetic coupling. However, at least for moderate concentrations, the compensation does not follow the expected nominal valences of Mn and As (that is, one As_{Ga} does not completely compensate the holes from two Mn ions). Moreover when two Mn ions are separated by only one As atom (so that they occupy two corners of a zincblende tetrahedron with an As atom in the center), ferromagnetic coupling is possible even far above compensation if As antisites are located at the other two tetrahedral positions to form a Mn_2As_3 complex (see Fig. 3).

Our calculations are performed using the code SIESTA,¹² which is an efficient implementation of DFT-LSDA based on pseudopotentials and a numerical localized atomic orbital basis set. This method combines good accuracy and small computational cost compared to other methods based on plane waves. Calculation details are given elsewhere.¹¹

We construct cubic 64 and rectangular 32 atom GaAs cells in which we include two Mn ions (giving Mn concentrations of $x=0.0625$ and $x=0.125$, respectively) and a variable number of As_{Ga} antisites. We investigate two different Mn configurations for each concentration: (1) the Mn ions occupy positions as far apart as possible (i.e., the corner and the middle of the cubic cell), (2) the Mn atoms occupy two corners of a tetrahedron and are coordinated through a single

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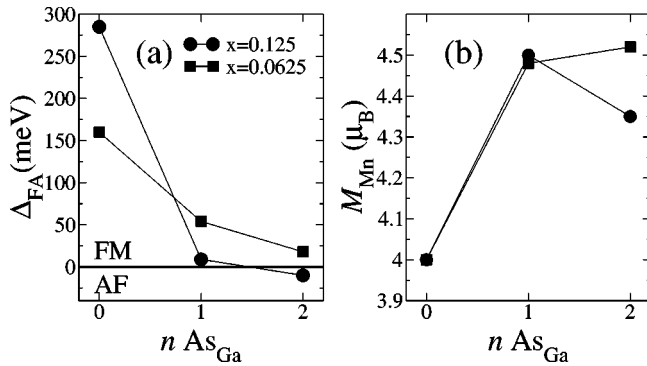


FIG. 1. (a) Energy difference between AF and FM alignments, Δ_{FA} , and (b) magnetization per Mn ion, M_{Mn} , as a function of the number of As_{Ga} antisites in the cell: *separated* configuration.

As ion. We call these two configurations *separated* and *close*, respectively. We calculate the ground-state properties of these systems for both ferromagnetic (FM) and antiferromagnetic (AF) alignment of the Mn ions within the cell.

The energy differences between the AF and FM aligned configurations, Δ_{FA} , and the magnetization per Mn ion, M_{Mn} , for the *separated* arrangement are presented in Fig. 1 as a function of the number of As_{Ga} antisites. The magnetization per Mn ion is defined to be half of the magnetization of the cell, calculated in the FM phase.

First, we note that the ferromagnetic coupling is strongly weakened by As_{Ga} antisite doping. This is consistent with the picture of magnetic coupling mediated by free carriers (holes): As_{Ga} antisites contribute electrons into the system and therefore compensate the holes. We also note that in the case of no antisites the ferromagnetic order is much stronger for large Mn concentration, which again supports the model of carrier-induced ferromagnetism. Within this model, the ferromagnetic coupling should disappear when the compensation is complete. However Fig. 1 suggests that the compensation mechanism does not follow the nominal atomic valence, since a single As_{Ga} antisite per cell is not sufficient to destroy the ferromagnetic coupling. Above compensation (one As_{Ga} for two Mn ions) antiferromagnetic coupling is obtained for large Mn concentration, while the system stays ferromagnetic at a low concentration. This is consistent with the onset of AF super-exchange coupling at compensation. Super exchange is a short range interaction, and therefore, is less important in the low concentration limit where the Mn ions are well separated. It is worth noting that for $x=0.125$ and large antisite concentrations ($n As_{Ga}=2$) the magnetic order is quite sensitive to the actual position of the antisite respect to the Mn ions. Different As_{Ga} arrangements may result either in FM or AF coupling.

If we now consider the magnetization per Mn ion [Fig. 1(b)] we note that there is a monotonic increase of the total magnetic moment on antisite doping. This can be understood by looking at the density of states of Fig. 2 (see also Ref. 11). At the Fermi energy, the density of states (DOS) of the majority spin band is the result of the hybridization between the Mn d states with t_2 symmetry and the p states coming mainly from As_{Ga} . The two donor levels of isolated As_{Ga} in GaAs are known to lie 0.54 and 0.75 eV above the GaAs valence band and to overlap with the exchange split Mn d levels of low dilution (Ga, Mn)As.¹¹ In contrast, the DOS of

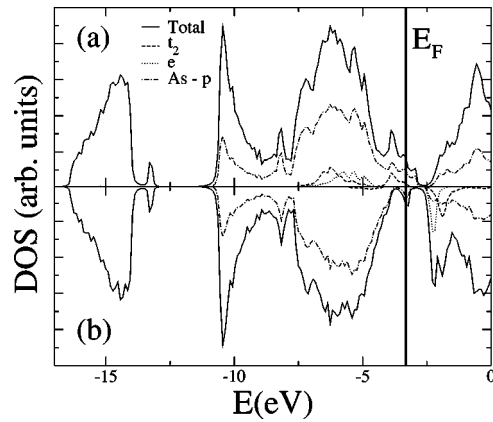


FIG. 2. DOS for (Ga, Mn)As obtained for a 64 atom unit cell with two Mn ions and one As_{Ga} antisite: *separated* configuration, FM alignment. (a) majority and (b) minority spins.

the minority spin band is dominated by antisite levels, the first Mn d states lying far above E_F . Therefore by increasing the antisite concentration, E_F is shifted towards higher energy, thus increasing the occupation of the Mn d shell in the majority spin band. This enhances the total magnetic moment of the system. Finally, note that a magnetization of $4.5\mu_B$ is in very good agreement with recent x-ray magnetic circular dichroism measurements.¹³

Let us now turn our attention to the *close* configuration. In this case, we expect the short range super exchange to play a more important role since the Mn ions are much closer to each other. Moreover the magnetic coupling is expected to be quite sensitive to the position of the antisites with respect to the Mn ions. We consider three different situations (Fig. 3): (a) the antisites are far from the $Ga_2Mn_2As_1$ complex, (b) one antisite occupies a tetrahedral site ($Ga_1Mn_2As_2$), and (c) two antisites occupy the tetrahedral sites (Mn_2As_3). In Fig. 3 we show Δ_{FA} and M_{Mn} as a function of the As_{Ga} concentration for these antisite arrangements. For the sake of brevity, we present data only for $x=0.0625$, noting that similar conclusions can be made also for $x=0.125$. From Fig. 3 it is very clear that, when the As_{Ga} defects are in the vicinity of the Mn ions [configurations (b) and (c)], the system is almost insensitive to the As_{Ga} concentration. In contrast, when the As_{Ga} antisites are far from the Mn ions the magnetic coupling undergoes a FM to AF transition with increasing antisite concentration.

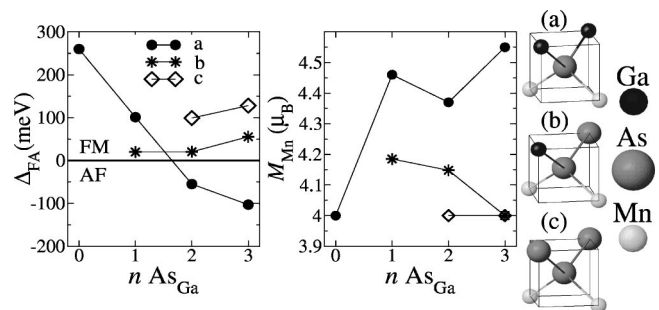


FIG. 3. (Left-hand side) energy difference between the AF and FM alignments Δ_{FA} and (right-hand side) magnetization per Mn ion M_{Mn} as a function of the number of As_{Ga} antisites in the cell: *Close* Mn configuration. The symbols \bullet , $*$, and \diamond represent arrangements (a), (b), and (c), respectively.

TABLE I. Mülliken atomic and orbital populations for the Mn ions and the intermediate As atom of the complexes of Fig. 3 ($x=0.0625$). The symbols \uparrow and \downarrow correspond to majority and minority spin respectively. The populations are in units of the electronic charge $|e|$.

n	As_{Ga}	Type	Mn- d_{\uparrow}	Mn- d_{\downarrow}	As- p_{\uparrow}	As- p_{\downarrow}	As- p	As
2	a	a	4.74	0.70	1.55	1.63	3.18	4.92
2	b	b	4.74	0.71	1.50	1.67	3.17	4.95
2	c	c	4.72	0.75	1.44	1.71	3.15	4.97
3	a	a	4.76	0.68	1.57	1.63	3.20	4.93
3	b	b	4.74	0.74	1.55	1.65	3.20	4.97
3	c	c	4.73	0.75	1.49	1.69	3.17	4.99

Consider first configuration (a). In this case both the Δ_{FA} and M_{Mn} curves look very similar to the curves we found for the *separated* arrangement (Fig. 1). However, in stark contrast with the *separated* case, an AF alignment can now be found for *large* As_{Ga} concentrations. Recalling the fact that the Mn d shell is more than half filled, and that it is antiferromagnetically coupled with the As p shell of the intermediate atom,¹¹ we propose that super-exchange coupling stabilizes the AF phase as soon as the free holes are completely compensated. However, this mechanism is extremely short range and therefore effective only when the Mn ions are separated by one As.

We now turn our attention to situations (b) and (c). In both cases, the FM alignment is stable and almost insensitive to the total As_{Ga} concentration. This is a strong indicator that the dominant interaction in these cases depends only on the local chemical properties. To shed some light on this aspect, we perform Mülliken population analyses.^{14,11} The Mülliken orbital (or atomic) population is the projection of the charge density onto a particular orbital (or atom). In Table I, we present the orbital population for the two Mn ions and the intermediate As ion of the complexes of Fig. 3. The most obvious feature is the larger polarization of the As p orbitals in Mn_2As_3 compared with $\text{Ga}_2\text{Mn}_2\text{As}_1$. This is accompanied by a small decrease in Mn d polarization, although this latter effect could be an artifact from the overlap component of the orbital population.¹¹ It is also interesting to note that the total atomic population of the As atom increases going from (a) to (b) to (c), while the p component of the population decreases. Therefore, if we start from the situation in which two As_{Ga} antisites are located far from the Mn-As-Mn complex, then we move each antisite in turn to one of the two other corners of the tetrahedron, then (i) the charge on the middle As atom increases, (ii) the spin polarization of the p shell of the middle As atom increases, and (iii) the total population of the p shell of the middle As atom decreases. And most importantly, the magnetic coupling changes from AF to FM.

In 1960, de Gennes observed¹⁵ that in an AF crystal, the presence of a bound carrier (electron or hole) which is Zener coupled to the local spins *always* induces a distortion in the AF lattice. In that spirit, we propose that the observed transition from AF to FM coupling between $\text{Ga}_2\text{Mn}_2\text{As}_1$ and Mn_2As_3 results from the onset of FM double-exchange coupling mediated by a bound Zener carrier. For $\text{Ga}_1\text{Mn}_2\text{As}_2$, we verified this hypothesis by performing a general spin calculation and found that the actual ground state is not given by perfect FM alignment, but instead, the Mn magnetic moments are canted with respect to each other.

In conclusion, we have shown that the inclusion of the As_{Ga} in (Ga, Mn)As can result in a variety of different behaviors depending on the microscopic arrangement of the Mn ions and the As_{Ga} antisites. In particular, we have shown that when the Mn ions are uniformly distributed in the crystal, As_{Ga} antisites weaken the ferromagnetic order. In contrast, if the Mn ions occupy two corners of the zincblende tetrahedron, several magnetic arrangements are possible depending on the positions of the antisites. In particular, FM coupling is obtained if antisites occupy the other positions in the tetrahedron. This suggests that a way to obtain high T_{C} in (Ga, Mn)As is to deposit Mn and As antisites with a strongly inhomogeneous distribution.

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