Prediction of enhanced ferromagnetism in (Ga,Mn)As by intrinsic defect manipulation

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Abstract

In the diluted magnetic semiconductor (Ga,Mn)As the excess of As incorporated as As antisites (AsGa) is responsible for the hole compensation. The AsGa defect can be transformed into a As interstitial–Ga vacancy pair (Asi–VGa) upon illumination. In this paper we study the effects of such a transition on the ferromagnetism of (Ga,Mn)As using density functional theory within the local spin density approximation. We find that the ferromagnetic order in (Ga,Mn)As is strongly enhanced if AsGa are transformed into Asi–VGa pairs, since the hole compensation is reduced. This suggests a valuable way to tune the carrier concentration and hence the \( T_c \) in (Ga,Mn)As, without changing the Mn concentration nor the microscopic configuration of the Mn ions. © 2002 Elsevier Science B.V. All rights reserved.

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The recent discovery of ferromagnetism in Mn-doped III–V semiconductors [1,2] has generated great enthusiasm because of their potential applications in magnetoelectronics [3]. In particular (Ga,Mn)As is a very promising material since it is compatible with the existing technology based on GaAs/(Al,Ga)As. In (Ga,Mn)As the Mn ions occupy the cation sites of the zincblende lattice, and generate free holes in the valence band due to the difference between the valence of Mn\(^{2+}\) and Ga\(^{3+}\). The free carriers are antiferromagnetically coupled to the local spins of Mn, through a strong p–d interaction [4]. This gives rise to carrier-mediated ferromagnetic coupling between the Mn ions [5].

The starting point for modeling the ferromagnetism of (Ga,Mn)As is mean field theory [5,6], in which the magnetizations of both carriers and Mn ions are considered to be uniform in space. Within this approach the critical temperature for the ferromagnetism \( T_c \) is given by [5,6]

\[
T_c = \frac{S(S+1)NJ_p^2}{8E_F} p, \tag{1}
\]

where \( S = \frac{7}{2} \) is the Mn spin, \( J_p \) is the exchange integral, \( N \) is the Mn concentration, \( \mu_B \) the Bohr magneton, \( E_F \) the Fermi energy and \( p \) the hole concentration. From Eq. (1) one sees that \( T_c \) increases as \( p^{1/3} \) (\( E_F \propto p^{2/3} \)), suggesting the possibility of arbitrarily large \( T_c \) upon heavy \( p \)-doping. However, a careful analysis of spin-wave
excitations [7] shows that for large hole concentration the dependence of $T_c$ on $p$ is more severe than $p^{1/3}$ in the weak coupling limit, posing a severe limit on the highest $T_c$ achievable.

From this short discussion it is clear that the ability to change the hole concentration, while keeping both the Mn concentration and the microscopic distribution fixed [8] will be very useful in understanding the basic mechanism of hole induced ferromagnetism. To date this has been achieved in (In,Mn)As by photo-excitation [9] and gate control [10]. However the same techniques are less applicable to (Ga,Mn)As because of the large hole concentration in as-grown samples. In this letter, we propose an alternative mechanism based on intrinsic defect engineering, which in principle can tune the hole concentration of (Ga,Mn)As in heavily $p$-doped samples.

We recall that in low-temperature (LT) molecular beam epitaxy grown (Ga,Mn)As the hole concentration is usually much smaller than the Mn concentration [1,2], and that the compensation is largely due to the excess of arsenic incorporated as As antisites, $A_{\text{Ga}}$. $A_{\text{Ga}}$ are also the largest source of donors in LT-GaAs grown under As rich conditions and/or acceptor-doping (e.g. Be) [11]. Consider for example Ga$_{1-x}$Mn$_x$As with $x = 0.053$ ($N = 1.3 \times 10^{21}$ cm$^{-3}$), which to date presents the highest $T_c$. In this case the hole concentration has been carefully measured to be $p = 3.5 \times 10^{20}$ cm$^{-3}$ [12]. $A_{\text{Ga}}$ are double donors and assuming they are the only source of compensation we obtain an $A_{\text{Ga}}$ concentration of $4.2 \times 10^{20}$ cm$^{-3}$ in such a sample. It is clear that if one can eliminate such defects without affecting the Mn concentration, part of the compensation will be removed and very large hole concentration can be reached.

Isolated $A_{\text{Ga}}$ in GaAs are responsible for the photoquenchable EL2 defect [13]. In fact $A_{\text{Ga}}$ upon illumination undergoes a structural transition to an As interstitial–Ga vacancy ($A_{\text{Si}}$–$V_{\text{Ga}}$) pair, which is obtained by moving $A_{\text{Ga}}$ along the $\langle 111 \rangle$ direction (see Fig.2). This complex is metastable since $A_{\text{Ga}}$ can be regenerated by heating. It is crucial to observe that the $A_{\text{Si}}$–$V_{\text{Ga}}$ pair is not electronically active in GaAs, since its only state in the bandgap is completely filled. In this letter, we show that this metastable complex is present, can be obtained by illumination and is also electronically inactive in (Ga,Mn)As.

With this goal, we perform density functional theory (DFT) calculations within the local spin density approximation (LSDA) using the code SIESTA [14]. SIESTA 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 [4,8].

In all the calculations presented here we consider 64 atom GaAs supercells in which we include Mn ions and intrinsic GaAs defects (either $A_{\text{Ga}}$ or $A_{\text{Si}}$–$V_{\text{Ga}}$ pair). The strength of the ferromagnetic coupling is calculated by introducing two Mn ions in the unit cell and by calculating the energy difference $\Delta_{\text{FA}}$ between the antiferromagnetic and ferromagnetic alignments [8]. We allow the system to relax and we stop the relaxation when the global stress on the unit cell is smaller than $2 \times 10^{-5}$ eV/Å$^3$ and the largest force on the individual atoms is smaller than $5 \times 10^{-3}$ eV/Å. We proceed as follows: first we prove the existence of the metastable complex $A_{\text{Si}}$–$V_{\text{Ga}}$ in (Ga,Mn)As, second we discuss how this complex can be generated from $A_{\text{Ga}}$, and finally we discuss the effect of such a transition on the ferromagnetism of (Ga,Mn)As.

In Fig.1, we present the total energy and the magnetization of an unrelaxed 64 atom unit cell containing one Mn ion ($x = 0.03125$) and one $A_{\text{Ga}}$ as a function of the displacement $l_{\langle 111 \rangle}$ of $A_{\text{Ga}}$ along $\langle 111 \rangle$. For comparison we also present the same curve for GaAs. From the picture it is clear that a metastable state exists in both cases for a displacement of about 1.5 Å. The energy barriers for the thermal regeneration (energy difference between the metastable state $l_{\langle 111 \rangle} \sim 1.5$ Å and the barrier maximum) are 0.50 and 0.45 eV, respectively for GaAs and (Ga, Mn)As. These values are reduced approximately by 0.1 eV if we allow the cell to relax, in good agreement with the regeneration temperature in GaAs ($T \geq 140$ K) [15] and with previous
theoretical calculations [13]. Therefore, we predict that the metastable Asi–VGa pair exists also in (Ga,Mn)As, and that the corresponding regeneration temperature is very similar to that of GaAs. The same calculation for Mn shows that no metastable Mni–VGa exists, in agreement with the fact that the transition is observed only if the $T_d$ impurity is a double donor [16].

In order to understand how this metastable state can be formed it is interesting to consider the energy levels of isolated AsGa and Asi–VGa in GaAs (Fig. 2). An isolated AsGa is a double donor, whose doubly occupied donor level (in the neutral configuration) belongs to the $A_1$ representation of the point group $T_d$. Although we use a large supercell, this state forms quite a dispersive impurity band. We take the position of its energy level by considering the impurity band center, and find a value of approximately 0.5 eV above the valence band (which reduces to $\sim 0.35$ eV for a relaxed cell). There is also a resonant state close to the conduction band edge with $t_2$ symmetry. The energy level of an Asi–VGa pair can be understood within a simple tight-binding picture by considering the interaction between an isolated Ga vacancy (point group $T_d$) and an isolated As interstitial (point group $C_{3v}$) [13]. This gives rise to only one doubly occupied energy level in the GaAs band-gap, and this level has $a$ symmetry. The corresponding impurity band is less dispersive than the $a_1$ band of AsGa and we calculate an impurity level of 0.3 eV above the valence band, which reduces to $\leq 0.1$ eV after relaxation.

The mechanism for transforming an isolated AsGa defect into a Asi–VGa pair has been explained by Scheffler et al. [16]. The main idea is that the excited electronic configuration $a'_1t'_2$ of a tetrahedral substitutional double donor (here AsGa) induces lattice distortion. The distortion is initiated because the many-electron wave function of the $a'_1t'_2$ configuration is orbitally degenerate. This means that the system is Jahn–Teller unstable, and it will lower the total energy by splitting the $t_2$ state into a lower $a$ state (half-filled) and a higher $e$ state (empty). It has been demonstrated that in GaAs the total-energy curve as a function of the displacement of AsGa along $<111>$ for the $a'_1t'_2$ configuration ($1a'_12a'$ when the defect assumes the
C_{3v} symmetry) has a minimum for l_{111} \approx 0.3 \text{ Å} [13]. Therefore, an optical excitation of the a_{1}^2 t_{2} ground-state to the a_{1}^1 t_{2} will initiate a distortion. Then the system has some probability to relax on the As_{i}–VGa side of the total-energy curve of Fig. 1, ending up considerably far from the antisite position. This mechanism leads to the creation of the As_{i}–VGa pair.

The same mechanism holds for (Ga,Mn)As since the only difference with respect to GaAs in the spin-splitting of the bands. This splitting however does not bring the a state of AsGa in the valence band nor the t_{2} state in the conduction band. Moreover as observed in Fig. 2 of Ref. [8] the midgap a level is partially occupied. With these considerations it is clear that the As antisite in (Ga,Mn)As presents the same features as that in GaAs and, therefore the mechanism described above is still applicable.

Finally, we discuss the effects of the As_{Ga} \rightarrow As_{i}–VGa transition on the ferromagnetism of (Ga, Mn)As. In Table 1, we present \Delta_{FA}, the M"{u}lliken orbital populations of the d-shell (\rho_{d}^{\uparrow}, with \sigma = \uparrow(\downarrow) for majority (minority) spin) and the corresponding spin polarization [4,8] for the ferromagnetic configuration. These are calculated for a 64 atom unit cell containing two Mn atoms and respectively no defects, one As_{Ga} and one As_{i}–VGa pair. The table clearly shows that the ferromagnetic coupling is strengthened considerably by the distortion and that both the energy splitting and the M"{u}lliken orbital population of As_{i}–VGa are very similar to those of defect-free (Ga,Mn)As. This suggests that the ferromagnetic order in (Ga,Mn)As is unaffected by the presence of As_{i}–VGa pairs.

Table 1
Antiferromagnetic to ferromagnetic energy splitting \Delta_{FA}, Mulliken orbital population \rho_{d}^{\downarrow} of d shell for spin \sigma and Mn d shell polarization \xi_{d} for a 64 atom (Ga,Mn)As cell (two Mn ions) with various defects

<table>
<thead>
<tr>
<th>Defect</th>
<th>\Delta_{FA} (meV)</th>
<th>\rho_{d}^{\uparrow} (e\text{\ angstrom}^{-1})</th>
<th>\rho_{d}^{\downarrow} (e\text{\ angstrom}^{-1})</th>
<th>\xi_{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>159</td>
<td>4.669</td>
<td>0.776</td>
<td>0.715</td>
</tr>
<tr>
<td>As_{Ga}</td>
<td>53</td>
<td>4.751</td>
<td>0.688</td>
<td>0.747</td>
</tr>
<tr>
<td>As_{i}–VGa</td>
<td>124</td>
<td>4.695</td>
<td>0.755</td>
<td>0.723</td>
</tr>
</tbody>
</table>

This result is in agreement with the hole-mediated picture of ferromagnetism, and can be understood by noting that the As_{i}–VGa energy levels show minimal splitting in (Ga,Mn)As. The energy level scheme for As_{i}–VGa in (Ga,Mn)As is that of Fig. 3, where we split only the valence band (the spin-splitting of the conductance band is small and not relevant for the present discussion). Since the highest occupied impurity state of As_{i}–VGa lies at only \sim 0.1 eV above the valence band of GaAs, the spin-splitting in (Ga,Mn)As moves such a state into the valence for the majority spin, and leaves it in the gap for the minority. This means that the As_{i}–VGa pair is not electrically active in (Ga, Mn)As. Therefore, it does not participate in the compensation of the holes supplied by the Mn ions, and therefore does not weaken the ferromagnetic coupling.

Our calculated band structure confirms this picture. In Figs. 4 and 5, we present the band structures for a cubic 64 atom unit cell (2 \times 2 \times 2 zincblende cubic cells) containing one Mn ion (x = 0.03125) and respectively one As_{Ga} and one As_{i}–VGa pair. We consider the band structure along the direction (\frac{1}{2} \pi/c_0,0,0) \rightarrow (0,0,0) \rightarrow (\frac{1}{2} \pi/c_0, \frac{1}{2} \pi/c_0, \frac{1}{2} \pi/c_0) with c_0 the unit vector of the cubic cell. We indicate these two directions respectively as X and M. The behavior of the two defects in (Ga,Mn)As is very different. In the case of As_{Ga} the Fermi energy cuts through the As_{Ga} impurity band, leaving the GaAs valence band.
band completely filled. Therefore, there are no holes mediating the ferromagnetic coupling between the Mn ions. This results in a strong reduction of $\Delta_{FA}$ with respect to the defect-free case. In contrast the band structure of (Ga,Mn)As with a $\text{As}_i-\text{V}_\text{Ga}$ pair is very similar to that of the scheme of Fig. 3. Although there is a small spin splitting of the impurity level, it is clear that this defect leaves holes in the majority spin band. The Fermi energy cuts through the top of the valence band and the impurity level. This situation is similar to the defect-free case, therefore the presence of $\text{As}_i-\text{V}_\text{Ga}$ pairs affects only weakly the ferromagnetic coupling between the Mn ions.

In conclusion, we propose that illumination of (Ga,Mn)As should be able to enhance the hole concentration, and in turn strengthen the ferromagnetic coupling. This is due to an optically induced transition of the $\text{As}_\text{Ga}$ antisites to metastable $\text{As}_i-\text{V}_\text{Ga}$ pairs. Such pairs are electronically inactive and reduce the hole compensation caused by the $\text{As}_\text{Ga}$ antisites. The effect suggested here constitutes a valuable way to tune the hole concentration in (Ga,Mn)As without changing either the Mn concentration or its microscopic distribution. However, since the $\text{As}_\text{Ga}$ regenerate for temperatures of the order of 140K, the mechanism cannot be used to obtain the high $T_c$’s required for technological applications. We suggest that illumination experiments in the spirit of this paper should be carried on with samples very close to compensation, therefore with quite low initial $T_c$.

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References