Do As antisites destroy the ferromagnetism of (Ga,Mn)As?

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(Dated: November 13, 2018)

The effect of the inclusion of As antisites in the diluted magnetic semiconductor (Ga,Mn)As is studied within density functional theory in the local spin density approximation. In the case of homogeneous distribution of Mn ions we find that the ferromagnetism is largely weakened by the presence of the antisites. This is due to 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, ferromagnetic and antiferromagnetic order compete. 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. The strong dependence of the ferromagnetic order on the microscopic configuration accounts for the large variation in experimental data.

PACS numbers: 75.50.Pp, 75.30.Et, 71.15.Mb, 71.15.Fv

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 \( \text{Ga}_{1-x} \text{Mn}_{x} \text{As} \). The potential utility of room temperature ferromagnetism in a semiconductor based system is enormous. On one hand, DMS could be replace the existing metallic magnetic elements in storage media. Here their better compatibility with existing semiconductors and MBE-growth technology over their metallic counterparts is a great advantage. On the other hand DMS can be used as spin injectors into semiconductors. This is a critical step in the physical realization of quantum computation based on the spin degree of freedom in a solid state device. In fact, although it has been shown that spin can be coherently transported over several micrometers in GaAs, its injection from metallic magnetic contacts is largely unsuccessful if not impossible. This is due to the large mismatch between the resistances of the metallic contacts and the semiconductor. The use of DMS solves this problem and \( \text{(Ga,Mn)}_{x} \text{As} \) together with GaAs and \( \text{(Al,Ga)}_{x} \text{As} \) represent to date the most promising material system 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 \( \text{(Ga,Mn)}_{x} \text{As} \), the detailed mechanism is still debated. The Zener model in the mean field approximation 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. Moreover recent density functional theory (DFT) results show that the \( p-d \) coupling in \( \text{(Ga,Mn)}_{x} \text{As} \) is very strong and the mean field approximation cannot be completely justified. Finally DFT calculations based on the coherent-potential approximation (CPA) suggest that the ferromagnetic order in \( \text{(Ga,Mn)}_{x} \text{As} \) may result from the competition between ferromagnetic double-exchange and antiferromagnetic super-exchange interactions.

Note that all these 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 Mn ions. 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 \( (\text{As}_{\text{Ga}}) \) or Ga vacancy-interstitial As pairs \( (\text{V}_{\text{Ga}}-\text{As}) \), which are usually found in low-temperature GaAs. In the above 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 paper we consider explicitly the effects of the inclusion of \( \text{As}_{\text{Ga}} \) in \( \text{(Ga,Mn)}_{x} \text{As} \) at different dilutions, 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 consider large GaAs cells in which Mn ions and \( \text{As}_{\text{Ga}} \) are inserted. We study the dependence of the magnetic coupling between Mn ions on: i) Mn concentration, ii) \( \text{As}_{\text{Ga}} \) concentration, iii) relative positions of the Mn ions and the \( \text{As}_{\text{Ga}} \) defects. The main result of our analysis is that, for a uniform distribution of Mn ions, \( \text{As}_{\text{Ga}} \) antisites strongly 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 \( \text{As}_{\text{Ga}} \) 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 levels.
if As antisites are located at the other two tetrahedral positions to form Mn$_2$As$_3$ complex (see Fig. 3).

Our calculations are performed using the code SIESTA [17, 18, 19], 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. We have described in a previous paper [14] the calculation details and the prescriptions one needs to optimize the basis set and the pseudopotentials. Here we just mention that we use Troullier-Martins pseudopotentials [20] with non-linear core corrections [21] and Kleinman-Bylander factorization [22], and the Ceperley-Alder [23] form of the exchange-correlation potential.

We construct 64 (cubic) and 32 (rectangular) atom GaAs cells in which we include two Mn ions and a variable number of As$_{Ga}$ antisites. These correspond to Mn concentrations of $x=0.0625$ (to date the largest concentration obtained experimentally) and $x=0.125$ respectively. 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 As ion (see Fig. 3). We call these two configurations separated and close respectively. The cells are then periodically repeated using 18 $k$-points in the irreducible cubic Brillouin zone. Note that the periodic boundary conditions fix the magnetic coupling between Mn ions that occupy equivalent positions in adjacent cells to be ferromagnetic but that the coupling between the two Mn ions in the same cell can be ferromagnetic or antiferromagnetic.

We calculate the ground-state properties of these systems for both ferromagnetic (FM) and antiferromagnetic (AF) alignment of the Mn ions within the cells.

The energy differences between the AF and FM aligned configurations, $\Delta_{AF}$, 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 aligned 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 in the case of 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 the figure 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 low concentration. This is consistent with the onset of antiferromagnetic super-exchange coupling, the mechanism which is believed to be responsible for the magnetic order in the II-VI DMS [24], 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 with respect to the Mn ions. Different As$_{Ga}$ arrangements may result either in ferromagnetic or antiferromagnetic coupling.

![FIG. 1: (a) Energy difference between AF and FM alignments, $\Delta_{AF}$, and (b) magnetization per Mn ion, $M_{Mn}$, as a function of the number of As$_{Ga}$ antisites in the cell: separated configuration. The horizontal line denotes the division between FM and AF alignment.](image)

![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 and ferromagnetic alignment. The upper graph represents the majority and the lower the minority spins.](image)
(see also Ref. [14]). At the Fermi energy the 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$_{Ga}$. In fact the two donor levels of isolated As$_{Ga}$ in GaAs are known to lie 0.54 eV and 0.75 eV above the GaAs valence band [14] and to overlap with the exchange split Mn $d$ levels of low dilution (Ga,Mn)$_3$As$_2$ [14]. In contrast the DOS of 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 [27].

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 rôlé since the Mn ions are much closer to each other. Moreover the magnetic coupling within a cell is expected to be quite sensitive to the position of the antisites with respect to the Mn ions. We consider the three different situations sketched in Fig. 3: a) the antisites are far from the Ga$_2$Mn$_2$As$_1$ complex, b) one antisite occupies a tetrahedral site (Ga$_1$Mn$_2$As$_2$), c) two antisites occupy the tetrahedral sites (Mn$_2$As$_3$). In Fig. 4 we show $\Delta_{FA}$ and $M_{Mn}$ as a function of the As$_{Ga}$ concentration for the different antisite arrangements of Fig. 3. The most obvious feature is the larger $\Delta_{FA}$ and $M_{Mn}$ concentration. This is accompanied by a small decrease of Mn-$d$ polarization, although this latter effect could be an artifact from the overlap component of the orbital population [14]. It is also interesting to note that 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 ferromagnetic alignment is stable and almost insensitive to the total As$_{Ga}$ concentration. This is a strong indicator that the dominant interaction in these cases is one that depends only on the local chemical properties. To shed some light on this aspect we present the results of Mulliken population analyses [14, 26] of the system. The Mulliken orbital (or atomic) population is the projection of the charge density onto a particular orbital (or atom). Although the absolute values depend on the chosen basis set, it is a useful quantity for understanding the charge distribution within a given material. In Table I we present the Mulliken orbital population for the Mn ions and the intermediate As atom of the complexes of Fig. 3. The Mn concentration is $x=0.0625$. The symbols $\uparrow$ and $\downarrow$ correspond to majority and minority spin respectively. The populations are in units of the electronic charge $|e|$.

![FIG. 3: Close Mn configuration. The three antisite arrangements considered in the text: a) Ga$_2$Mn$_2$As$_1$, b) Ga$_1$Mn$_2$As$_2$, c) Mn$_2$As$_3$.](image)

| $n$ As$_{Ga}$ | Type | Mn-$d$ | Mn-$d$ | As-$p_{\uparrow}$ | As-$p_{\downarrow}$ | As-$p$ |
|-------------|------|--------|--------|----------------|----------------|--------|
| 2           | a    | 4.74   | 0.70   | 1.55          | 1.63           | 3.18   |
| 2           | b    | 4.74   | 0.71   | 1.50          | 1.67           | 3.17   |
| 2           | c    | 4.72   | 0.75   | 1.44          | 1.71           | 3.15   |
| 3           | a    | 4.76   | 0.68   | 1.57          | 1.63           | 3.20   |
| 3           | b    | 4.74   | 0.74   | 1.55          | 1.65           | 3.20   |
| 3           | c    | 4.73   | 0.75   | 1.49          | 1.69           | 3.17   |

![FIG. 4: (a) Energy difference between the AF and FM alignments $\Delta_{FA}$, and (b) magnetization per Mn ion $M_{Mn}$ as a function of the number of As$_{Ga}$ antisites in the cell: Close Mn arrangement. The symbols $\bigcirc$, $\star$ and $\bigotimes$ represent arrangements (a), (b) and (c) of Fig. 3 respectively.](image)
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 $\text{As}_{\text{Ga}}$ 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 antiferromagnetic to ferromagnetic.

In 1960 de Gennes observed that in an antiferromagnetic crystal the presence of a bound carrier (electron or hole) which is Zener coupled to the local spins always induces a distortion in the antiferromagnetic lattice. In that spirit we propose that the observed transition from antiferromagnetic to ferromagnetic coupling between Ga$_2$Mn$_2$As$_3$ and Mn$_2$As$_3$ results from the onset of ferromagnetic double-exchange coupling mediated by a bound Zener carrier. This is further supported by recent calculations in which we show that the actual ground state for Ga$_1$Mn$_2$As$_2$ is not one of perfect ferromagnetic alignment, but instead the Mn magnetic moments are canted with respect to each other.

In conclusion we have shown that the As$_{\text{Ga}}$ antisites’ inclusion in (Ga,Mn)As can result in a variety of different behaviors depending on the microscopic arrangement of the Mn ions and the As$_{\text{Ga}}$ antisites. In particular we have shown that when the Mn ions are uniformly distributed in the crystal, As$_{\text{Ga}}$ antisites weaken the ferromagnetic order. In contrast if the Mn ions occupy two corners of the zineblende tetrahedron several magnetic arrangements are possible depending on the positions of the antisites. In particular ferromagnetic 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 either to reduce the As antisite concentration, or to deposit Mn and As antisites with a strongly inhomogeneous distribution.

This work made use of MRL Central Facilities supported by the National Science Foundation under award No. DMR96-32716. This work is supported by the DARPA/ONR under the grant N0014-99-1-1096, by ONR grant N00014-00-10557, by NSF-DMR under the grant 9973076 and by ACS PRF under the grant 33851-G5.

[1] H. Ohno, H. Munekata, T. Penney, S. von Molnar and L.L. Chang, Phys. Rev. Lett. 68, 2666 (1992)
[2] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo and S. Kutsumoto, Appl. Phys. Lett. 69, 363 (1996)
[3] H. Ohno, J. Magn. Magn. Mater 200, 110 (1999)
[4] H. Ohno, Science 281, 951 (1998)
[5] G. Prinz, Science 282, 1660 (1998)
[6] Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura and H. Ohno, D.D. Awschalom, Nature 402, 790 (1999)
[7] R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag and L.W. Molenkamp, Nature 402, 787 (1999)
[8] D.P. Di Vincenzo, Science 270, 255 (1995)
[9] J.M. Kikkawa and D.D. Awschalom, Phys. Rev. Lett. 80, 4113 (1998)
[10] J.M. Kikkawa and D.D. Awschalom, Nature 397, 139 (1998)
[11] G. Schmidt, D. Ferrand, L.W. Molenkamp, A.T. Filip and B.J. van Wees, Phys. Rev. B 62, R4790 (2000)
[12] T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, Science 287, 1019 (2000)
[13] J. König, H.-H. Lin and A.H. MacDonald, cond-mat/0010471 submitted to PRB
[14] S. Sanvito, P. Ordejón and N.A. Hill, cond-mat/0011050 submitted to PRB
[15] H. Akai, Phys. Rev. Lett. 81, 3002 (1998)
[16] J. Dabrowski and M. Scheffler, Phys. Rev. B 40, 10391 (1989) and references therein
[17] P. Ordejón, D. Sánchez-Portal, E. Artacho and J.M. Soler, SIESTA, Spanish Initiative for Electronic Simulations with Thousands of Atoms
[18] D. Sánchez-Portal, P. Ordejón, E. Artacho and J.M. Soler, Internat. J. Quantum Chem. 65, 453 (1997) and references therein
[19] P. Ordejón, Phys. Stat. Sol. B 217, 335 (2000)
[20] N. Troullier and J.L. Martins, Phys. Rev. B 43, 1993 (1991)
[21] S.G. Louie, S. Froyen and M.L. Cohen, Phys. Rev. B 26, 1738 (1982)
[22] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)
[23] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45, 566 (1980)
[24] Diluted Magnetic Semiconductors, edited by J.K. Furdyna and J. Kossut, Semiconductor and Semimetals Vol. 25 (Academic, New York, 1988); Diluted Magnetic Semiconductors, edited by M. Balkanski and M. Averous (Plenum, New York, 1991)
[25] H. Ohldag, V. Solinus, F.U. Hillebrecht, J.B. Goedkoop, M. Finazzi, F. Matsukura and H. Ohno, Appl. Phys. Lett. 76, 2928 (2000)
[26] R.S. Mülliken, J. Chem. Phys. 23, 1833 (1955), ibidem J. Chem. Phys. 23, 1841 (1955)
[27] P.-G. de Gennes, Phys. Rev. 118, 141 (1960)
[28] S. Sanvito and N.A. Hill, in preparation