

## Spin interactions of interstitial Mn ions in ferromagnetic GaMnAs

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(Received 4 December 2002; published 17 March 2003)

The recently reported Rutherford backscattering and particle-induced x-ray emission experiments have revealed that in low-temperature molecular beam epitaxy grown  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  a significant part of the incorporated Mn atoms occupies tetrahedral interstitial sites in the lattice. Here we study the magnetic properties of these interstitial ( $\text{Mn}_i$ ) ions. We show that they do not participate in the hole-induced ferromagnetism. Moreover,  $\text{Mn}_i$  double donors may form pairs with the nearest substitutional ( $\text{Mn}_{\text{Ga}}$ ) acceptors—our calculations evidence that the spins in such pairs are antiferromagnetically coupled by the superexchange. We also show that for the Mn ion in another, hexagonal, interstitial position (which seems to be the case in the  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{As}$  samples) the  $p$ - $d$  interactions with the holes, responsible for the ferromagnetism, are very much suppressed.

DOI: 10.1103/PhysRevB.67.121204

PACS number(s): 75.70.-i, 75.25.+z

The incorporation of transition metal ions into the III-V host semiconductors by low-temperature molecular beam epitaxy (LT MBE), i.e., the discovery of ferromagnetic dilute magnetic semiconductors (DMS) in the pioneering work by Munekata *et al.*,<sup>1</sup> was a major step towards the integration of the spin degrees of freedom with the semiconducting properties in the same material. Still, the prospects for practical applications of DMS in “spintronic” devices depend crucially on the possibilities to increase in these materials the temperature of the transition to the ferromagnetic phase. The highest Curie temperatures  $T_C$  in DMS have been obtained by a substitution of Mn for Ga in GaAs, which was complemented by a post-growth annealing in temperatures only slightly exceeding the LT MBE growth temperature. Until recently the  $T_C = 110$  K seemed to be the upper limit for this material.<sup>2-5</sup> In the last months, however, considerably higher values of  $T_C$  in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , even exceeding 150 K for thin films, have been reported by several groups.<sup>6-9</sup> This progress has been made basically by an optimization of the annealing time and temperature.

In the theoretical models describing the ferromagnetism in DMS (e.g., in Ref. 10–12) the  $T_C$  is expected to increase with both, the magnetic ions and hole concentrations. In LT MBE grown  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  this was indeed experimentally established for Mn concentrations up to about  $x = 0.07$ .<sup>2</sup> The Mn ion in the substitutional position in the GaAs lattice ( $\text{Mn}_{\text{Ga}}$ ) acts as an acceptor, but in all  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  samples the hole concentration is substantially lower than the Mn content. This has been ascribed to the presence of compensating donors, in particular to the formation of arsenic antisites ( $\text{As}_{\text{Ga}}$ ) during the epitaxial growth of  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  at As overpressure.<sup>13,14</sup> In Ref. 3, 5, and 15 the observed annealing-induced changes of the  $T_C$  were attributed solely to the decrease of the concentration of arsenic antisites leading to the increase of the hole concentration. These antisites, however, are relatively stable defects—it was shown that to remove  $\text{As}_{\text{Ga}}$  from LT MBE grown GaAs the annealing temperatures above 450 °C are needed.<sup>16</sup> Recently, simultaneous

channeling Rutherford backscattering and particle-induced x-ray emission experiments shed new light on this problem.<sup>17</sup> Namely, they have revealed that in LT MBE grown ferromagnetic  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  with high  $x$  a significant fraction of incorporated Mn atoms (ca 15% for the as-grown  $\text{Ga}_{0.91}\text{Mn}_{0.09}\text{As}$  sample) occupies well defined, commensurate with the GaAs lattice interstitial positions.

In the diamond cubic crystal lattice there are three possible interstitial positions, two tetrahedral sites and one hexagonal, in which the atoms are shadowed along  $\langle 100 \rangle$  and  $\langle 111 \rangle$  direction and exposed in the  $\langle 110 \rangle$  axial channel, as seen at the experiment. They can be distinguished by studying angular scans around the  $\langle 110 \rangle$  axial direction.<sup>18</sup> The scans presented in Ref. 17 suggested that the  $\text{Mn}_i$  ions observed in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  occupy the tetrahedral sites, in which the interstitial is surrounded by four nearest neighbors. These can be cations or anions. As pointed out already by Yu *et al.*,<sup>17</sup> the electrostatic attraction between positively charged  $\text{Mn}_i$  donors and negative  $\text{Mn}_{\text{Ga}}$  acceptors stabilizes the otherwise highly mobile  $\text{Mn}_i$  in the interstitial sites adjacent to  $\text{Mn}_{\text{Ga}}$ , i.e., the tetrahedral position between four cations, e.g., as presented in Fig. 1, is chosen.

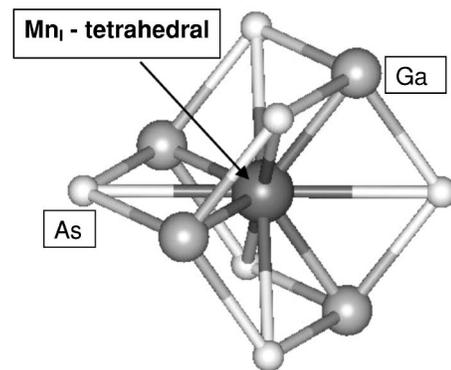


FIG. 1. The nearest four cation and six anion neighbors for an ion in the tetrahedral interstitial position in the zinc-blende lattice.

The  $Mn_I$  serve, like  $As_{Ga}$ , as double donors, decreasing the hole concentration. The results presented in Ref. 17 directly showed that in the process of LT annealing the  $Mn_I$  ions are moved to random, incommensurate with the GaAs lattice positions (e.g.,  $MnAs$  clusters), in which the Mn ions are electrically inactive. Thus, in the annealed samples the concentration of the compensating  $Mn_I$  donors decreases considerably whereas the hole concentration increases and the observed Curie temperature is much higher. Moreover, it was demonstrated that the appropriate annealing increases the saturation magnetization, i.e., that the presence of  $Mn_I$  reduces the net magnetic moment.<sup>6,17,19,20</sup>

The described above experimental results stimulated theoretical studies on the formation and properties of  $Mn_I$  in the GaMnAs ternary compound. First, the electronic structure of the GaMnAs with  $Mn_{Ga}$  and  $Mn_I$  was calculated by *ab initio* methods, showing that indeed Mn interstitials act as double donors.<sup>21</sup> In a recent paper<sup>22</sup> the self-compensation of Mn in such semiconductors was studied within the density-functional theory. In Ref. 22 it was shown that  $Mn_I$  can be easily formed near the surface.

Here we consider the spin properties of interstitial magnetic ions. We study the spin interactions for the  $Mn_I$  ion surrounded by four cations, i.e., in the tetrahedral interstitial position, in order to provide theoretical basis for the understanding of the experimental findings concerning the magnetic behavior of the as-grown and annealed  $Ga_{1-x}Mn_xAs$  samples. We analyze the hybridization of the  $d$  orbitals of these ions with the valence-band  $p$  states. This effect is essential for both, the superexchange and the RKKY-type, dominant ion-ion interactions in DMS. It is widely accepted that the latter mechanism is responsible for the hole-induced ferromagnetism in III-V DMS and that the  $T_C$  depends crucially on the  $p-d$  hybridization—within the Zener model<sup>10</sup>  $T_C$  is proportional to the square of the kinetic  $p-d$  exchange constant  $\beta$ , i.e., to the fourth power of the hybridization constant  $V$  at the center of the Brillouin zone.

The valence-band states in  $Ga_{1-x}Mn_xAs$  are built primarily from the anion  $p$  orbitals, thus the  $p-d$  hybridization for a given magnetic ion is determined by the positions of its nearest-neighbor anions. In zinc-blende lattice of GaAs, the Mn ion in the cation substitutional position has four anion nearest neighbors at the distances  $a\sqrt{3}/4$  (where  $a$  is the lattice constant) along the  $[1, 1, 1]$ ,  $[1, -1, -1]$ ,  $[-1, 1, -1]$ , and  $[-1, -1, 1]$  directions. For these positions the interatomic matrix elements,  $E_{x,xy}$ ,  $E_{x,yz}$ ,  $E_{x,zx}$ , etc., expressed in terms of the Harrison parameters  $V_{pd\sigma}$  and  $V_{pd\pi}$ ,<sup>23</sup> add up constructively to the hybridization constant  $V$  in the hybridization Hamiltonian  $\hat{H}_h$ , with different weights for different points of the Brillouin zone. At the point  $\vec{k}=0$  of the Brillouin zone they sum up to the value:  $4(V_{pd\sigma} - 2/\sqrt{3}V_{pd\pi})$ .

In contrast, the ion in the tetrahedral interstitial position, e.g.,  $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$  as in Fig. 2, has 6 anion neighbors on  $[0, 0, \pm 1]$ ,  $[0, \pm 1, 0]$ , and  $[\pm 1, 0, 0]$  directions, at the distances  $a/2$  (see Fig. 1). In this case all not equal zero interatomic matrix elements are proportional to the appropriate  $\sin(ak_i/2)$  (where  $k_i$ ,  $i=x,y,z$ , are the components of the wave-vector  $\vec{k}$ ) and they vanish at the center of the Brillouin

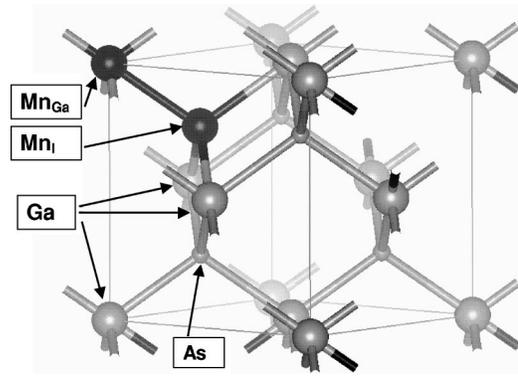


FIG. 2.  $Mn_{Ga}$ - $Mn_I$  pair in the GaAs structure.

zone. Thus, the  $Mn_I$   $d$  orbitals do not hybridize with the  $p$  states of the holes at the top of the valence band (i.e., for the tetrahedral interstitials the kinetic exchange constant  $\beta_I=0$ ) and they do not contribute to the hole-induced ferromagnetism. This means that the formation of Mn interstitials decreases not only the hole concentration but also the number of Mn ions participating in the Zener-type ferromagnetism. Still, these effects do not explain why the removal of interstitials leads to the increase of magnetization and to the higher  $T_C$  than expected from the rise of the hole concentration.<sup>19</sup>

As the  $Mn_I$  is situated close to the  $Mn_{Ga}$  ion, due to the electrostatic attraction, these two ions form in fact a  $Mn_{Ga}$ - $Mn_I$  pair, as shown in Fig. 2. One notices that despite the fact that for the interstitials the  $p-d$  kinetic exchange and, consequently, the hybridization mediated spin interactions with holes in the vicinity of the top of the valence-band vanish, the ionic spins in the pair can be coupled by superexchange mechanism. In the latter process the spins of the two ions,  $\vec{S}_1$  and  $\vec{S}_2$ , are correlated due to the spin-dependent  $p-d$  exchange interaction between each of the ions and the valence-band electrons in the entire Brillouin zone. The superexchange Hamiltonian

$$\hat{H}_{superexchange} = -2J(\vec{R}_{12})\hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

can be obtained by a proper selection of spin-dependent terms in the matrix of the fourth-order perturbation with respect to the hybridization for a system of two ions in the crystal.<sup>24</sup>

$$- \sum_{l,l',l''} \frac{\langle f|\hat{H}_h|l''\rangle \langle l''|\hat{H}_h|l'\rangle \langle l'|\hat{H}_h|l\rangle \langle l|\hat{H}_h|i\rangle}{(E_{l''}-E_0)(E_{l'}-E_0)(E_l-E_0)} \quad (2)$$

Using the virtual transition picture, one can say that the superexchange is a result of four virtual transitions of an electron—from the band onto the  $d$  shell of the ion and from the ionic  $d$  shell to the band, in different sequences.<sup>25</sup> The quantitative determination of the superexchange constant  $J$  requires the knowledge of the energies of these virtual transitions, which are represented by the energy differences between the intermediate and initial states of the system of two

ions and the completely filled valence bands, in the denominator of Eq. (2). Of primary importance it is, however, to determine the sign of the superexchange interaction for the  $\text{Mn}_{\text{Ga}}\text{-Mn}_{\text{I}}$  pair. In the following, we calculate the exchange

constant  $J$  within a simplified model, in which we neglect the dispersion of the valence bands but we account for the wave-vector dependence of the hybridization matrix elements. The resulting formula for the exchange constant  $J$  reads:

$$J(\vec{R}_{12}) = -\frac{1}{25} \left[ \frac{1}{E_{a_1} E_{a_2}} \left( \frac{1}{E_{a_1}} + \frac{1}{E_{a_2}} \right) + \frac{1}{E_{a_1}^2 (E_{a_1} + E_{d_2})} + \frac{1}{E_{a_2}^2 (E_{a_2} + E_{d_1})} \right] \\ \times \sum_{\nu_1, \nu_2, \vec{k}_1, \vec{k}_2, m, n} V_{\nu_1, \vec{k}_1, m}^* V_{\nu_2, \vec{k}_2, m}(2) V_{\nu_2, \vec{k}_2, n}^* V_{\nu_1, \vec{k}_1, n}(1). \quad (3)$$

In Eq. (3) the summation runs over the valence-band indices  $\nu_1$  and  $\nu_2$ , the wave-vectors  $\vec{k}_1$ ,  $\vec{k}_2$  from the entire Brillouin zone, and over the Mn  $d$  orbitals  $m$ ,  $n$ . The energies  $E_{a_i}$  and  $E_{d_i}$  ( $i=1,2$ ) are the transfer energies for the electron from the valence band onto the ion  $i$  (“acceptor”) and from the ion  $i$  to the valence band (“donor”), respectively. It should be noted that these energies for the interstitial Mn ion are completely unknown. Still, since all these energies as well as the sum, which we calculated numerically, are positive, we can conclude that the  $\text{Mn}_{\text{Ga}}\text{-Mn}_{\text{I}}$  pair is *antiferromagnetically* coupled. Thus, Mn ions when in tetrahedral interstitial positions not only do not contribute to the hole-induced ferromagnetism but they also make some of the substitutional Mn ions magnetically inactive by forming with them close pairs, in which the spins of the ions are antiferromagnetically coupled by the superexchange mechanism. This explains the experimental observations that the removal of  $\text{Mn}_{\text{I}}$  ions by low-temperature annealing leads not only to an increase of the hole concentration, but also to a significant increase of the magnetization.

To estimate the strength of this coupling we compare  $J$  with the superexchange constant  $J'$  for a  $\text{Mn}_{\text{Ga}}\text{-Mn}_{\text{Ga}}$  closest pair, obtained within the same simple model. Using the same transition energies for both  $\text{Mn}_{\text{Ga}}$  and  $\text{Mn}_{\text{I}}$  ions, we obtain  $J/J' \approx 1.6$ . This is not surprising in view of the small distance between the interstitial and the nearest substitutional Mn ions and the larger number of anion neighbors for  $\text{Mn}_{\text{I}}$ . With a reasonable value of 3 eV for the  $\text{Mn}_{\text{Ga}}$  charge transfer energies, with the values of Harrison parameters  $V_{pd\sigma} = 1.1$  eV,<sup>26</sup> and  $V_{pd\pi} = -\frac{1}{2}V_{pd\sigma}$ , (which for the  $\text{Mn}_{\text{I}}$  we scale according to the Harrison’s prescription)<sup>23</sup> the absolute values of  $J$  and  $J'$  constants are by far not negligible:  $J \approx 71$  K and  $J' \approx 43$  K. We note that these values, although much larger than those observed in canonical II-VI DMS, seem to be reasonable in view of the extremely strong dependence of the hybridization mediated exchange interactions on the size of the lattice cell of the material.<sup>23</sup> Still, it should be stressed again that this is only a crude estimate as these values depend strongly also on the charge-transfer energies for the Mn ion in GaAs lattice, here all taken 3 eV.

The role of interstitial Mn ions occurred to be even more pronounced in  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{As}$  samples, grown at Notre Dame with the hope to increase the hole concentration, and hence  $T_C$ , by introducing another acceptor.<sup>27</sup> Instead, it turned out that adding Be to  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  increases the concentration of  $\text{Mn}_{\text{I}}$  at the expense of  $\text{Mn}_{\text{Ga}}$ .<sup>20,28</sup> At the same time, although the hole concentration does not change significantly, the  $T_C$  drops dramatically,<sup>27,29</sup> in agreement with the presented above result that the  $\text{Mn}_{\text{I}}$  do not participate in the hole-induced ferromagnetism. Recently performed angular scans seem to suggest, however, that the  $\text{Be}_{\text{Ga}}$  acceptor stabilizes the Mn interstitial donor not in the tetrahedral but in the hexagonal,  $(\frac{3}{8}, \frac{5}{8}, \frac{3}{8})$  position.<sup>30</sup> In this site the  $\text{Mn}_{\text{I}}$  has three anion nearest neighbors, as shown in Fig. 3, on the  $[-1, -3, -1]$ ,  $[3, 1, -1]$  and  $[-1, 1, 3]$  directions, at the distance  $a\sqrt{11}/8$ . In such case one does not expect the kinetic  $p$ - $d$  exchange constant  $\beta$  to be equal to zero—it can be rather expected that the hybridization for the ion in this site should be stronger, due to the smaller distance to the anions, what increases the Harrison parameters  $V_{pd\sigma}$  and  $V_{pd\pi}$ . Surprisingly enough, the most of the interatomic matrix elements in the hybridization constant  $V$  for the hexagonal in-

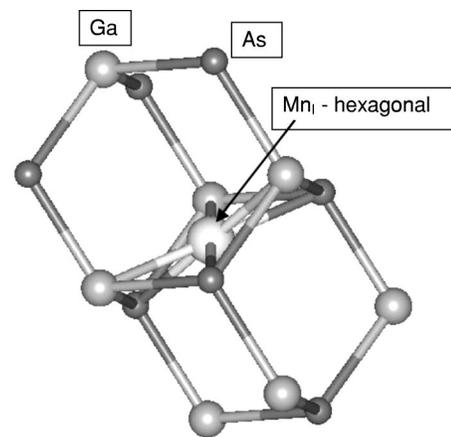


FIG. 3. The six (three cations and three anions) nearest neighbors and the next four cations and four anions for an ion in the hexagonal interstitial position in the zinc blende lattice.

stitial Mn mutually cancel at the center of the Brillouin zone. This leads to a considerably smaller than for the substitutional Mn ion value of the kinetic exchange constant  $\beta_{I_h}$ , i.e.,  $\beta/\beta_{I_h} \approx 5$ . As the Curie temperature in the Zener model depends on  $\beta^2$ , we conclude that the contribution to the hole-induced ferromagnetism from the Mn ions occupying the hexagonal interstitial sites is very much suppressed.

In conclusion, we have shown that not only the compensating properties of the interstitial magnetic ions impose a limit to the Curie temperature in the ferromagnetic  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  and  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{As}$  samples. Also their magnetic properties in both (tetrahedral and hexagonal) in-

stitial sites, i.e., the negligible kinetic exchange constant and strong antiferromagnetic superexchange with the adjacent substitutional Mn ion, act towards diminishing the transition temperature.

The authors are very much obliged to J. Furdyna, T. Wojtowicz, and W. Walukiewicz for making their unpublished results available to us and for valuable discussions and comments. Support of the FENIKS project (Grant No. EC:G5RD-CT-2001-00535) and of the Polish State Committee for Scientific Research Grant No. PBZ-KBN-044/P03/2001 is also gratefully acknowledged.

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