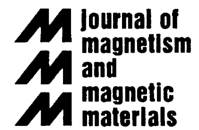
ELSEVIER

Journal of Magnetism and Magnetic Materials 242–245 (2002) 441–446


www.elsevier.com/locate/jmmm

Invited paper

First principles study of intrinsic defects in (Ga,Mn)As

Stefano Sanvito*, Nicola A. Hill

Materials Department, University of California, Santa Barbara, CA 93106-5050, USA

Abstract

We present density functional calculations of the structural, electronic and magnetic properties of various intrinsic defects in (Ga,Mn)As. Our main finding is that As excess generally weakens the ferromagnetic coupling between Mn ions. Moreover, we find that the interaction is strongly dependent on the microscopic configuration of the Mn ions and the defects, suggesting that a mean field description is not always appropriate. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diluted magnetic semiconductors; Defects; Density functional calculation

1. Introduction

The GaAs/(Al,Ga)As system has been the benchmark for new physics and devices for many years. The discovery of ferromagnetism in (Ga,Mn)As [1,2] has opened up the possibility of adding magnetism to this material system. $Ga_{1-x}Mn_xAs$ can be grown by low-temperature molecular beam epitaxy (LT-MBE) achieving Mn concentrations up to $x=0.07$, far above the solubility limit of Mn in GaAs. The low-temperature growth is necessary to avoid the formation of MnAs clusters with NiAs-type lattice structure, which is the stable structure at equilibrium [3]. However low-temperature growth leads to the incorporation of an As excess as large as 1.5%. This is stored in the form of intrinsic defects: As antisites (As_{Ga}), Ga vacancies (V_{Ga}), As interstitial (As_i), and their combinations.

Although there is a general agreement that (i) Mn^{2+} ions with spin $S=\frac{5}{2}$ substitute the Ga^{3+} cations in the zincblende lattice, and (ii) there are free holes in the system, the exact role of the intrinsic defects and their distribution with respect to the Mn ions is not clear. Certainly they are responsible for the observed hole concentration, which is much lower than the Mn concentration, in spite of the fact that Mn should be a single acceptor in GaAs. This drastically reduces hole-mediated ferromagnetic coupling between the Mn ions. Moreover, the relative positions of the Mn ions with respect to each other and to the GaAs intrinsic defects can drastically affect the magnetic, electronic and transport properties of (Ga,Mn)As. Two sets of experiments illustrate this. On the one hand low-temperature annealing experiments [4,5] and growth at ultra-low temperature [6] clearly show that microscopic defect rearrangement can change the Curie temperature, the lattice constant and the magnetization of (Ga,Mn)As. Also, if (Ga,Mn)As is grown as zincblende MnAs monolayers separated by GaAs regions [7] (so called digital ferromagnetic heterostructures, DFH), the Curie temperature is independent of the separation between the MnAs planes, therefore of the bulk Mn concentration after few monolayers. Moreover, ferromagnetism can also be found in isolated zincblende MnAs monolayers [7].

These experiments suggest that the microscopic configuration of the Mn ions and eventually of the GaAs intrinsic defects strongly affect the properties of (Ga,Mn)As. On the one hand, the annealing experiments show that the ferromagnetism of (Ga,Mn)As is the result of a delicate interplay between long-range hole-mediated interaction between Mn ions, and local effects mainly driven by the presence of intrinsic defects. On the other, the dependence of T_c on the MnAs layer separation in the digital ferromagnetic heterostructures

*Corresponding author. Tel.: +1-8050893-7934; fax: +1-805-893-8502.

E-mail address: ssanvito@mrl.ucsb.edu (S. Sanvito).

0304-8853/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0304-8853(01)01073-3

is convincing evidence of two-dimensional ferromagnetism in these structures. This means that the Mn chemical potential is rather strong in GaAs, and that the local arrangement of the Mn ions is very important in determining the properties.

The local chemical environment is neglected in the mean-field approach to the ferromagnetism of (Ga,Mn)As [8,9]. In these models the ferromagnetic Mn–Mn interaction is mediated by free holes at the top of the GaAs valence band, which in turn are antiferromagnetically coupled to the Mn through kinetic p–d coupling [10]. The presence of compensating intrinsic defects is taken implicitly into account by allowing the Mn and the hole concentrations to be different. Although this represents a good starting point, recent density functional calculations cast some doubts on the full applicability of mean-field theories. First of all the exchange coupling appears to be rather large [11]. This alone can invalidate the mean-field approach, since its basic assumption is that the p–d coupling must be much smaller than the relevant bandwidth. Secondly, if As antisites are explicitly introduced, then close to compensation the relative microscopic position of the Mn ions and the As antisites determines most of the properties. In a recent paper [12] we have shown that the ferromagnetic coupling of the two Mn ions in the $Ga_{2-n}Mn_2As_{1+n}$ (with $n=1,2$) tetrahedral cluster embedded into GaAs is almost independent of the degree of compensation of the crystal for both $n=1$ and 2.

In this paper we focus on two aspects. First we consider how intrinsic defects affect the magnetic properties of a random alloy of (Ga,Mn)As. Then we propose direct defect manipulation as a valuable way of changing the degree of compensation, and therefore the magnetic coupling between the Mn ions in (Ga,Mn)As.

We perform density functional theory (DFT) calculations in the local spin-density approximation (LSDA). The numerical implementation in the code SIESTA [13] uses a very convenient localized atomic orbitals basis set, which allows us to treat large systems without massive computational overheads. Details of the technique have been presented extensively elsewhere [11]. Here we just point out that we allow structural relaxation. We stop the relaxation when the total stress on the unit cell is smaller than $2\times10^{-5}\,\mathrm{eV/\AA^3}$ and the largest force on individual atoms is smaller than $5\times10^{-3}\,\mathrm{eV/\AA}$.

2. Intrinsic defects

We study the effect of intrinsic defects on the ferromagnetic coupling between Mn ions by constructing a cubic 64 atom unit cell in which we introduce two Mn ions (in the center and at the corner of the cell) and one intrinsic defect. The energy difference Δ_{FA} between the total energy of the antiferromagnetic (E_{AF}) and ferromagnetic (E_{FM}) states of the unit cell gives a measure of the coupling strength between the Mn ions. The energy level diagrams of the various defects in GaAs we consider are presented in Fig. 1, along with the corresponding symmetry labels. Note that all these defects introduce an As excess into (Ga,Mn)As. In Table 1 we report Δ_{FA}, the total magnetization of the cell in the ferromagnetic ground state (M_{FM}), and the spin polarization of the Mn d-shell ξ_d for cells containing the defects of Fig. 1. The spin polarization ξ_d is calculated from the Mülliken orbital population ρ_d^σ (with $\sigma=\uparrow(\downarrow)$ for majority (minority) spin) [11,14] as $\xi_d=(\rho_d^\uparrow-\rho_d^\downarrow)/(\rho_d^\uparrow+\rho_d^\downarrow)$.

From the table it is immediately clear that the presence of intrinsic defects reduces the ferromagnetic coupling between Mn ions. However, the mechanisms can be rather different for different defects. As a general guideline for understanding the different mechanisms consider the fact that the defect levels do not spin split upon Mn doping. This hypothesis is confirmed by our bandstructure calculations of (Ga,Mn)As supercells with single GaAs intrinsic defects. Hence the energy scheme for an intrinsic defect in (Ga,Mn)As can be obtained from that of GaAs by simply spin splitting the valence band of GaAs symmetrically with respect to its center (the spin splitting of the conduction band is unimportant for the present discussion). For the Mn concentration considered here ($x=0.0625$) this split is of the order of 0.6 eV [11], which leads to a valence band edge ~0.3 higher (lower) for the majority (minority) band of (Ga,Mn)As with respect to the valence band edge of GaAs. Moreover, since we always consider two Mn ions per cell, the Fermi energy cuts through the majority valence band leading to the formation of two spin holes (see Fig. 3a). It is worth noting that if no intrinsic defects are present, the aforementioned spin splitting causes (Ga,Mn)As to be half-metallic [11].

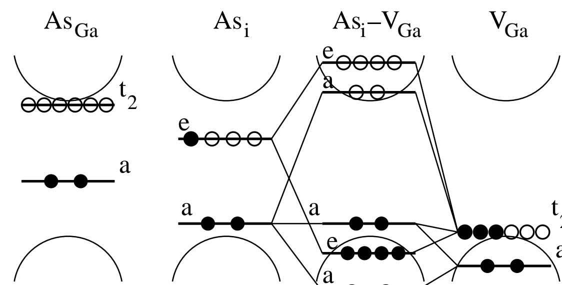


Fig. 1. Energy scheme for intrinsic defects in GaAs. The open circles represent the unoccupied states and the full circles the occupied ones. The labels indicate the energy level point group representation.

Table 1
Energy splitting between AF and FM configuration Δ_{FA}, magnetization of the cell M_{FM} and spin polarization of the Mn d-shell for a cell containing two Mn ions and one intrinsic defect.[a]

Defect	Δ_{FA} (meV)	M_{FM} (μ_B)	ξ_d
No defect	160	8.00	0.715
As_{Ga}^{a}	40	8.96	0.738
As_{Ga}^{b}	93	8.88	0.734
V_{Ga}	30	7.22	0.684
$As_i + V_{Ga}$	123	8.00	0.723

[a] For As_{Ga}: (a) the antisite is equidistant from the Mn, (b) the antisite is a second nearest neighbor to one of the Mn ions, forming a $Ga_1Mn_2As_2$ complex.

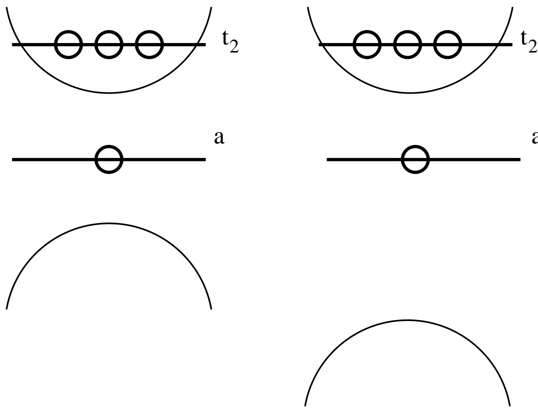


Fig. 2. Energy scheme for As_{Ga} in (Ga,Mn)As: majority (left) and minority (right) band.

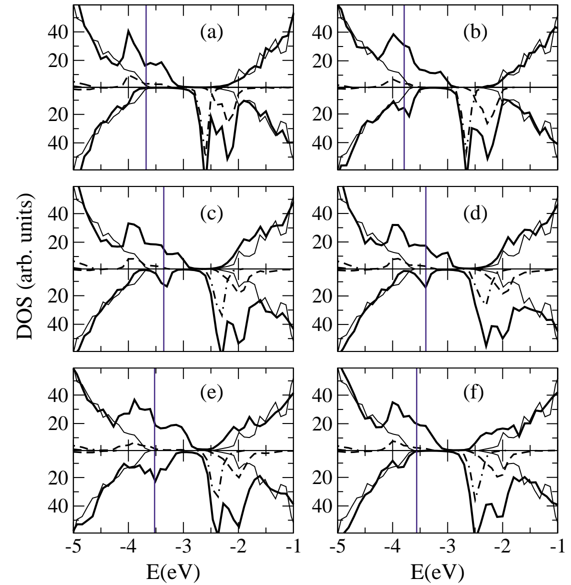


Fig. 3. Density of states for a 64 atom GaAs unit cell with two Mn ions and one intrinsic defect: (a) defect-free; (b) V_{Ga}, (c) As_{Ga} equidistant from the two Mn ions; (d) As_{Ga} close to one of the two Mn ions; (e) As_{Ga}–V_{Ga} pair, and (f) As_i–V_{Ga} pair. The upper panels are for the majority spin and the lower for the minority. The bold line is for the total DOS, the dashed and the dashed–dotted lines are for the projections of the DOS onto the Mn d t_2 and Mn d e orbitals, respectively, and the thin line is the DOS of GaAs. The latter is calculated with a GaAs 64 atom unit cell. The relative positions of the DOS of GaAs and (Ga,Mn)As are obtained by aligning the lower lying As s bands. The vertical line denotes the position of the Fermi energy.

2.1. As antisite: As_{Ga}

From direct experimental evidence in p-doped LT-GaAs [15], As_{Ga}'s are probably the most abundant defects in (Ga,Mn)As, with concentrations up to $10^{20}\,cm^{-3}$. As_{Ga} is a double donor in GaAs with a doubly occupied deep level at midgap and an empty resonant state at the edge of the conduction band. These states belong, respectively, to the A_1 and T_2 symmetry of the T_d point group. The corresponding energy scheme for As_{Ga} in (Ga,Mn)As is reported in Fig. 2. Since the spin splitting of the valence band is smaller than the position of the impurity levels, both the A and the T_2 states are in the gap. However, at zero temperature both the states will be unoccupied, leaving no holes in the (Ga,Mn)As valence band. The system is therefore compensated and the coupling between the Mn ions strongly weakened. This confirms the widely held view that the ferromagnetism in (Ga,Mn)As is hole-mediated. However, the situation is not as ideal as that pictured in Fig. 2. The top of the valence band for the majority spin of (Ga,Mn)As is in fact hybridized with the a defect level. Therefore the compensation is not quite complete and a residual magnetic coupling is left. This can be clearly seen in Fig. 3c and d where we show the density of states for a 64 atom unit cell with two Mn ions and one As_{Ga}. Note that the Fermi energy is close to midgap, pinned by the a level of As_{Ga}; for this reason (Ga,Mn)As loses its half-metallicity. Moreover, there is a large increase in the magnetization per unit cell and in the spin polarization of the Mn d-shell ξ_d. This is a direct result of the position of the Fermi energy. In fact the valence band edge of the majority band is now almost entirely occupied. Recalling that in (Ga,Mn)As the top of the majority band has a large Mn d component (t_2 states), this also increases the occupation of the Mn d level. The same argument does not hold for the minority band, since there are no Mn d states below the Fermi energy. This of course increases the spin polarization.

We also consider different positions of the As_{Ga} with respect to the Mn ions. The densities of states of Fig. 3c and d correspond, respectively, to the situations in which

the As_{Ga} is equidistant from the Mn ions, and in which it is a second nearest neighbor to one of the Mn ions, thus forming a $Ga_1Mn_2As_2$ complex. The $Ga_1Mn_2As_2$ is a tetrahedron with an As atom in the center and two Mn ions, one Ga ion and one As_{Ga} at the four corners (see Fig. 3(b) of Ref. [12]). Although the DOS look quite similar a closer look reveals that in the latter case the Fermi energy cuts through a region where there is still a contribution from the Mn d t_2 states. This contribution, which accounts for 16% of the total DOS, is due to the hybridization of the Mn d states with the As_{Ga} impurity band, which is stronger when Mn and As_{Ga} are closer. The spin polarization of the $Ga_1Mn_2As_2$ complex is much smaller ($\xi_d = 0.72$) then that of other Mn ion in the cell ($\xi_d = 0.75$), suggesting that the two Mn centers can have slightly different energy levels. It is also important to observe that the ferromagnetic coupling between the Mn ions gets stronger when the As_{Ga} moves towards the Mn, with Δ_{FA} increasing from 40 to 93 meV (see Table 1). Finally, $Ga_1Mn_2As_2$ has lower total energy than that of two Mn ions and one As_{Ga} equidistant from those. The energy difference is about 100 meV and this suggests that, if the As_{Ga} have enough kinetic energy to diffusive within (Ga,Mn)As, the ground state is formed when the antisites pair up with the Mn ions forming $Ga_1Mn_2As_2$ complexes. This strengthens the ferromagnetic coupling between the Mn, eventually enhancing T_c. We believe that this effect is a first step towards the understanding of the improvement of T_c in (Ga,Mn)As upon short-time low-temperature annealing [4,5].

2.2. Ga vacancy: V_{Ga}

From formation energy calculations [16] these are believed to be quite rare defects in LT-GaAs, although they may appear in complexes with As_{Ga}'s and be responsible for the As excess migration in GaAs upon annealing [17]. An ideal Ga vacancy causes the sp^3 dangling bonds to hybridize and form bonding and antibonding states. The antibonding states belong to the threefold-degenerate T_2 representation of the T_d group and in GaAs are located very close to the valence band edge. In contrast the bonding state belongs to the A_1 representation and lies well within the valence band. If we now introduce the Mn ions and spin split the valence band, the t_2 states also shift below the valence band edge for the majority spin. This leads to three extra holes at the top of the spin-split valence band as indicated in Fig. 4. However, in contrast with what would be naively expected for a p-doping level higher than that of the defect-free case, the magnetic coupling between the Mn ions is reduced (see Table 1). Moreover the large depletion of the top of the valence band, strongly hybridized with the Mn d-shell, produces a drastic reduction of both the magnetization and the Mn d-shell

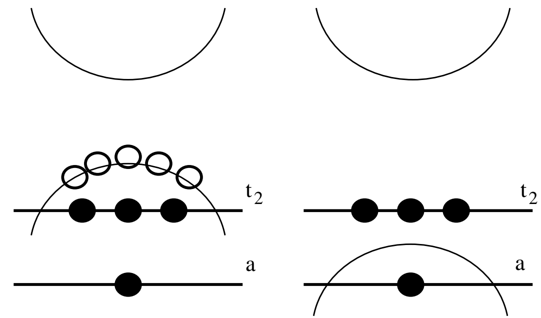


Fig. 4. Energy scheme for V_{Ga} in (Ga,Mn)As: majority (left) and minority (right) band.

spin polarization. This is the opposite effect than that occurring with As_{Ga}'s. Bearing in mind that one V_{Ga} per two Mn ions in a 64 atom unit cell results in an unrealistically large vacancy concentration the present result is rather important. It says that a large p-doping does not necessary enhance the magnetic coupling and hence the T_c in (Ga,Mn)As.

We also investigate the effect of introducing an As_{Ga}–V_{Ga} pair at different positions with respect to the Mn ions. Using arguments analogous to those for isolated As_{Ga} and V_{Ga}, we conclude that a single hole per unit cell is present. In all the cases studied Δ_{FA} is drastically reduced from the defect-free case although the magnetization of the cell and the spin polarization of the Mn d-shell are almost unchanged. It is worth noting that in general Δ_{FA} depends on the microscopic arrangement of the Mn ions and the defects. This highlights the fact that the ferromagnetism is not solely driven by the hole concentration but, that the microscopic configuration is also crucial.

2.3. As_i–V_{Ga} pairs

Finally, we consider the case of As interstitial–Ga vacancy pairs. Such complex can be obtained by moving an As antisite along the $\langle 1\,1\,1 \rangle$ direction and has the energy scheme shown in Fig. 5. In LT-GaAs this structural transition is believed to be responsible for the photoquenchable EL2 defect [18]. In a recent paper [19] we have shown that the same transition is possible in (Ga,Mn)As and that it can drastically improve its magnetic properties. Here we concentrate on the electronic properties of the As_i–V_{Ga} pair in (Ga,Mn)As.

From the density of states of Fig. 3f it is clear that the inclusion of an As_i–V_{Ga} pair in (Ga,Mn)As does not destroy the half-metallic behavior. This is quite a spectacular result, which can be easily explained by considering the position of the a defect level in (Ga,Mn)As. We have calculated such an impurity level in GaAs to be $\leqslant 0.1$ eV above the valence band. This

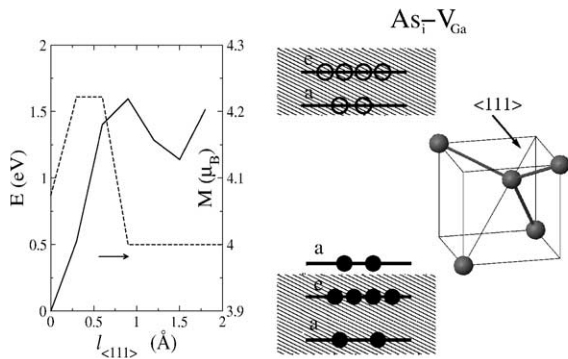


Fig. 5. Total energy as a function of the displacement of As_{Ga} along ⟨1 1 1⟩ and energy scheme for a As_i–V_{Ga} pair.

means that if we now spin split the valence band as in (Ga,Mn)As, such an impurity level shifts below the valence band edge and remains occupied. This means that the defect is electronically neutral in (Ga,Mn)As. The DOS of Fig. 3f, which looks remarkably similar to the defect-free case, clearly confirms this behavior. We observe that there is a small peak in the minority band just below to the band edge, which corresponds to the a impurity level. However, this does not modify the GaAs band edge nor its occupation, and the magnetic coupling between the Mn ions is basically identical to that of the defect-free case (see Table 1).

As anticipated, this defect can be optically induced from As_{Ga}. The mechanism has been explained by Dabrowski and Scheffler [18]. The main idea is that the excited electronic configuration $a^1t_2^1$ (see Fig. 1 for the energy levels) of a tetrahedral substitutional double donor (here As_{Ga}) induces a lattice distortion. The distortion is initiated because the many-electron wave function of the $a^1t_2^1$ 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 [18] that in GaAs the total-energy curve as a function of the displacement of As_{Ga} along ⟨1 1 1⟩ for the $a^1t_2^1$ configuration ($1a^12a^1$ when the defect assumes the C_{3v} symmetry) has a minimum for $l_{\langle 1 1 1\rangle} \sim 0.3\AA$. Therefore an optical excitation of the $a^2t_2^0$ ground-state to the $a^1t_2^1$ will initiate a distortion. Then the system has some probability of relaxing into the As_i–V_{Ga} side of the total-energy curve, ending up far from the antisite position (see Fig. 5). This mechanism leads to the creation of the As_i–V_{Ga} pair. The same mechanism holds for (Ga,Mn)As since the only difference with respect to GaAs is in the spin splitting of the bands. This splitting however is not large enough to move the a state of As_{Ga} into the valence band nor the t_2 state in the conduction band. Therefore the mechanism described above is still applicable [19].

We then suggest that photoillumination can be a valuable way to change the magnetic properties of (Ga,Mn)As, since some of the As_{Ga}'s can be transmuted in As_i–V_{Ga} pairs. This will lead to a different p-doping level and consequently to a different T_c. However it is worth noting that this mechanism cannot give rise to very high T_c's, since the energy barrier for the As_{Ga} regeneration is rather small and the As_i–V_{Ga} pairs are destroyed at about 140°K.

3. Conclusion

We have studied the magnetic and electronic properties of various intrinsic defects in (Ga,Mn)As. The main finding is that As excess usually weakens the magnetic coupling between Mn ions, although the details depend upon the kind of defects and the their relative position with respect to the Mn ions. We identify As_i–V_{Ga} as a neutral intrinsic defect in (Ga,Mn)As, which can be generated from As_{Ga}. This suggests the possibility of ferromagnetic coupling engineering via defect manipulation.

Acknowledgements

This work made use of MRL Central Facilities supported by the National Science Foundation under award no. DMR96-32716. This work is supported by ONR (grant N00014-00-10557), by NSF-DMR (grant 9973076) and by ACS PRF (grant 33851-G5).

References

[1] H. Ohno, Science 281 (1998) 951.
[2] H. Ohno, J. Magn. Magn. Mater 200 (1999) 110.
[3] S. Sanvito, N.A. Hill, Phys. Rev. B 62 (2000) 15553.
[4] T. Hayashi, Y. Hashimoto, S. Katsumoto, Y. Iye, Appl. Phys. Lett. 78 (2001) 1691.
[5] S.J. Potashnik, K.C. Ku, S.H. Chun, J.J. Berry, N. Samarth, P. Schiffer, cond-mat/0105541 Appl. Phys. Lett. 79 (2001) 1495.
[6] J. Sadowski, R. Mathieu, P. Svedlindh, J.Z. Domagala, J. Bak-Misiuk, K. Światek, M. Karlsteen, J. Kanski, L. Ilver, H. Åsklund, U. Södervall, Appl. Phys. Lett. 78 (2001) 3271.
[7] R.K. Kawakami, E. Johnston-Halperin, L.F. Chen, M. Hanson, N. Guébels, J.S. Speck, A.C. Gossard, D.D. Awschalom, Appl. Phys. Lett. 77 (2000) 2379.
[8] T. Dietl, H. Ohno, F. Matsukura, J. Cibèrt, D. Ferrand, Science 287 (2000) 1019.
[9] J. König, H.-H. Lin, A.H. MacDonald, in: R. Haug, H. Schoeller (Eds.), *Interacting Electrons in Nanostructures*, Springer, Berlin, 2001, also J. Schliemann, J. König, H.-H. Lin, A.H. MacDonald, Appl. Phys. Lett. 78 (2001) 1550

[10] B.E. Larson, K.C. Hass, H. Ehrenreich, A.E. Carlsson, Phys. Rev. B 37 (1998) 4137.
[11] S. Sanvito, P. Ordejón, N.A. Hill, Phys. Rev. B 63 (2001) 165206.
[12] S. Sanvito, N.A. Hill, Appl. Phys. Lett. 78 (2001) 3493.
[13] D. Sánchez-Portal, P. Ordejón, E. Artacho, J.M. Soler, Int. J. Quantum Chem. 65 (1997) 453 and references therein
[14] R.S. Mülliken, J. Chem. Phys. 23 (1955) 1833.
[15] P. Specht, R.C. Lutz, R. Zhao, E.R. Weber, W.K. Liu, K. Bacher, F.J. Towner, T.R. Stewart, M. Luysberg, J. Vac. Sci. Technol. B 17 (1999) 1200.
[16] S.B. Zhang, J.E. Northrup, Phys. Rev. Lett. 67 (1991) 2339.
[17] D.E. Bliss, W. Walukiewicz, E.E. Haller, J. Electron. Mat. 22 (1993) 1401.
[18] J. Dabrowski, M. Scheffler, Phys. Rev. B 40 (1989) 10391.
[19] S. Sanvito, N.A. Hill, J. Magn. Magn. Mater. 238 (2002) 252.