Hole $sp^3$-character and delocalization in (Ga,Mn)As revised with pSIC and MLWF approaches - newly found spin-unpolarized gap states of $s$-type below 1% of Mn

Karolina Z. Milowska*
Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, ul. Hoża 69, 00-681 Warszawa, Poland
Photonics and Optoelectronics Group, Faculty of Physics, Ludwig-Maximilians-University Munich, Amalienstrasse 54, 80799 Munich, Germany

Małgorzata Wierzbowska†
Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, ul. Hoża 69, 00-681 Warszawa, Poland

The dilute magnetic semiconductor (Ga,Mn)As is ferromagnetic in accordance with the p-d Zener model. Hole density function (HDF) localization has been previously studied by means of the density functional theory (DFT) and non-standard DFT methods; however not for dopings near 1%. We have revised (Ga,Mn)As using the DFT with the pseudopotential self-interaction correction (pSIC) and maximally-localized Wannier functions (MLWFs), which show the $sp^3$ character of a HDF. Nature of HDF is extended - for low dopings and the pSIC, 70% of the HDF is located within the inter-impurities region, and contribution of the 3d-Mn states is 3-5% for 1-3% of Mn with the pSIC, and 11% with the DFT. We found that for dopings below 1%, the spin-unpolarized $s$-type impurity states segregate from the conduction band to the energy gap - in contrast to earlier publications. This implies that donor co-doped dilute samples would be both insulating and nonmagnetic.

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I. INTRODUCTION

The dilute magnetic semiconductors (DMS) possess combined semiconducting and magnetic properties, hence their potential application in spintronics have been extensively investigated over past 30-years. A prototype DMS used to explain a mechanism of the ferromagnetic order in this class of magnetic materials is (Ga,Mn)As. It is a half-metal, with a metallic phase in majority-spin band, and with a spin-polarized hole introduced to the host GaAs by a substitution of Ga with Mn. The nature of this hole rules magnetic and transport properties. Therefore, deep understanding of a type and localization of empty states near the Fermi level and within the energy gap is a subject of hot debate.

In the pioneering work, Dietl et al. assumed the extended-hole scenario, with a HDF delocalized within the valence band, and applied the p-d Zener model to successfully explain high Curie temperature, reaching 110 K, in GaAs with 5% of Mn. Since then, many papers based on this model have been written and very intensive ab-initio studies on the (Ga,Mn)As system have been performed (see a review). However, perfect consensus about this system is not achieved, and very low dopings were not studied in detail by means of first-principles methods, while there are many experimental papers considering this type of systems.

It is also stated in a few works that some impurity states at low dopings appear within the energy gap. Their character is believed to be of valence band origin and spin-polarized and the $d$-type. In contrast to those investigations, we have found that the gap states close to 1% doping originate from the conduction band and their character is spin-unpolarized and the $s$-type.

In our studies, we have employed the following two additional methods beyond standard implementations of DFT (like GGA), which have not been previously applied to the hole localization problem at very low concentrations:

1. pSIC scheme, which corrects the electronic self-interaction problem for all atomic shells, giving a more balanced treatment than just the $d$-shell correlations included in the DFT+U approach

2. MLWFs analysis

These two methods complete the HDF localization description in the real-space manifold of localized functions centred at atoms or bonds. We have focused on two Mn concentrations of 1% and 3%, showing that, at some co-doping with donors, the samples may exhibit different magnetic and conducting properties.

Next in the scope of this work, we have listed earlier studies on the HDF localization in (Ga,Mn)As in section 2, given details of our calculations in section 3, presented our results in section 4, and drawn conclusions in section 5.

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*karolina.milowska@gmail.com
†malgorzata.wierzbowska@fuw.edu.pl
II. BRIEF SUMMARY OF EARLIER STUDIES

The earlier DFT and DFT+U calculations for (Ga,Mn)As at dopings of 6% and 12% already have shown that the highest contribution to the HDF originates from the As-neighbours of Mn, and this result was confirmed in the system with 3% of Mn. Further studies for concentrations 3-12% showed that the HDF extends beyond the second As neighbours of the impurity. First application of the pSIC method to this system for dopings of 6-12% presented the contribution of the 4p-Mn states to the top of the valence band.

Other self-interaction corrected scheme, namely SIC-LSD, has been applied to (Ga,Mn)As at 3-25% of Mn, and only the majority-spin d-states have been treated with this method, beyond standard DFT. That work, however, focuses on critical temperature and a comparison of (Ga,Mn)As to Mn doped GaP and GaN, showing the total density of states (DOS) and the d-projected DOS of Mn only. The standard DFT calculations for lower Mn doping of 2% have been also performed.

None of the publications mention the gap states, since the considered dopings were too high to find them. Those works did not focus on the chemical character of a hole, as it was considered in previous studies for a different system: Mn in Ge. Very detailed investigations of chemical character of the 3d-Mn states in work do not consider explicitly a contribution of the 4p-Mn states to the HDF. We found these states dominating over the $t_{2g}$-Mn contribution when the pSIC scheme was applied.

Nevertheless, all listed above publications agree about the HDF delocalization scenario, which leads to justification of the p-d Zener model for $T_\text{c}$ in (Ga,Mn)As. Our results presented here support this model too.

Recently, a contradicting hypothesis, with the Fermi level localized within the 3d-Mn impurity states, is discussed by the experimental group, and followed by a theoretical work, with similar conclusions to earlier publication. These works examine the double-exchange mechanism as possible in (Ga,Mn)As.

As for the gap states at lower dopings, some publications imply that the origin of these states is from the valence band and their spin-polarization is of the d-type. We have found that these states are spin-unpolarized and of the s-type, and they are formed by a separation from the conduction band.

III. THEORETICAL DETAILS

We have started performing the calculations within the density functional theory framework, employing the QUANTUM ESPRESSO code, with the pseudopotentials (PPs) and the plane-wave basis. For the exchange-correlation functional, we have chosen the generalized gradient approximation (GGA) by means of the Perdew-Burk-Ernzenhof parametrization. We have used the ultrasoft pseudopotentials with the semicore 3s- and 3p-shell of Mn and the 3d-shell of Ga included in the valence bands, and with nonlinear core correction for the Ga and the As PPs. The energy cutoffs of 35 Ry and 350 Ry were set for the plane-waves and the density, respectively.

The calculations were done for two Mn concentrations: 1% with one Mn atom in the 216-atoms cell and 3% with a single impurity in the 64-atoms cell. Dense k-point grids of (6,6,6) and (12,12,12) points generated according to the Monkhorst and Pack scheme were used, for these dopings respectively. For a quadrature over the Brillouin zone, the metallic-smearing technique close to the Fermi surface was used with the Gaussian broadening of 0.01 Ry. The experimental lattice constant of 5.65 Å was fixed for all calculations, and the atomic positions in the cells were optimized. The largest relaxation, found close to the Mn impurity, was smaller than 0.6% of the Ga-As bond length.

The pSIC scheme results were compared to the GGA results. The self-interaction corrections have been applied to all atomic shells of all atoms in the calculated cells and to both spins.

To imagine a character of the hole, we performed the detailed analysis of the projected density of states onto the atomic shells. The hole occupation numbers $n_h^{\text{Pdos}}$ were obtained from a quadrature of the projected DOS, $N(\varepsilon)$, in a range from the Fermi level $\varepsilon_F$ to the energy at which the DOS vanish first time for the unoccupied states:

$$n_h^{\text{Pdos}} = \int_{\varepsilon_F}^{N(\varepsilon)=0} N(\varepsilon) \, d\varepsilon.$$  \hspace{1cm} (1)

The shape of HDF and the degree of localization in the real space have been examined using the maximally-localized Wannier functions (MLWFs) for which calculations are made with the aid of the Wannier code. The electronic localization degree can be estimated from the MLWFs spreads, $\Omega_n$, defined as:

$$\Omega_n = |(r^2)_n - \bar{R}_n^2|,$$  \hspace{1cm} (2)

where $\bar{R}_n^2 = \langle 0|n|0\rangle^2 = \langle r_n^2 \rangle$ and $|(r^2)_n = \langle 0|n|r^2|0\rangle$, with $|0n\rangle$ being the Wannier function with number $n$ and centered in the original cell with the direct-lattice vector $\mathbf{R} = 0$, and $\mathbf{r}$ is the real-space position operator. The sum of above defined quantities $\Omega = \sum_n \Omega_n$ is minimized in the MLWFs-finding procedure.

To get a closer insight into the Mn-As bonds, we calculated the MLWFs on the GGA and the pSIC Bloch-functions obtained for the 64-atoms cell. For minimization of the total spread, we have chosen the 133- and 128-band space in the spin up and down, respectively. Bottom of the energy window was set within the gap between the localized 3d-Ga derived bands and the delocalized sp-bands of (Ga,Mn)As. Top of the energy window was fixed just above the 133-rd band counted for the spin up from the bottom of the energy window. From this band-manifold, we obtained 133 and 128 MLWFs in the spin up and down, respectively.
In analogy to the hole occupation numbers obtained from the DOS, \( n_{h}^{P DOS} \), we analyse contributions of the HDW from the MLWFs, \( n_{h}^{MLWF} \), defined via the MLWFs occupations as \( n_{h}^{MLWF} = 1 - f_{n}^{MLWF} \). Concept of the Wannier occupations has been introduced recently for proper symmetries of some systems, which need a few unoccupied states (usually the anti-bonding counterparts to the valence states) in the manifold of Bloch functions to be used for the MLWFs construction.\(^{37}\) These occupation numbers \( f_{n}^{MLWF} \) are defined with the use of two unitary transformation matrices \( U_{pq}^{dis} \) and \( U_{ij} \), where the first acts in the disentangling procedure to obtain the optimal subspace of Bloch-like functions possessing proper symmetries and the second is obtained during the MLWFs optimization process. Thus the occupation matrix is as follows:

\[
\sum_{k \in BZ} \sum_{p} \sum_{s,r} U_{rm}^{k} U_{pr}^{k} U_{sn}^{k} U_{ps}^{k}, \tag{3}
\]

where 'win' runs over all states in the outer window (including some unoccupied states) and 'occ' runs over states up to the Fermi level. Since the off-diagonal occupations sum to zero in the whole system, we use only the diagonal occupations \( f_{n} = f_{nn} \) in the definition of MLWFs contributions to the HDF.

IV. RESULTS

The Mn impurity, replacing Ga in the GaAs host, offers two electrons from the 4s-shell and five electrons from the 3d-shell instead of the Ga configuration \( 4s^{2}3d^{10}4p^{1} \). Since the valence of As is 5 and that of Ga is 3, the substitution of Ga with Mn creates a hole in the valence band, because five 3d electrons of Mn almost do not take a part in binding with the As neighbours.

In Figure 1, the density of states (DOS), projected on the \( t_{2g} \), \( e_{g} \) and \( 4p \) Mn-orbitals, is presented. The Fermi level cuts through the valence band top, for two concentrations and both theoretical methods applied. The DOS centre of mass, for the \( t_{2g} \) and \( e_{g} \) states, moves in the pSIC approach. The sum of contributions from Mn and its neighbours in the cells in units of the lattice constant are given in parenthesis. The sum of contributions from Mn and its neighbours along four tetragonal easy-axes are given in the last row.

TABLE I: Contribution to the hole occupations \( n_{h}^{P DOS} \) from the projected DOS [in %], for two doping levels: 3% and 1%, obtained with the GGA and the pSIC. Wyckoff positions in the cells in units of the lattice constant are given in parenthesis.

| States (Atomic Position) | GGA | pSIC |
|--------------------------|-----|------|
| 64 atoms                 | 216 atoms |
| \( t_{2g} \)-Mn (0,0,0)  | 10.75 | 6.45 | 11.10 | 3.03 |
| \( 4p \)-Mn (0,0,0)      | 4.97  | 4.05 | 4.78  | 2.34 |
| \( 4p \)-As (1/4,1/4,1/4)| 7.17  | 7.18 | 6.67  | 4.41 |
| \( 4p \)-Ga (1/2,1/2,0) | 0.52  | 0.65 | 0.47  | 0.36 |
| \( 4p \)-As (3/4,3/4,1/4)| 2.05  | 2.89 | 1.34  | 1.32 |
| Total from 4 easy axes   | 54.68 | 51.58 | 49.80 | 29.73 |

FIG. 1: (Color online) Projected density of states (DOS) for \( t_{2g} \), \( e_{g} \) and \( 4p \) states of Mn in (Ga,Mn)As at doping levels of 3% (64-atom cell) and 1% (216-atom cell). The Fermi level is marked by the vertical dashed line.
The HDF is distributed over all bonds in the supercell. This is the signature of the HDF being localized close to the As atoms. The Mn substitution effect was blowing them. It might be due to the Mn-As and Ga-As bonds analysed with the MLWFs for the spin-up channel, obtained with the GGA, are drawn in Figure 3.

The spreads for some representative MLWFs for (Ga,Mn)As, obtained from the GGA- and the pSIC Blochs, are collected in Table II and compared to the MLWFs obtained for the isolated Mn atom and pure GaAs. It is clear, that characters of the sp-lobes centred on the Mn-As bonds are very similar to those on the As-Ga bonds, except slightly smaller spreads of the As-Mn MLWFs caused by a little shift away from Mn. The 3d-Mn MLWFs are much more localized than the sp3 functions, although, spreads of the d-type functions are twice larger, for eg, and three times larger, for t2g, than for the corresponding functions of the isolated atom.

Plots also show that a contribution of the t2g-symmetry functions to the As-Mn bond is small, and even with a tendency to escape from the bondline, as one can see from the asymmetry of plus- and minus-sign lobes of the dxy MLWF (dxy and dyz have the same property). Spreads of the sp3 MLWFs on the As-Ga bonds (Ga,Mn)As are larger than these in pure GaAs, like Mn-substitution effect was blowing them. It might be a signature of the HDF being localized close to the As atoms. Finally, an effect of the pSIC shows better localization around atoms. This causes decrease of atomic spreads, and increase of the distance between lobes of the interatomic MLWFs, and decrease of covalence. When bands are infinitely thin, and there is no k-points dispersion, then an effect of the pSIC on the MLWF-spreads is vanishing (Mn atom).

To give a measure of the HDF localization with the MLWFs approach, we present, in Table III the hole occupation numbers n^MLWF in, defined in the previous section. The HDF is distributed over all bonds in the supercell. It’s half-localization, in the 64-atoms supercell, extends to the second As-neighbours of the impurity (this volume contains 13 atoms). Far away from the impurity (which is placed in the corner of a supercell), at four central As atoms in the 64-atom supercell, there is about 4×(0.37+3×0.39)=6.16% of a HDF obtained with the GGA method and 8.8% by means of the pSIC. These

For accuracy, Table I collects the hole occupation numbers, n^DOS, defined in the previous section. We conclude, that the HDF is composed of many states and the contribution of the 4p-As states is the highest by means of the pSIC. If we take into account the fact that there are four As nearest neighbours of Mn, then it is obvious that the HDF is mainly located around the impurity neighbours and not at the impurity. The 4p-Mn donation to the HDF is almost as high as from the 3d-Mn states (pSIC) or about half of the Mn-3d input (GGA). Interestingly, the HDF extends beyond the second As-neighbours of Mn, and only half or less of the hole occupation is summed over the Mn atom and its twelve neighbours from the Mn-As-Ga-As chains along four easy axes. Half of the HDF extends over the inter-impurity part of the supercells at doping 3%, or it is even 70% in case of 1% Mn calculated within the pSIC approach. Similar analysis has been performed in the publications 18,20, by means of the DFT, the DFT+U and the pSIC approaches.

Chemical bond of Ga with As-neighbours is built by 4s and 4p electrons. For the Mn impurity, occupations of the 4s-states are about 0.34 (↑) and 0.27 (↓) for both the GGA and the pSIC, and for the 4p-states the corresponding numbers are 0.70 (↑) and 0.50 (↓) (GGA) and 0.89 (↑) and 0.60 (↓) (pSIC), independently of impurities concentrations.

The Mn-As and Ga-As bonds analysed with the MLWFs appear as sp3-type lobes centred closely to each of 32 As atoms in the cell, these centres are slightly on the back bonds. The 3d-type functions centred at Mn rather do not take a part in bonding. Similar sp3-hybridization has been discussed by Stroppa et al.22 for the Mn impurity in Ge. Because of the chosen energy window, the Wanniers obtained by us contain the HDF. Plots for some MLWFs for the spin-up channel, obtained with the GGA, are drawn in Figure 3.

FIG. 2: (Color online) Projected density of states (DOS) close to the Fermi level at dopings of 3% and 1%, obtained with the GGA and the pSIC. The total DOS is marked by the grey colour. As-1 and As-2 denote the first- and second-neighbour As-atoms along the Mn-As-Ga-As chain in 110-direction, the Ga-atomic site is (1/2,1/2,0) in units of the lattice constant and Mn is at the origin.

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numbers are similar to the picture obtained from the projected DOS analysis.

It is significant that after taking a closer look at the hole bandwidth, i.e. $E_F - E_N(\varepsilon) = 0$, for different dopings, we find that in every considered case the system is not strictly insulating. For 3% of Mn, the hole bandwidth is 0.3 eV (GGA) or 0.4 eV (pSIC), and for 1% of Mn, it amounts to 0.18 eV (GGA) or 0.28 eV (pSIC). The hole bandwidth reduction with decreasing doping is due to increasing number of states in larger supercells while the number of holes is kept the same (namely one) - this is independent on whether the 3d-states of Mn reside at the Fermi level or not. We remind, that the maximum of the DOS of the 3d-Mn levels is located 3-4 eV below the Fermi level.

From ab-initio calculations, we do not observe separation of the DOS from the top of the valence bands, which was suggested in few previous works\textsuperscript{39,40}. For very low doping, the impurity band within the gap originates from the conduction states. Detailed picture of the gap region is included in Figure 4. Composition of the impurity band within the gap, for the 216-atoms cell and for both the GGA and the pSIC, consists of the 4s-functions of Mn, As and Ga atoms, and there is no d- or p-type add. Anyway, due to their small bandwidths, these impurity states can act as traps for electrons from the Mn interstitials, which are known to be donors\textsuperscript{40,41}, or these bands can be populated via absorption of photons.

Experimentally, some of diluted samples are conducting and a few among all samples are insulating; the conducting samples have extended HDF and the insulating samples are characterized by the localized HDF\textsuperscript{26}. This matches perfectly with our Figure 4 and donor scenario of Ref\textsuperscript{40,41}:

1. If there is a low concentration of interstitials then
holes are not compensated, Fermi level lays within the valence band, and samples are conducting.

2. If there are many donors, then the holes within the valence band are compensated, the unpolarized states of the s-type within the gap (see Figure 4 in 216-atoms cases) become partially or totally occupied, the Fermi level cuts through these states, or between them and the valence band, or between the gap states and the conduction band, and the samples are insulating.

V. SUMMARY

We have used two approaches: the pSIC and the MLWF, in order to analyse in detail the Fermi level and the gap regions of the (Ga,Mn)As density of states, and the hole localization and its chemical character.

It is demonstrated that the HDF is very delocalized, especially within the self-interaction corrected scheme. In diluted case, the HDFs are mainly spread over the crystal volume among the impurities, not close to the impurities regions. Only at higher concentrations the HDF resides mainly at the Mn-As complex, and this part of the HDF has mainly $sp^3$-character centred on the As-neighbours of Mn.

For very low dopings, the hole states (low energy unoccupied bands) are still merged with the valence band, and the impurity band within the gap forms via separation from the conduction states. These gap states are unpolarized and purely of the s-type. Our new result requires experimental confirmation.

Fermi level is pinned within the valence band for donor-free samples, or within the localized gap states of s-type for donor-rich samples and low Mn dopings - these samples are insulating and nonmagnetic. With the above findings, models for Curie temperature in dilute magnetic semiconductor (Ga,Mn)As, which assume an extended hole density function over the valence band\cite{1,2,3,4,5,6,7}, are clearly justified.

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