Exchange coupling and Mn valency in GaN doped with Mn and co-doped with Mg

Mostefa Djermouni  
Laboratoire de Physique Computationnelle des Matériaux (LPCM),  
Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès 22000 & Département de physique,  
Centre Universitaire Ahmed ZABANA de Relizane, Algeria

Ali Zaoui  
Laboratoire de Physique Computationnelle des Matériaux (LPCM),  
Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès 22000, Algeria

Roland Hayn  
Aix-Marseille Univ., CNRS, IM2NP-UMR 7334, 13397 Marseille Cedex 20, France

Abdelkader Boukortt  
Université de Mostaganem, Faculté des Sciences et de la Technologie, ECP3M, Algeria

(Dated: October 31, 2020)

We study 1 or 2 neighboring Mn impurities, as well as complexes of 1 Mn and 1 or 2 Mg ions in a 64 atoms supercell of GaN by means of density functional calculations. Taking into account the electron correlation in the local spin density approximation with explicit correction of the Hubbard term (the LSDA+U method) and full lattice relaxation we determine the nearest neighbor exchange $J$ for a pair of Mn impurities. We find $J$ to be ferromagnetic and of the order of about 18 meV in the Hamiltonian $\hat{H} = -2J \hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2$. That $J$ is only weakly influenced by the $U$ parameter (varying between 2 and 8 eV) and by the lattice relaxation. From a detailed analysis of the magnetization density distribution we get hints for a ferromagnetic super-exchange mechanism. Also the Mn valence was found to be 3+ without any doubt in the absence of co-doping with Mg. Co-doping with Mg leads to a valence change to 4+ for 1 Mg and to 5+ for 2 Mg. We show that the valence change can already be concluded from a careful analysis of the density of states of GaN doped with Mn without any Mg.

I. INTRODUCTION

The quest for a diluted magnetic semiconductor (DMS) having ferromagnetic order with high Curie temperature is heavily disputed in the scientific literature. Several candidate materials had been proposed with contradicting results. Up to now, the highest transition temperature of about 200 K was confirmed in GaAs doped with about 10 percent Mn. It is generally agreed that in that compound the Zener p-d exchange mechanism is at work. That mechanism demands the presence of localized magnetic moments and of p-type hole charge carriers to align the magnetic moments in a ferromagnetic state. In the compound GaAs:Mn the Mn$^{2+}$ ion is stable providing at the same time a magnetic moment and a charge carrier. Soon after the discovery of ferromagnetism in GaAs:Mn, T. Dietl and co-workers proposed two other materials having the prospective of room temperature ferromagnetism: GaN:Mn and ZnO:Co. Both materials were widely discussed in the scientific literature and we are going to concentrate here on GaN:Mn.

Unfortunately, the proposal of room temperature ferromagnetism in GaN:Mn could not be generally confirmed. Some authors found indeed a high transition temperature close or even higher than room temperature, whereas others found only low Curie temperatures of about 10 K for 10 percent Mn doping or antiferromagnetic exchange couplings between Mn ions. Also the theoretical analysis of that material is far from being well advanced and accepted.

Also the theoretical analysis of that material is far from being well advanced and accepted. Despite a large number of ab-initio studies devoted to Mn doped GaN, there are still important controversies and the values of the exchange couplings are highly disputed. Nowadays, the importance of the strong Coulomb repulsion in the incompletely filled d-shell of Mn is rather well accepted. One way of properly taking into account the Coulomb interaction is the introduction of the Hubbard $U$ term in the density functional as it is done by the LSDA+$U$ method. But even within this LSDA+$U$ method the ground state of GaN:Mn is disputed. If one considers one Mn atom in a supercell with cubic symmetry and a valence band in difference to the situation in GaAs:Mn. Whether the lattice relaxation also leads to an energy gap for a pair of Mn impurities

\[ \text{arXiv:1710.02056v1 [cond-mat.mtrl-sci]} \quad 5 \text{ Oct 2017} \]
and whether it would significantly influence the magnetic exchange coupling was not clarified up to now.

All the numerous ab-initio studies of exchange coupling between two neighboring Mn atoms in GaN point to a ferromagnetic one (see Ref. 17 for an overview). Nevertheless, there remain several problems and inconsistencies. First of all, there is a considerable discrepancy between the ab-initio values of the order of 10 to 20 meV and the more analytical ferromagnetic superexchange calculations giving values being 10 times smaller but leading to the experimentally observed Curie temperatures. On the other hand, an experimental analysis of the Curie constant confirms the rather large ab-initio values of exchange couplings. Also, the character of the exchange coupling is disputed between the ferromagnetic super-exchange mechanism or the Zener double exchange. And finally, even the Mn$^{3+}$ valency was recently questioned in a theoretical study.

It is a famous knowledge that Mg doping in GaN leads to hole carriers. The discovery of $p$-type GaN was a crucial step to develop the now well known light emitting diodes and was re-compensated by the Nobel prize in 2014. Therefore, it is a tempting idea to co-dope GaN with Mn and Mg to combine local magnetic moments with hole-doping and to eventually increase the ferromagnetic Curie temperature by the Zener $p$-$d$ exchange mechanism. Unfortunately, that is not what happens. In fact, the doped holes are immediately captured by the Mn$^{3+}$ ions changing its valence to Mn$^{4+}$ or even Mn$^{5+}$. That was recently established in a combined experimental and theoretical study.

In view of this large number of inconsistencies we are addressing here several questions in an ab-initio supercell study of GaN doped with Mn or co-doped with Mn and Mg. In extension to previous literature reports we investigate the combined influence of Coulomb correlations in the Mn $d$-shell and of lattice relaxations on the magnetic exchange coupling $J$ between neighboring Mn ions and on the Mn valence in GaN co-doped with Mg. We used the LSDA+$U$ functional as implemented in the WIEN2k code and a 64 atoms supercell with cubic zinc-blende structure. The Hubbard $U$-parameter was exclusively applied to the incompletely filled $d$-shell of Mn and varied in between 0 and 10 eV.

Due to the good accuracy of the all-electron full potential augmented plane wave code and the proper inclusion of Coulomb interaction and lattice relaxation we are able to determine the nearest neighbor exchange coupling $J$ with high precision. We are going to clarify whether the lattice relaxation which opens a gap for one Mn atom in a 64 atom supercell of GaN also leads to a gap for a pair of Mn impurities and whether it would significantly influence the magnetic exchange couplings. From the magnetic moment values, the $d$ shell filling, and from the densities of states we can deduce the Mn valency in case of co-doping with Mg. We find that one Mg ion in the supercell changes the valence from Mn$^{3+}$ to Mn$^{4+}$ and two Mg-ions lead to Mn$^{5+}$. As we will show below, the deceiving effect of Mg co-doping can already be concluded from an analysis of the DOS of GaN:Mn without any Mg.

II. COMPUTATIONAL METHODS

All calculations were done with the Density Functional Theory (DFT) implemented in the Wien2k code. The atoms were represented by the hybrid full-potential (linearized) augmented plane-wave plus local orbitals (LAPW+lo) method. A very careful analysis is done to ensure convergence of the total energy in terms of the variational cutoff-energy parameter. The total energy was determined using a set of 63 $k$-points in the irreducible sector of Brillouin zone, equivalent to an $5 \times 5 \times 5$ Monkhorst-Pack grid in the supercell. A value of 7 for $R_{MT(KMAX)}$ was used. The zinc-blende lattice of GaN (numerically optimized to $a = 4.47$Å for the primitive unit cell) is constructed by use of a $2 \times 2 \times 2$ supercell in primitive lattice structure, resulting in a basis of 64 atoms. To solve the Kohn-Sham equations, the exchange-correlation energy, $E_{XC}$, was calculated using the Perdew-Wang LSDA and the LSDA+$U$ method in the rotationally invariant form of Liechtenstein et al. The $U$-parameter of the Mn $3d$ orbital was used as a free one between 0 and 10 eV. But the relevant results depend on $U$ in an unimportant way. Any value between 2 and 8 eV leads to similar results.

III. MANGANESE DOPING

In a first step we investigated one Mn impurity in the 64 atom supercell and calculated the gap at Fermi level for the fully relaxed situation, i.e. including the Jahn-Teller effect. The gap value as a function of the Hubbard-$U$ is shown in Table I and the spin-resolved partial DOS projected onto the Mn $3d$ and the $2p$ orbitals of two different N atoms for $U_{eff} = 4$ eV in Fig. 1.

In cubic symmetry, the Mn $3d$ electrons are split into a lower $e_g$ doublet and a higher $t_{2g}$ triplet. The $e_g$ doublet is usually merged with the valence band (of mostly N $2p$ character) and not seen as a distinguished peak. On the other hand, the $t_{2g}$ multiplet peaks are clearly visible in the neighborhood of the Fermi level. They have a capacity of three electrons but are only filled by two. Without Jahn-Teller effect, in pure cubic symmetry, the $t_{2g}$ levels are perfectly degenerate, even within the LSDA+$U$ method. But the local lattice distortion around the Mn impurity, i.e. the Jahn-Teller effect, leads to a gap at the Fermi level which is good visible in Fig. 1. The filling of the $t_{2g}$ multiplet with two electrons corresponds to a Mn valency of $3^+$. The fact that the $t_{2g}$ peaks at Fermi level have a significant (30 per cent) $p$-contribution means that the Mn$^{3+}$ valent state is in reality a rather extended molecular-orbital like state. Therefore, it was recently interpreted as a bound state of a local $S = 5/2$
Mn state in $d^5$ configuration ($\text{Mn}^{2+}$) with a surrounding hole having antiparallel spin on the four neighboring N ligands.\textsuperscript{13} However, for that interpretation to be valid, there should be a local Mn moment close to 5 $\mu_B$, which is not confirmed by our calculations (see also later).

It is interesting to note that only the LSDA result ($U_{\text{eff}} = 0$) is half-metallic but already a small Hubbard correction of $U_{\text{eff}} = 2$ eV leads to a gap which is stable in a large range of $U_{\text{eff}}$ values. So, we confirm the result of Refs.\textsuperscript{15} and \textsuperscript{16} that the combined influence of Hubbard-$U$ and Jahn-Teller effect (lattice relaxation) leads to insulating behavior. The gap we found is slightly smaller than in Ref.\textsuperscript{16} but the general tendency is the same. Calculating the optical data in such a manner corrects the artificial Drude-peak behavior of a seemingly metallic solution.\textsuperscript{12}

The super-exchange mechanism between two magnetic ions in an insulating host leads in most of the cases to an antiferromagnetic exchange coupling. It is therefore highly interesting to check the influence of the lattice relaxation on a pair of Mn impurities. For that purpose, we investigated two Mn atoms substituting for two neighboring Ga atoms in the 64 atom supercell (2x2x2 cells of 8 atoms) and compared the energy difference between ferromagnetic and antiferromagnetic arrangements $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ as a function of the Hubbard-$U$ parameter (see Table II). It can be seen that $\Delta E$ is positive in all cases corresponding to ferromagnetic exchange and it is nearly 4 times larger in LSDA than in LSDA+$U$. It varies very slightly with $U_{\text{eff}}$ once the Hubbard correlation is included. We can conclude from Tables I and II that all values of $U_{\text{eff}}$ between 2 and 8 eV can be taken as relevant ones.

It is very instructive to investigate the influence of lattice relaxation and to look at the total DOS for a pair of Mn impurities (Fig. 2 for $U_{\text{eff}} = 4$ eV which is also chosen for all the other DOS figures in the present article). Without relaxation, the DOS is rather high at $E_F$. But a pseudo gap opens due to lattice relaxation leading to a very small DOS at $E_F$. On the other hand, the lattice relaxation has no essential influence on $\Delta E$, i.e. on the exchange coupling. It is also remarkable that the rather slim $t_{2g}$ double peak for 1 Mn impurity broadens considerably into several sub-peaks for a pair of Mn impurities.

The energy difference $\Delta E$ can be used to calculate the exchange coupling $J$ in the Hamiltonian

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad \text{(1)}$$

with the two spin operators $\hat{S}_{1,2}$ corresponding to the two Mn-moments. We prefer to use the definition of $J$ in (1) in agreement with the classical works of Larson et al.,\textsuperscript{9} meaning that our $J$-values have to be multiplied by two to be compared with the values given in Refs.\textsuperscript{17} and \textsuperscript{19}. Treating the spin operators as classical vectors of length $S_{1,2} = S = 2$ in agreement with the Mn-valency of $+3$ in GaN:We obtain for the energy difference

$$\Delta E = E_{\text{AFM}} - E_{\text{FM}} = 4JS_{\text{class}}^2 = 16J_{\text{class}} \quad \text{(2)}$$

leading to $J_{\text{class}} = (21.2 \ldots 23.8)$ meV for $\Delta E = (340 \ldots 380)$ meV in the representative region for $U_{\text{eff}}$ (2 to 8 eV).

**TABLE I.** Gap energies of GaN:Mn with one Mn-atom doped in a 64 atom supercell as a function of $U_{\text{eff}} = U - J$.

| $U_{\text{eff}}$ (eV) | $E_g$ (spin up) (eV) | $E_g$ (spin down) (eV) |
|-----------------------|----------------------|------------------------|
| 0                     | –                    | 2.04                   |
| 2                     | 0.19                 | 2.04                   |
| 4                     | 0.42                 | 2.09                   |
| 6                     | 0.41                 | 2.02                   |
| 8                     | 0.41                 | 2.01                   |
| 10                    | 0.30                 | 2.00                   |

**TABLE II.** Energy difference $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ between AFM and FM arrangements of Mn spins for one pair in a 64 atom supercell as a function of $U_{\text{eff}} = U - J$. Also given are total magnetic moment $M_{\text{total}}$, as well as the magnetic moments at the Mn-sites and at the bridging N.

| $U_{\text{eff}}$ (eV) | $\Delta E$ (meV) | $M_{\text{total}}$ ($\mu_B$) | $M_{\text{Mn}}$ ($\mu_B$) | $M_{\text{N}}$ ($\mu_B$) |
|-----------------------|------------------|-------------------------------|--------------------------|--------------------------|
| 0                     | 1212.84          | 7.97                          | 3.1                      | -0.01                    |
| 2                     | 356.00           | 8.01                          | 3.35                     | -0.05                    |
| 4                     | 339.42           | 8.00                          | 3.58                     | -0.15                    |
| 6                     | 350.79           | 8.00                          | 3.81                     | -0.19                    |
| 8                     | 383.19           | 8.02                          | 3.98                     | -0.23                    |
| 10                    | 456.95           | 8.00                          | 4.13                     | -0.27                    |
It is more justified to treat the spins as quantum operators and $\Delta E$ becomes

$$\Delta E = 2S(2S + 1)J_{\text{quant}} = 20J_{\text{quant}} \quad (3)$$

with $J_{\text{quant}} = (17.0 \ldots 19.0)$ meV. Our results agree well with former ab-initio values.$^{14}$

To provide more detailed information and to get some ideas about the possible exchange mechanism we analyzed carefully the magnetization density distribution (Fig. 3) and the local magnetic moments on the Mn and ligand sites (Fig. 4 left and Table II). It can be observed that the magnetization density is well concentrated at the Mn sites and the space in between. The local moment at the Mn sites is $3.58 \mu_B$ far from the $5 \mu_B$ of a local $S = 5/2$ spin. Considerable magnetization contribution anti-parallel to the Mn ones can be found on the bridging N ($-0.15 \mu_B$) and smaller ones at the other N ligands. The total magnetic moment of $4 \mu_B$ per Mn ion confirms the $S = 2$ of a Mn$^{3+}$ state. The good localisation of the magnetization density on the space in between the two Mn ions in connection with the pseudo gap feature point to a ferromagnetic super-exchange mechanism.

The partial DOS for a pair of Mn impurities in GaN is shown in Fig. 5 (left hand side). It confirms the general picture for an isolated Mn impurity with the main difference of a significant broadening of the $t_{2g}$ complex at the Fermi level.

**IV. CO-DOPING WITH MAGNESIUM**

To investigate the influence of co-doping Mn and Mg to GaN we studied a 64 atoms supercell of GaN with 1 Mn and 1 or 2 Mg ions. The corresponding total and partial DOS are shown in Figs. 5, 6, and 7. Fig. 5 shows nicely how a gap opens due to relaxation in the supercell with 1 Mn and one Mg. Figs. 6 and 7 show the changes of total and partial DOS by adding 1 Mg or 2 Mg, respectively. The corresponding magnetic moment distributions are presented in Tables III and IV. All these results show that co-doping of GaN with Mn and Mg leads to a valence change of Mn. Without Mg, the Mn valence is +3. That means that no charge carriers are doped into GaN. But by substituting one, or two Mg atoms for Ga, the Mn valence changes to +4 or +5, correspondingly. At the same time the local magnetic moment of Mn diminishes from a value corresponding to roughly $S = 2$ (four unpaired electrons) to $S = 3/2$ or $S = 1$. That is best visible in the total magnetic moment values per Mn ion for $U = 4$ eV (see Tables II, III, and IV) which decrease from $4 \mu_B$ to $3.01 \mu_B$ and $2.04 \mu_B$ for the supercells without, with 1 or 2 Mg ions. The corresponding values of magnetization values at the Mn sites are different, namely $3.58 \mu_B$, $2.77 \mu_B$ and $2.12 \mu_B$, since part of the total magnetic moment is distributed on the neighboring N-sites with different orientation. That is shown in Fig. 4 for the example of a pair of Mn or Mn/Mg impurities and also presented in Tables II-IV.

The magnetization values of Tables III and IV can be compared with the former study of Devillers of all$^{24}$ which used the Quantum Espresso code.$^{13}$ The general tendency is the same but the local values can be quite dif-
FIG. 5. Total DOS projected onto one spin direction for the 64 atom supercell of GaN co-doped with 1 Mn and 1 Mg at neighboring positions in the unrelaxed (top) and relaxed (bottom) structure.

![Graph showing total and partial density of states for GaN:Mn:Mg](image)

FIG. 6. Total and partial DOS projected onto spin up (upper part) and spin down (lower part) for the relaxed structures of GaN with 2 Mn (left) or 1 Mn and 1 Mg (right). Shown are the partial DOS of the Mn $d$ orbitals, the Ga and Mg $p$ orbitals, as well as the N $p$ orbitals for a N atom close to the Mn impurity ($N_{\text{in}}$) and another one far of it ($N_{\text{out}}$).

![Graph showing total and partial density of states for GaN:Mn:Mg](image)

FIG. 7. Same as Fig. 5 but comparing 1 Mn co-doped with 1 Mg (left) and 1 Mn co-doped with 2 Mg (right).

![Graph showing total and partial density of states for GaN:Mn:Mg](image)

FIG. 8. Local magnetic moments at the Mn, Mg ions and the neighboring ligands for a complex of 1 Mn and 2 Mg.

### TABLE III. Magnetic moments for a complex consisting of 1 Mn and 1 Mg in GaN as a function of $U_{\text{eff}}$. Given are the total magnetic moment $M_{\text{total}}$ as well as the local moments at the Mn, Mg and the bridging N sites.

| $U_{\text{eff}}$ (eV) | $M_{\text{total}}$ ($\mu_B$) | $M_{\text{Mn}}$ ($\mu_B$) | $M_{\text{Mg}}$ ($\mu_B$) | $M_{\text{N}}$ ($\mu_B$) |
|----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 0                    | 3.007                       | 2.289                       | 0.004                       | 0.035                       |
| 2                    | 2.996                       | 2.512                       | 0.003                       | 0.008                       |
| 4                    | 3.007                       | 2.773                       | 0.003                       | -0.025                      |
| 6                    | 3.003                       | 3.235                       | 0.000                       | -0.143                      |
| 8                    | 3.006                       | 3.657                       | -0.002                      | -0.219                      |
| 10                   | 2.968                       | 3.663                       | -0.002                      | -0.231                      |

### TABLE IV. Magnetic moments for a complex consisting of 1 Mn and 2 Mg in GaN for $U_{\text{eff}} = 4$ eV. Given are the total magnetic moment $M_{\text{total}}$ as well as the local moments at the Mn, Mg and the bridging N sites.

| $U_{\text{eff}}$ (eV) | $M_{\text{total}}$ ($\mu_B$) | $M_{\text{Mn}}$ ($\mu_B$) | $M_{\text{Mg}}$ ($\mu_B$) | $M_{\text{N}}$ ($\mu_B$) |
|----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 4                    | 2.039                       | 2.124                       | 0.002                       | -0.050                      |

Different. For instance, the local Mn moment in the study of Villars et al for the complex with one Mn and one Mg is 4.02 $\mu_B$ and considerably larger than our values in Table III. That discrepancy can be explained by the different ways of calculating local moments in the Wien2k or the Quantum Espresso code.

Much more convincing, and free of methodological details is the analysis of the Mn valency by means of the DOS (see Figs. 6 and 7). The Mn valency is determined by the filling of the above mentioned $t_{2g}$ peaks at Fermi level. As it was already mentioned, the filling of the $t_{2g}$ peaks with two electrons corresponds to a Mn valency of $3^+$. If we now dope additionally one Mg ion, the $t_{2g}$ multiplet can only be filled with one electron. And since it is the Mn $3d$ peak which is located at the Fermi level and since that peak is very well separated from the valence orbitals, the Ga and Mg $p$ orbitals, as well as the N $p$ orbitals for a N atom close to the Mn impurity ($N_{\text{in}}$) and another one far of it ($N_{\text{out}}$).
band even for $U$ values between 2 and 8 eV (in difference to the situation in GaAs:Mn) it is quite natural that the doped holes due to Mg doping sit at Mn and are not distributed in the valence band. That is already visible in the DOS. Correspondingly, the Mn valency is 4+ for the supercell with one Mg. And it is a logic consequence, that doping a second Mg ion into the supercell leads to the loss of the last electron in the $t_{2g}$ level and to the Mn$^{5+}$ valence.

V. CONCLUSION

We analyzed numerically a 64 atom supercell of zincblende GaN with 1 or 2 Mn ions, as well as with 1 Mn ion and 1 or 2 Mg ions. The nearest neighbor exchange of two Mn was found to be ferromagnetic with the magnetization density concentrated in between the two Mn sites (see Figure 3). The exchange coupling constant $J$ (in the Hamiltonian $\hat{H} = -2J\vec{S}_1 \cdot \vec{S}_2$) was found to be about 18 meV. The lattice relaxation leads to a decrease of the density of states at the Fermi level (pseudo gap feature, Fig. 2) but does not influence the magnetic coupling in a significant way.

Co-doping with Mg leads to holes which sit, however, at the Mn sites and change the Mn valency from Mn$^{4+}$ without Mg to Mn$^{4+}$ with 1 Mg and Mn$^{5+}$ with 2 Mg.

We showed that this valence change can already be concluded from a careful analysis of the DOS without Mg co-doping since the relevant peak at Fermi level is of Mn character, well separated from valence or conduction band and filled with 2 electrons for GaN:Mn.

We can even deduce more conclusions from our analysis of the DOS. Let us suppose a complex with 1 Mn and 3 Mg ions in GaN which would lead to further p doping. But the Fermi level is then expected to enter into the main valence band with low Mn character. As a consequence, the valence of Mn is expected to stay 5+ for such a complex which explains the experimental observation. It should also be noted that the Mn-Mg complexes in GaN show highly interesting optical properties especially in the near infrared. Even stimulated emission could recently be shown. The analysis of the optical properties of these materials could be an interesting subject of further studies.

VI. ACKNOWLEDGEMENTS

We thank NATO SPS program (grant SIP-984735) for financial support. R.H. thanks A. Bonanni, D. Kyslychyn, A. Nikolenko, and V. Strelchuk for stimulating discussions.
30 V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B 44 , 943 (1991).
31 A.I. Liechtenstein, V. I. Anisimov, J. Zaanen, Phys. Rev. B 52 , R5467 (1995).
32 A. Boukortt, R. Hayn, and F. Virot, Phys. Rev. B 85 , 033302 (2012).
33 P. Giannozzi et al., J. Phys.: Condensed Matter 21 , 395502 (2009)
34 G. Capuzzo, D. Kysylychyn, R. Adhikari, T. Li, B. Faina, A. Tarazaga, M. Luengo, and A. Bonanni, Sci. Rep. 7 , 42697 (2017).