Electronic structure and Jahn–Teller effect in GaN:Mn and ZnS:Cr

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Abstract

We present an ab initio and analytical study of the Jahn–Teller effect in two diluted magnetic semiconductors with d4 impurities, namely Mn-doped GaN and Cr-doped ZnS. We show that the correct insulating electronic structure may be obtained by a proper treatment of the strong electron correlation in the 3d shell in combination with the Jahn–Teller distortion which breaks the local symmetry. Using the LSDA + U approach, we treat the zinc-blende and the wurtzite crystal structures of GaN:Mn, as well as zinc-blende ZnS:Cr. We show that the trigonal distortion due to the wurtzite structure is less important than the Jahn–Teller deformation. This observation allows us to construct a simplified phenomenological ligand field theory (trigonal influence is neglected) which completes the ab initio part. Our work corrects previous studies and the obtained energy gain due to the Jahn–Teller effect (from both the LSDA + U calculation and the ligand field theory) is in good agreement with the experimental data. The same is true for the complete set of crystal field parameters obtained from the phenomenological model which agrees well with previous optical measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Jahn–Teller effect of molecules or impurity ions in semiconductors with degenerate ground states has been well known for a long time [1]. Most of its theoretical treatments were based on crystal field (CF) theory. A well-studied example of the Jahn–Teller effect is the Cr2+ ion in ZnS [2]. That ion is in the 3d4 configuration, has spin S = 2 and a partially filled t2 level. The same 3d4 configuration is realized for the Mn3+ ion in GaN. On the other hand, GaN:Mn is actually a highly disputed material for spintronics applications. The whole class of diluted magnetic semiconductors has at present a lot of interest, and high Curie temperatures were predicted for GaN:Mn [3]. Corresponding experimental [4] or ab initio studies [5] seemed to confirm these predictions. However, the experimental results are not commonly accepted since they might be caused by small inclusions of secondary phases [6]. Also most of the previous ab initio studies obtained a partially filled band of only one spin direction at the Fermi level (half-metallic behaviour) which will be shown to be an artefact of those calculations.

The electronic structure calculations of GaN:Mn, which are based on density functional theory (DFT) within the local spin density approximation (LSDA), lead to a half-metallic ferromagnetic ground state [5, 7, 8]. There were several attempts to include the effects of strong electron correlations on the electronic structure by means of the LSDA + U method but they lead to the same ground state [9, 10]. It was found that the magnetic couplings in GaN:Mn are more short range than in GaAs:Mn, leading to smaller values of the predicted Curie temperatures [8]. A half-metallic state would correspond to hole doping in GaN:Mn. That is equivalent to the fact that some of the Mn ions (or all of them) should be in the Mn2+ charge state. However, as will be shown in this paper, this will not happen since the strong Coulomb correlation in combination with the Jahn–Teller lattice distortion stabilizes the Mn3+ state (in contrast to the behaviour of Mn in GaAs).

As a matter of fact, none of the previous LSDA + U calculations for GaN:Mn were performed with broken local cubic symmetry. In that case, the t2 level remains degenerate by symmetry and the Coulomb correlation cannot open up a gap. As will be demonstrated below, only the combined treatment of Jahn–Teller distortion and strong electron correlations leads to the correct electronic structure. The electron correlations turn out to be the leading interaction, but the lattice distortion is necessary to break the symmetry.
The Jahn–Teller effect of GaN:Mn was previously treated in LSDA (which leads to no substantial gap, however) [11] or by taking into account the strong electron correlation within the Heyd–Scuseria–Ernzerhof hybrid functional [12]. However, some questions remained open in those previous studies. First of all, they considered zinc-blende GaN:Mn, whereas nearly all experimental studies deal with wurtzite GaN:Mn. (Actually, GaN:Mn can exist in both modifications.) Second, and even more important, they missed establishing a relationship between ab initio studies of the Jahn–Teller effect on the one hand, and experimental as well as theoretical crystal field (CF) studies on the other. For that reason we investigate in the present paper not only GaN:Mn but also ZnS:Cr for which the Jahn–Teller effect is well established and the corresponding CF parameters are well known [2]. A detailed calculation of crystal field parameters is important for the interpretation of optical, electron spin resonance (ESR) and spectroscopic data and allows a much better understanding than just a calculation of atomic displacements.

Our paper is organized as follows. After presenting our method of ab initio calculations we show the DFT results for zinc-blende structures (GaN:Mn and ZnS:Cr) in section 3.1 and the results for wurtzite GaN:Mn in section 3.2. All calculations were performed within the supercell method. We obtain the lattice displacements, the Jahn–Teller energy gain $E_{JT}$ and the density of states (DOS). The resulting DOS is dramatically different from previous electronic structure calculations (which did not take into account the combined effect of Jahn–Teller distortion and Coulomb correlation), neither for Mn-doped GaN [7, 13–16, 9, 17–23, 10, 24–28] nor for Cr-doped ZnS [29–31]). Instead of half-metallic behaviour we obtain an insulating ground state with a considerable excitation gap. Similar results for zinc-blende GaN:Mn were reported earlier but using different methods than in our study [32, 12].

For wurtzite GaN:Mn, the Jahn–Teller displacements around the Mn impurity are much more important than the trigonal distortions corresponding to the difference between wurtzite and zinc-blende host lattices. Therefore, we neglect this trigonal distortion in the more phenomenological ligand field theory which is outlined in section 4. That ligand field approach properly takes into account the Coulomb correlation by a many-electron multiplet approach and considers the ‘crystal field’ splitting which arises due to the hybridization with the ligands [34]. It was already successfully applied to ZnO:Co and it represents an important complement to the ab initio part, since it is the only theoretical method which provides us with the complete set of crystal field parameters. We obtain this set of parameters in good agreement with previous optical measurements for ZnS:Cr [2, 33] and GaN:Mn [35].

2. Method of calculation

Our calculations are performed using the full potential local orbital (FPLO) [36] method with the LSDA + $U$ (local spin density approximation with strong Coulomb interaction) [37] approximation in the atomic limit scheme. The lattice constants are optimized for pure semiconductors using the LSDA method. We obtain for the zinc-blende structure $a_0 = 4.48$ Å for GaN and $a_0 = 5.32$ Å for ZnS. The optimal lattice parameters for GaN in a wurtzite structure are $a = 3.162$ Å, $c = 5.179$ Å and $u = 0.375$. To study the Jahn–Teller effect, we use a supercell of 64 atoms for both structures, zinc-blende and wurtzite. The supercell is constructed by $4 \times 2 \times 2$ (in the $a$, $b$ and $c$ directions) elementary cells of four atoms in the wurtzite structure, and by $2 \times 2 \times 2$ elementary cells of eight atoms for zinc blende. In all cases, we use a $4 \times 4 \times 4$ $k$-point mesh. The LSDA+$U$ parameters are introduced as Slater parameters: for Mn [37], $F_2 = 7.41$ eV, $F_4 = 4.63$ eV and for Cr [38], $F_2 = 7.49$ eV, $F_4 = 4.68$ eV. The $F_0$ parameter is equal to $U$, and is chosen to be 4 eV. This value is in good agreement with other works and it corresponds to the value which gives the maximum splitting of the triplet manifold at the Fermi level for GaN:Mn and ZnS:Cr in the zinc-blende structure with local D$_{2h}$ symmetry around the impurity. We have verified that our results are not very sensitive to the actual choice of the $U$ parameter. The value $U = 4$ eV gives representative results for a rather large range of $U$ parameters, reaching from 3 up to 8 eV. For each material and each structure we performed a series of calculations with different displacements of the ligands around the impurity in order to find the configuration which minimizes the total energy of the supercell.

3. Ab initio results

3.1. Zinc-blende structure

In the zinc-blende structure, the transition metal ions (Mn or Cr) substitute one atom in the centre of the crystal and there is a complete tetrahedron of ligands around the magnetic ion. Without distortion, the tetrahedron is in the $T_d$ symmetry group (cubic). This symmetry allows two tetragonal (point groups $C_{2v}$ and $D_{2h}$) and one trigonal ($C_3v$) Jahn–Teller distortions. We have verified that the most important energy gain is obtained with the pure tetragonal distortion where the symmetry reduces from $T_d$ to $D_{2d}$. That is in agreement with a previous study of the Jahn–Teller effect in GaN:Mn where, however, the electron correlation had not been taken into account [11]. The displacements of ligands in $D_{2d}$ symmetry are shown in figure 1, using the ligand $N_3$ (which moves to $N_{3JT}$) as an example. The $D_{2d}$ symmetry is defined by $\delta_x = \delta_y \neq \delta_z$ (see figure 1).

Within the zinc-blende phase, we find the distance between Mn and N to be 1.948 Å (with cubic symmetry, it is 1.938 Å) with the displacement coordinates $\delta_x = 1.68$ pm and $\delta_z = 1.76$ pm. The Jahn–Teller effect induces a lowering of the total energy by 38.13 meV and a splitting of the triplet state by 0.81 eV. For Cr-doped ZnS, the results are similar; the distance Cr–S is 2.314 Å (2.304 Å without the Jahn–Teller effect), with $\delta_z = 3.36$ pm and $\delta_x = -0.32$ pm. The total energy decreases by 58.1 meV and the splitting of the triplet level is 1.44 eV.

Without $U$, in the LSDA method, we also find a Jahn–Teller effect for GaN:Mn but the energy gain is smaller by nearly two orders of magnitude, only 0.71 meV. It is very
Figure 1. Definition of coordinate axes and lattice displacements for the Jahn–Teller effect in the zinc-blende structure. The example of MnN₄.

Instructive to compare the resulting densities of states (DOS) for zinc-blende GaN:Mn in LSDA or LSDA + U (figure 2). In the LSDA method, all the 3d levels are located in the gap with a rather small mixing to the 2p orbitals. The doublet of e orbitals is located at about −1.4 eV and the triplet of t₂ character is at the Fermi level. It is partially filled (with two electrons) and one finds half-metallic behaviour. The Hubbard correlation opens up a considerable gap in the one-particle spectral density which is well approximated by the LSDA + U DOS. The width of the gap is 0.6 eV for GaN:Mn and 1.32 eV for ZnS:Cr (figure 3). The empty state (singlet) is mainly of 3d character for the two compounds and the doublet, just below the Fermi level, is mainly of 2p character originating from ligand orbitals. That doublet should not be mixed up with the doublet of e orbitals in the LSDA calculation which is pushed to much lower energy to lie deep within the valence band due to the electron correlation. It is also the electron correlation which leads to the change of orbital character. As a consequence, the transition from the doublet (in LSDA + U) to the first excited state has a considerable p–d character and should be visible as an optical interband transition. That allows a reinterpretation of the optical transition at 1.4 eV (for GaN:Mn) which is usually considered as a pure d–d transition [35]. In agreement with a proposal of Dietl it should be better interpreted as a transition from the d⁴ configuration to d⁵ and a ligand hole [39].

There are two peaks in the unoccupied, minority DOS at about 2.5 eV for GaN:Mn. They are also visible in the LSDA calculation at 1.16 and 1.62 eV and correspond to crystal-field-split 3d levels which were well seen in x-ray absorption spectroscopy. Up to now, they were interpreted by means of an LSDA calculation [40], but our DOS shows that these peaks occur also in the more realistic LSDA + U approach where, however, a detailed calculation of the matrix element effects is still lacking [40].

For GaN:Mn, the total magnetic moment is equal to 4 μₜ, corresponding to S = 2. That fits well with the ionicity 3+ for manganese. The local magnetic moment at the manganese site is slightly enhanced, Mₜ₁ = 4.042 μₜ, which is compensated by small induced magnetic moments of opposite sign at the neighbouring ligands and further neighbours.

Another interesting result is presented in figure 4. In this case we introduced the local Coulomb correlation but no lattice deformation. The local cubic symmetry was, however, broken by the occupation of the triplet manifold. The calculation still shows an insulating case with nearly the same splitting of the triplet state. This observation is not visible within the LSDA method. Therefore, we can say that the splitting of the triplet state is mainly due to the strong correlation of 3d electrons. The Jahn–Teller distortion introduces a small additional splitting of the triplet state: 60 meV for Mn-doped GaN and −11.4 meV for Cr-doped ZnS (in the opposite sense,
Figure 3. Total and partial densities of states (DOS). ZnS:Cr (zinc-blende), LSDA + \( U = 4 \) eV. The dashed line represents the partial 3d DOS of the transition metal ion and the solid line represents the total DOS. The Fermi level is set to 0 eV.

Figure 4. DOS of zinc-blende GaN:Mn resulting from the LSDA + \( U \) calculation (\( U = 4 \) eV). The dashed line represents the DOS without Jahn–Teller distortion but breaking local cubic symmetry and the solid line represents the DOS with Jahn–Teller effect. The Fermi level is set to 0 eV.

Figure 5. The tetrahedron of ligands around the magnetic ion in wurtzite structure. The dashed arrows represent the displacement similar to \( C_{2v} \) (denoted \( \delta \) in the text).

Table 1. Change of the distances between the magnetic ion and its ligands \( d_{\text{JT}-\text{JT}} \) (in pm) due to the trigonal wurtzite distortion or the Jahn–Teller effect in both phases.

| Structures | N_1 | N_2 | N_3 | N_4 |
|-----------|-----|-----|-----|-----|
| \( d_{\text{ZB-JT}} - d_{\text{ZB}} \) | 0.95 | 0.95 | 0.95 | 0.95 |
| \( d_{\text{ZB-JT}} - d_{\text{ZB}} \) | 0.35 | -0.16 | -0.16 | -0.16 |
| \( d_{\text{ZB-JT}} - d_{\text{ZB}} \) | 2.08 | 2.06 | 2.06 | 2.09 |

displacements, there is still a mirror symmetry between \( N_2 \) and \( N_3 \). There is no reason why this mirror symmetry should be conserved in the Jahn–Teller effect. We tried additional displacements around the minimum which was found in the geometry described above. But the additional energy gain was very small and the corresponding displacements of only a few tenths of a picometre. Therefore, we neglected these additional distortions in the following.

For Mn-doped GaN in the wurtzite phase, the Jahn–Teller displacements of figure 5 lead to a total energy decrease of 27.1 meV for the optimal displacement \( \delta = 2.53 \) pm. The calculations are performed with the same parameter values as in the zinc-blende phase, i.e. with \( U = 4 \) eV. Already in the ideal wurtzite structure, the \( t_2 \) manifold is split into a lower singlet and an upper doublet which is partially occupied with one electron. The Jahn–Teller effect leads to the splitting of the doublet and to insulating behaviour. This splitting is seen at the \( \Gamma \)-point of the resulting band structure (not shown) by an amount of 0.81 eV, very similar to the splitting in the zinc-blende phase.

Table 1 summarizes the influence of the distortions (trigonal and Jahn–Teller) on the distances between the magnetic ion and its ligands for both structures, zinc blende and wurtzite. One remarks, first of all, that the Jahn–Teller distortions are much larger than the trigonal distortions of the ideal wurtzite structure. There is a factor between 3 and 6 for the different distances. The Jahn–Teller effect compensates nearly the trigonal distortion and all four distances become approximately equal. The distances change more in the wurtzite structure than in the zinc-blende one. However, it is better to compare the norm of the displacement vectors \( \| \delta \| \) which is \( \| \delta \| = \delta = 2.53 \) pm in wurtzite and

3.2. Wurtzite structure

In the case of the wurtzite structure, the local tetrahedron is no longer an ideal one, even without Jahn–Teller distortion. It is elongated along the \( c \) direction (see figure 5) and the position of the central ion is given by the \( u \) parameter and it is not exactly at the centre of the tetrahedron. In the ideal wurtzite crystal, the tetrahedron of ligands has a threefold symmetry axis along \( c \) (\( C_{3v} \) symmetry group). The Jahn–Teller effect breaks this symmetry. In our study, we investigated the displacements which are indicated by arrows in figure 5 (all are of the same amount \( \delta \)). Without trigonal distortion these displacements would correspond to a local \( C_{2v} \) symmetry. With these
The Jahn–Teller effect of $D_{2d}$ symmetry leads to a splitting of the $t_2$ levels into a doublet and a singlet and the $e$ multiplet is split as well (figure 7). An energy gain for a $d^4$ configuration differs less than the distance change of table 1.

Very similar to the zinc-blende case, the LSDA DOS shows half-metallic behaviour (not shown) whereas the LSDA + $U$ with Jahn–Teller deformation (figure 6) opens up a gap. However, the gap is smaller in the wurtzite structure than in zinc blende (compare with figure 2(b)). The reason is the top of the 2$p$ valence band which has a trigonal splitting in the wurtzite structure. Therefore, the 3$d$ quasi-doublet just below the Fermi level is superimposed with a broader p-band. Its constant DOS indicates a nearly ideal 2D character which arises from the $N$ $p_x$ and $p_y$ orbitals in the $a$–$b$ plane (see figure 5). The splitting of the 3$d$ levels of 0.81 eV is clearly visible in figure 6 but the gap at the Fermi level is only 0.3 eV. As in section 3.1, we also introduced the local Coulomb correlation but no lattice deformation. Now, it is the trigonal symmetry which is broken by the occupation. Very similar to the zinc-blende case (figure 4) the resulting DOS changes only slightly in comparison to figure 6 (but is not shown). The lattice displacements introduce only a small change of the splitting of 3$d$ levels of $\sim 40$ meV (opposite to GaN:Mn in the zinc-blende phase) corresponding to a stretching of the tetrahedron. But once again, the main reason for the 0.81 eV splitting consists in the strong Coulomb correlation of 3$d$ electrons.

The symmetry analysis of the wurtzite case is different (figure 8). Here, already the trigonal wurtzite distortion leads to a splitting of the $t_2$ multiplet. But without lattice distortion, the doublet is higher than the singlet and partially filled for a $d^4$ configuration. The Jahn–Teller effects lifts this degeneracy and leads to an energy gain and insulating behaviour. One can also understand why the Jahn–Teller effect compensates partially the trigonal distortion since the two occupied $t_2$ orbitals build a quasi-doublet similar to the doublet of the $D_{2d}$ Jahn–Teller level structure in the zinc-blende case (compare with figure 7).

The ligand field theory allows a deeper understanding of the Jahn–Teller effect. We apply here a theory which was formerly developed for ZnO:Co [34]. It correctly takes into account the Coulomb correlation and the hybridization with the ligands. Since the trigonal distortion was found to be much smaller than the Jahn–Teller distortion in our $ab$ $initio$ study of wurtzite GaN:Mn, we will neglect it in this analytical part. In ligand field theory, the degeneracy of the impurity 3$d$ level is split due to hybridization with the neighbouring ligands. In the following we neglect the electrostatic contributions, which will be shown to be justified for GaN:Mn and to a lesser extent for ZnS:Cr. The level structure of the 3$d^4$ multiplet (figure 9) is just the inverse of figure 7. The splitting of the lowest $^3T_2$ triplet is denoted as $\Delta_{T_2}$. The local Hamiltonian in ligand field or crystal field theory can be expressed as

$$
H_{\text{CF}} = H_{\text{cub}} + H_{\text{tetra}}
= B_4(O_4^2 + 5O_2^2) + (B_2^0O_2^0 + B_4^0O_4^0)
$$

where $B_4^0$ and $O_4^0$ are Steven’s parameters and Steven’s operators, respectively [41]. The first part represents the Hamiltonian of an ideal tetrahedron and the second describes

![Figure 6. DOS of Mn-doped GaN in wurtzite structure resulting from the LSDA + $U$ calculation ($U = 4$ eV). The Fermi level is set to 0 eV.](image)

![Figure 7. Schematic level spectrum of the 3d multiplet in one-electron mean-field theory. Jahn–Teller effect in the zinc-blende structure.](image)

![Figure 8. Same as figure 7 but in wurtzite structure.](image)
the linear Jahn–Teller effect. The eigenvalues of $H_{\text{CF}}$ correspond to the 3d electronic levels of the magnetic ion (they represent the spectrum). $B_4$ is the parameter of the cubic crystal field and it is equal to $\Delta_g/120$.

The crystal field Hamiltonian (1) has the same form for the one-particle problem (with parameters $B_3$, $B_2$, and $B_0$) or for the 3d multiplet (with parameters $B_3$, $B_2$, and $B_0$) \cite{[41, 34]}. The fundamental multiplet state is $^5D$ ($L = 2$ and $S = 2$). In this fundamental state, the orbital moment for one electron ($l = 2$) is equal to the total orbital moment. This particular case shows that the one-electron spectrum is opposite to the multiplet spectrum (example: $B_2 = -B_1$). In the superposition model \cite{[34, 42, 43]} the crystal field Hamiltonian (1) can be calculated by adding up the hybridization contributions of all the ligands. Then, the matrix elements of $H_{\text{CF}}$ with respect to the projection $m$ of the total orbital momentum $L = 2$ are given by

$$V_{nm'} = \sum_i [A_{mm'}b_4(R_i)Y_4^{m-m'}(\theta_i, \phi_i)]$$
$$+ \sum_i [B_{mm'}b_2(R_i)Y_2^{m-m'}(\theta_i, \phi_i)]$$
$$+ \sum_i [b_0(R_i)b_{mm'}]$$

with

$$A_{mm'} = \frac{(-1)^m5\sqrt{4\pi} c^{224}_{-m,m} c^{224}_0}{27}$$
$$B_{mm'} = \frac{(-1)^m5\sqrt{4\pi} c^{222}_{-m,m} c^{222}_0}{\sqrt{5}}$$

and where $C^{ijkl}_{mm'm'}$ are Clebsch–Gordon coefficients and $Y_i^m$ are spherical harmonics. The $i$ index corresponds to the ligand number. The axis system is defined in figure 1.

By identifying the eigenvalues of $H_{\text{CF}}$ with the equivalent values of $V_{nm'}$, we obtain the expressions of Steven’s parameters as a function of the ligand coordinates:

$$\hat{B}_4 = \frac{-b_4(R_i)Y_4^0(\theta_i, \phi_i)}{120}$$
$$\hat{B}_4^0 = \frac{b_2(R_i)Y_2^0(\theta_i, \phi_i) + 7Y_4^0(\theta_i, \phi_i)}{12}$$
$$\hat{B}_4^0 = \frac{-2b_2(R_i)Y_2^0(\theta_i, \phi_i)}{49}$$

with

$$Y_4^0(\theta_i, \phi_i) = 6 - 30\cos^2\theta_i + 35\cos^2\theta_i$$
$$Y_4^0(\theta_i, \phi_i) = \sin^2\theta_i + 3\sin^2\theta_i$$
$$Y_4^0(\theta_i, \phi_i) = -2 + 3\cos^2\theta_i + 3\cos^2\theta_i$$

$$b_2(R_i) = \frac{-3h^2R^3}{\Delta_{pd} m^2} (\eta_{pd}^2 + \eta_{pd}^2)$$

where $b_2(R_i)$ and $b_4(R_i)$ are expressed by means of the Harrison parameterization of p–d hopping. The values of $\eta_{pd} = -2.95$ and $\eta_{pdr} = 1.36$ are extracted from his book (first edition) \cite{[44]}. In the case of D$_{3h}$ symmetry, the distances $R$, between the magnetic ion and the four ligands is identical. $\Delta_{pd}$ is the charge transfer energy. It is treated as an adjustable parameter in this theory.

The Hamiltonian (1) concerns the electronic degrees of freedom only. The tetragonal distortion results from the coupling to the lattice. As is shown in figure 9 any tetragonal distortion leads to a splitting of the lowest triplet $^5T_2$ and to an energy gain. We note that the many-electron multiplet spectrum of figure 9 cannot be compared with figure 4 since it corresponds to excitations with a constant number of electrons, in contrast to the one-particle spectral density. The energy gain is linear in the lattice displacements, whereas the vibronic energy loss $E_{\text{vibronic}}$ is a quadratic term. One has to minimize the total energy

$$\Delta_{\text{total}} = \frac{2}{3} (E(\hat{C}B_2) - E(\hat{C}E_2)) + E_{\text{vibronic}}.$$  

For the sake of simplicity we approximate $E_{\text{vibronic}}$ by the breathing mode energy, extracted from the LSDA + $U$ calculation. We find the lattice contribution for GaN:Mn to be $E_{\text{vibronic}}[\text{eV}] = 36.7708||\delta||^2$ and for ZnS:Cr $E_{\text{vibronic}}[\text{eV}] = 30.4887||\delta||^2$ with $||\delta||$ in Å. One should note that there is no difference between LSDA and LSDA + $U$ methods for the lattice energy. Also, we have tested the lattice energy for the more specific tetragonal mode with no essential difference. The energy gain, which is induced by the Jahn–Teller effect, corresponds to

$$E_{\text{JT}} = \min(\Delta_{\text{total}}).$$

The results of the ligand field model are presented in table 2. For GaN:Mn, we have exclusively used the ligand hybridization as the microscopic origin for the level splitting. The value of $\Delta_{pd}$ is adjusted such that $\Delta_g$ equals the experimental value. The results are very convincing which proves that the exceptionally large value of $\Delta_g = 1.4$ eV in the case of GaN:Mn is predominantly caused by the hybridization energy to the ligands. On the other hand, neglect of the electrostatic contribution is certainly an approximation which shows its limits for ZnS:Cr. The procedure described above gives no satisfactory results. We interpret this deficiency such that the electrostatic corrections become more important for ZnS:Cr which has a much smaller value of $\Delta_g$, indicating a smaller hybridization. As discussed in \cite{[46]}, the higher-order...
Table 2. Summary of parameters.

|                      | GaN:Mn | ZnS:Cr |
|----------------------|--------|--------|
| Our work             | 187    | 111    |
| Experiment           | 167.1  | 213.9\(^{111}\)11.6\(^b\) |
| \(E_{JT}\) (meV)     | 59.9   | 37     |
| \(E_{JT}\) (meV)     | 58.4   | 71.3\(^{25}\)37.2\(^b\) |
| \(\Delta T_2\) (meV) | -1.88  | -1.05\(^b\), -1.02\(^d\) |
| \(\Delta T_2\) (meV) | -1.26  |        |
| \(\Delta_3\) (eV)   | 1.4    | 0.57   |
| \(\Delta_3\) (eV)   | 0.58\(^b\), 0.59\(^b\) |
| \(R\) (\(\AA\))     | 1.932  | 2.303  |
| \(\Delta_2\) (eV)   | 2.31   |        |
| \(b_2/b_4\)         | 3.3    |        |

\(^a\) Optical measurements [45]. \(^b\) Optical measurements [33].
\(^c\) Optical measurements for wurtzite GaN:Mn [35].
\(^d\) Magnetic measurements for wurtzite GaN:Mn [50].

The lattice distortions obtained from the ligand field theory (table 2) approximately fulfill the relationship \(\delta = \delta_2 = \frac{1}{4}\delta_x\). This occurs not by accident since the relationship characterizes a pure tetragonal mode \(Q_0\). In general, up to now, we considered \(\delta_x = \delta_y \neq \delta_z\), which corresponds to a mixture of tetragonal and breathing mode \(Q_b\). The normal coordinates of the two modes are defined as \(Q_0 = -2\sqrt{2}(\delta_x + \delta_y)\) and \(Q_b = \sqrt{3}(2\delta_y - \delta_z)\), respectively [47]. But it is only the tetragonal mode which leads to a splitting of the \(5T_2\) level. That is described in the Hamiltonian which was used by Vallin et al [2, 45, 33] to analyze their data obtained by optical measurements and electron paramagnetic resonance (EPR):

\[
H_D = V Q_0 e_\theta + \frac{\kappa}{2} Q_0^2.
\]

Here, the \(V\) parameter is the Jahn–Teller coupling coefficient and \(e_\theta\) is a diagonal \(3 \times 3\) matrix which describes the splitting of the \(5T_2\) triplet into the upper \(5E_2\) doublet and the lower \(5B_2\) singlet. Its diagonal elements are 1/2 (corresponding to \(5E_2\)) and -1 (corresponding to \(5B_2\)). The parameter \(\kappa\) describes the lattice stiffness and is connected with the phonon frequency by \(\omega = \sqrt{\kappa/m}\), where \(m\) is the mass of one ligand. Minimizing the energy (8) we find the relationship \(V = \kappa Q_0\) and the Jahn–Teller energy

\[
E_{JT} = \frac{V}{2} Q_0.
\]

Therefore, if we know the Jahn–Teller energy \(E_{JT}\) and the lattice distortion \(Q_0\), we may calculate the coupling coefficient \(V\) and the phonon frequency \(\omega\) and compare it with other works. The comparison is not an ideal one since our LSDA + \(U\) results do not correspond to a pure tetragonal distortion. They contain an important part of the breathing mode which comes about due to recharging effects around the impurity being not treated in the ligand field theory or in the analysis of the optical data in [2, 33]. Nevertheless, we compare in table 3 our ab initio and ligand field results with other theoretical or experimental work from the literature. We may remark on a rather good agreement for the Jahn–Teller energy \(E_{JT}\) between our work and the optical data of Vallin et al for ZnS:Cr [2]. However, our estimate of the phonon frequency is much larger. A detailed analysis of this discrepancy is beyond the scope of the present work. We just remark that higher phonon frequencies would mean a more profound tendency towards the dynamic Jahn–Teller effect. There are indeed discussions (but not for ZnS:Cr) whether the experimental data of GaN:Mn should be interpreted as a static [35] or a dynamic [49] Jahn–Teller effect. Such nonadiabatic effects can, however, not at all be treated in density-functional-based methods.

6. Discussion and conclusion

Many ab initio studies of Mn-doped GaN or Cr-doped ZnS, mostly based on the LSDA approximation, result in a half-metallic behaviour. In those calculations, the Fermi level is located in a small 3d band of majority spin within the middle of the gap of the host semiconductor [7, 13, 29, 30]. We have shown that such a result is an artefact of the LSDA method and can be repaired by taking into account the strong Coulomb correlation in the 3d shell and the Jahn–Teller displacements simultaneously. Allowing for a Jahn–Teller distortion only, but neglecting the Coulomb correlation, leads to a tiny gap at the Fermi level [11]. Also, the opposite procedure of taking into account the Coulomb correlation by the LSDA + \(U\) method (i.e. the same method which we have used) but remaining in cubic symmetry is insufficient [9]. The origin of this deficiency in the given case of a d\(^4\) impurity is a threefold degenerate level of \(t_2\) symmetry at the Fermi level which is occupied with one electron only. It is sufficient to break the local cubic symmetry in the presence of a strong electron correlation to obtain insulating behaviour with a gap of the order of 1 eV. Such an electronic structure is in agreement with the known experimental data for both compounds. Using the LSDA + \(U\) method we found the Jahn–Teller energy gain \(E_{JT}\) in good agreement with known optical data [33, 35].

In addition to the ab initio calculations, we applied a many-electron ligand field theory [34] to reach a deeper understanding of the Jahn–Teller effect. It uses the p–d hybridization between the 3d impurity and ligands as the principal origin of the crystal field splitting [34]. This hybridization is parametrized by the Harrison scheme [44] and the lattice energy as obtained from our ab initio calculation is added. The resulting energy gain is very close to the ab initio results but the ligand field theory allows, in addition, the determination of the complete set of crystal field parameters. We found good agreement with the experimental parameter set for GaN:Mn [35]. Our ab initio results confirm the
experimental observation that the trigonal splitting is much smaller than the Jahn–Teller splitting. We have observed that our ligand field method works better for GaN:Mn than for ZnS:Cr due to the very large cubic crystal field splitting $\Delta q = 1.4$ eV in the former case (in contrast to $\Delta q = 0.58$ eV for ZnS:Cr).

Our combined ab initio and analytical study allows also a comparison with the ‘classical’ work on ZnS:Cr. The Jahn–Teller effect of that model compound had already been studied in the 1970s in great detail by optical and EPR measurements [2, 33, 45]. We obtained here an energy gain $E_{JT}$ very close to the experimental data but for higher phonon frequencies.

Finally, we would like to discuss the importance of our results for spintronics applications. First of all, the Jahn–Teller mechanism which we describe is not restricted to the two compounds of our study. It may occur in all cases where the impurity level is well separated from the valence band but only partially filled. The separation from the valence band is important since it makes all the difference between GaAs:Mn and GaN:Mn. We confirm with our method the result of [12] that GaAs:Mn remains half-metallic even if we take into account the strong electron correlations and the Jahn–Teller displacements. For GaN:Mn, the Jahn–Teller effect leads to insulating behaviour, which questions many previous ab initio studies in the literature. In the case of GaN:Mn all available information points to the stability of Mn$^{5+}$ which hinders an intrinsic hole doping by Mn [50] (experimentally, one may find Mn$^{3+}$ in electron-doped samples, which is not well suited for spintronics applications either). One still has the possibility to reach hole doping by a second impurity besides Mn (co-doping). That would probably allow the classical mechanism for ferromagnetism in diluted magnetic semiconductors with $S = 2$ local moments at the Mn sites.

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References

[1] Jahn H A and Teller E 1937 Proc. R. Soc. A 161 220

Table 3. Comparison of parameters. When possible, the complete set of parameters was calculated from the literatures values by the relations given in section 5. HSE: Heyd–Scuseria–Ernzerhof hybrid functional, GGA: generalized gradient approximation, GFC: Green-function calculation, W: wurtzite, ZB: zinc blende, LFT: ligand field theory.

| Method      | Structure | $E_{JT}$ (meV) | $Q_0$ (Å) | $V$ (eV Å$^{-1}$) | $\hbar\omega$ (cm$^{-1}$) |
|-------------|-----------|----------------|-----------|-------------------|--------------------------|
| GaN:Mn     | Present LFT ZB | 59.4 | −0.0828 | −1.44 | 579 |
|            | LSDA + U ZB | 38.1 | −0.0562 | −1.35 | 680.5 |
| Literature | LSDA + U W | 27.1 |  |  |  |
| GGA [11]   | ZB         | 100 | −0.1365 | −1.46 | 454 |
| HSE [12]   | ZB         | 184 |  |  |  |
| Optics [35] | W         | 37 |  |  |  |
| ZnS:Cr     | Present LFT ZB | 58.4 | −0.0834 | −1.4 | 375.8 |
|            | LSDA + U ZB | 58.4 | −0.0496 | −2.35 | 631.5 |
| Literature | GFC [48] ZB | 185.98 | −0.16 | −2.32 | 349.4 |
| Optics [33] | ZB         | 37.2 | −0.279 | −0.266 | 90 |
[31] Jia X, Qin M and Xang W 2009 J. Phys. D: Appl. Phys. 42 235001
[32] Schulthess T C, Temmerman W M, Szotek Z, Butler W H and Stocks G M 2005 Nat. Mater. 4 838
[33] Kaminska M, Baranowski J M, Uba S M and Vallin J T 1979 J. Phys. C: Solid State Phys. 12 2197
[34] Kuzian R, Dure A M, Satii P and Hayn R 2006 Phys. Rev. B 74 155201
[35] Wolos A, Wysmolek A, Kaminska M, Twardowski A, Bockowski M, Grzegory I, Porowski S and Potemski M 2004 Phys. Rev. B 70 245202
[36] Koepernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[37] Anisimov V I, Zaanen J and Andersen O K 1991 Phys. Rev. B 44 943
[38] Korotin M A, Anisimov V I, Khomskii D I and Sawatzky G A 1998 Phys. Lett. 80 4305
[39] Dietl T 2008 Phys. Rev. B 77 085208
[40] Titov A et al 2005 Phys. Rev. B 72 115209
[41] Abragam A and Bleaney B 1970 Electron Paramagnetic Resonance of Transition Ions (Oxford: Clarendon)
[42] Bradbury M I and Newman D J 1967 Chem. Phys. Lett. 1 44
  For a review see Newman D J and Ng B 1989 Rep. Prog. Phys. 52 699
[43] Kuzmin M D, Popov A I and Zvezdin A K 1991 Phys. Status Solidi b 168 201
[44] Harrison W A 1980 Electronic Structure and the Properties of Solids (San Francisco: Freeman)
[45] Vallin J T and Watkins G D 1974 Phys. Rev. B 9 2051
[46] Savoyant A, Stepanov A, Kuzian R, Deparis C, Morhain C and Grasza K 2009 Phys. Rev. B 80 115203
[47] Sturge M D 1967 Solid State Phys. 20 91
[48] Oshiyama A, Hamada N and Katayama-Yoshida H 1988 Phys. Rev. B 37 1395
[49] Marcet S et al 2006 Phys. Rev. B 74 125201
[50] Stefanowicz W et al 2010 Phys. Rev. B 81 235210