Jahn-Teller distortion and ferromagnetism in the dilute magnetic semiconductors GaAs:Mn and cubic GaN:Mn

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Using first-principles total-energy methods, we investigate Jahn-Teller distortions in III-V dilute magnetic semiconductors, GaAs:Mn and GaN:Mn in the cubic zinc blended structure. The results for an isolated Mn impurity on a Ga site show that there is no appreciable effect in GaAs, whereas in GaN there is a Jahn-Teller effect in which the symmetry around the impurity changes from T_d to D_{2d} or to C_{2v}. The large effect in GaN occurs because of the localized d^4 character, which is further enhanced by the distortion. The lower symmetry should be detectable experimentally in cubic GaN with low Mn concentration, and should be affected by charge compensation (reductions of holes and conversion of Mn ions to d^5 with no Jahn-Teller effect). The Jahn-Teller effect is greatly reduced because the symmetry at each Mn site is lowered due to the Mn-Mn interaction. The tendency toward ferromagnetism is found to be stronger in GaN:Mn than in GaAs:Mn and to be only slightly reduced by charge compensation.

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I. INTRODUCTION

Electronics based upon the spin of the electron (spintronics) seeks to exploit the spin of charge carriers in semiconductors.[1–3] It is widely expected that new functionalities for electronics and photonics can be derived if the injection, transfer, and detection of carrier spin can be controlled above room temperature in these dilute magnetic semiconductors (DMSs).[4] Most of the work in the past has focused on InAs:Mn,[5–8] GaAs:Mn,[9–25] and Ge:Mn.[26,27] Novel control of magnetism has already been achieved in these host materials. However, the reported Curie temperatures[1] are too low to have significant practical impact. Recently, there has been interest in wide band gap semiconductors, such as GaN,[28–35] which may exhibit higher Curie temperatures.[36–42] Since there has been tremendous progress on the growth of high-quality (Ga, Mn)N epitaxial layers,[43–45] GaN:Mn is a promising high-T_c ferromagnetic semiconductor. Using the Zener model of ferromagnetism,[46] Dietl *et al.*[36] predicted that cubic GaN doped with 5 atomic percentage of Mn and containing a high concentration of holes (3.5×10^{20} cm^{-3}) should exhibit a Curie temperature exceeding room temperature. However, the mechanisms of ferromagnetism in DMS materials is still an open question.

Theoretically, there are many proposals for the electronic configuration which have focused the ferromagnetic mechanism upon the coupling between the host p and Mn $3d$ states;[47–51] suggestions include Mn $3d^5$+hole induced ferromagnetism in GaAs:Mn,[47] whereas in GaN:Mn the spin-spin interaction has been proposed to be driven by a double exchange mechanism involving d electrons in Mn $3d^4$ states.[48] It has been suggested that $3d^5$, $3d^5$+hole, and $3d^4$ coexist in GaAs:Mn based upon evidence in the dilute regime that there is a Jahn-Teller[52] distortion associated with the $3d^4$ state.[50] However, to our knowledge only one work has proposed that there should be a strong Jahn-Teller effect in the GaN:Mn system,[51] and there have been no quantitative theoretical studies of the Jahn-Teller effect in either GaAs:Mn or GaN:Mn.

In this paper, we report first-principles calculations of the magnitude of the Jahn-Teller effect and the consequences for ferromagnetism in GaAs:Mn and GaN:Mn in the cubic zinc blende structure. Although GaN is normally found in the hexagonal wurtzite structure, there are reports that GaN:Mn can be stabilized in the cubic structure.[31,45] This is relevant for the magnetic properties which are believed to be controlled by the states at the Fermi level. As we discuss below, magnetic interactions are enhanced by the degeneracy of the partially filled states at the Fermi level in cubic symmetry, whereas a splitting of the states can lead to a gap at the Fermi energy. Indeed we find a Jahn-Teller effect which should be observable for isolated Mn impurities in cubic GaN; however, the effect is not large enough to affect the magnetic interactions in GaN:Mn at doping concentration levels in magnetic semiconductors. We also point out that our results suggest possible consequences for GaN:Mn in the wurtzite structure, since the symmetry of the electronic states found in other work[30,53] implies that Jahn-Teller effects may occur also in the wurtzite structure.

II. CALCULATION METHODS

Our calculations were performed using the density-functional theory within the generalized gradient approximation (GGA) of the Perdew-Wang 91 form.[54] We used the Vanderbilt ultrasoft pseudopotentials[55] and the Vosko-Wilk-Nusair interpolation for the correlation functional in the spin-polarized calculations, as implemented by the plane-wave total energy VASP code.[56] The calculated lattice constants are $a=5.751$ Å for GaAs and $a=4.542$ Å for GaN, and all calculations with supercells are done keeping the supercell lattice vectors fixed as multiples of the primitive lattice vectors. All cell-internal structural parameters are fully relaxed until the forces are converged to within 0.005 eV Å^{-1} for all calculations for an isolated Mn (Sec. III). A larger tolerance of 0.05 eV Å^{-1} is used in the calculations involving Mn-Mn pairs (Sec. IV). The cutoff energy for the plane wave expan-

sion is 170 eV for calculations involving Mn in GaAs and 270 eV for Mn in GaN, with checks using 400 eV. For self-consistent total energy calculations, we used a 64-atom supercell and a $4\times4\times4$ Monkhorst-Pack k-point mesh (which has been verified to be sufficient[33]), and selected cases were checked with a $6\times6\times6$ k-point mesh. Density of states plots were made using a finer $8\times8\times8$ k-point mesh.

III. ISOLATED MN IMPURITIES

The Jahn-Teller effect was first proposed to occur in open-shell molecules,[52] and there are many examples in impurity states in II-VI (Ref. 57) and III-V (Ref. 58) semiconductors. The effect is caused by a distortion that lowers the symmetry and leads to a splitting of a degenerate state that is linear in the magnitude of the distortion. If the state is partially occupied, the total energy is always lowered by some distortion since all other contributions to the energy are quadratic in the distortion, and the total energy is minimum in a distorted configuration. It may also happen that a large distortion occurs leading to a new bonding configuration separated by an energy barrier, such as the DX center[59] and AX center.[60] Although the existence of a Jahn-Teller effect is determined only by symmetry, we have to do a quantitative calculation of the magnitude. If the splitting is less ≈0.01 eV, we estimate that the effect is smaller than the effect of quantum fluctuation or temperature and therefore can be ignored.

In order to study isolated Mn impurities, we have carried out calculations on 64-atom cells with one Mn substituted for a Ga atom in GaAs and in GaN. We have calculated the total energy and the eigenvalues of the Kohn-Sham Hamiltonian for various cases. First we have considered the ideal geometry with all atoms at the ideal positions of the GaAs or GaN tetrahedral lattices, and breathing distortions in which the bond lengths change but the symmetry is constrained to remain T_d. We have also considered three different lower symmetry distortions as shown in Fig. 1: (a) T_d to D_{2d} (b) T_d to C_{2v}, (c) T_d to C_{3v}. All cases can be compared if we define symmetry-adapted variables. In order to disentangle the effects of the distortions, we define the positions of the four nearest-neighbor N (or As) atoms around a Mn atoms to be $\mathbf{R}_i^0$, $i=1,4$, in the ideal tetrahedral structure, and the displacements of the neighbors relative to the Mn, as:

$$\Delta\mathbf{R}_i = (\Delta x_i, \Delta y_i, \Delta z_i). \tag{1}$$

The displacement of the neighbors can be projected into two parts. One part is a symmetric radial "breathing" component, which preserves the tetrahedral symmetry, given by

$$\Delta\mathbf{R}_i^B = \Delta R^B \hat{\mathbf{R}}_i^0, \tag{2}$$

where the magnitude ΔR^B is easily extracted for a given displacement pattern $\Delta\mathbf{R}_i$ using

$$\Delta R^B = \frac{1}{4}\sum_i \hat{\mathbf{R}}_i^0 \cdot \Delta\mathbf{R}_i. \tag{3}$$

The remaining parts of the displacement are symmetry-breaking Jahn-Teller distortions, given by

$$\Delta\mathbf{R}_i^{JT} = \Delta\mathbf{R}_i - \Delta\mathbf{R}_i^B. \tag{4}$$

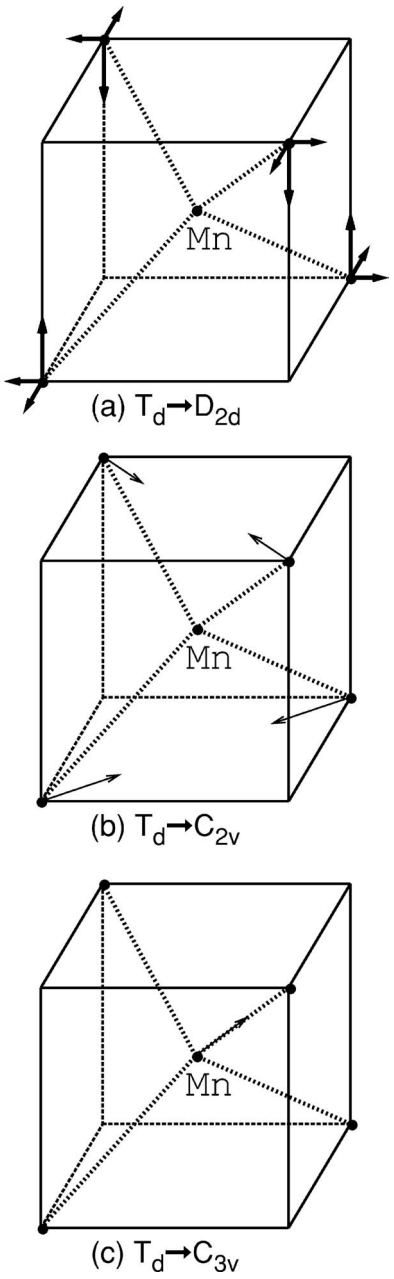

FIG. 1. A schematic drawing of three different atomic configurations, which lower symmetries in Jahn-Teller distortion (a) T_d to D_{2d}, (b) T_d to C_{2v}, and (c) T_d to C_{3v}.

In one set of calculations, we have considered only breathing, varying the magnitude of ΔR_i^B and forcing the symmetry to remain T_d. Comparing to ideal tetrahedral positions, for GaN all four N nearest neighbors of the Mn atom move closer to the Mn by the amount $\Delta R_i^B=0.034$ Å and the energy decreases by $\Delta E=0.05$ eV. For GaAs all four As nearest neighbors of the Mn atom move closer to the Mn by only a small amount $\Delta R_i^B=0.007$ Å and the energy decreases by $\Delta E=0.008$ eV. The difference between GaAs and GaN is readily explained by the different size of As and N atoms.

In the remaining calculations the atoms are allowed to distort and lower the symmetry. In the case of GaAs the energy was never found to decrease. Therefore, we conclude

TABLE I. The comparison of total energy among four different symmetries in GaN:Mn. Here the total energy E_{tot} of T_d symmetry (with breathing relaxation) is set to zero.

Symmetry	T_d	D_{2d}	C_{2v}	C_{3v}
E_{tot} (eV)	0.00	−0.10	−0.08	−0.02

that there is no appreciable Jahn-Teller effect in GaAs. However, in GaN the energy is found to decrease substantially. The decrease in the total energy for the three different symmetries is listed in Table I. There we have defined the energy relative to the minimum energy of T_d symmetry as described above. In the distortion shown in Fig. 1(a), the four nearest neighbors of the Mn atom move to lower the symmetry from T_d to D_{2d} with displacements ($|\Delta x_i| = |\Delta y_i| \neq |\Delta z_i|$). The distortion results in a 0.10 eV lower energy in GaN:Mn (see Table I the D_{2d} column). (This energy difference changes by only 6 meV if the energy cutoff is increased from 270 to 400 eV.) In Fig. 1(b), two neighbors of the Mn atom move along [110] and another two neighbors of the Mn atom move along the $[\bar{1}10]$ direction. This atomic configuration has 0.08 eV total energy lowering in GaN:Mn (Table I, C_{2v} column). However, there is not an obvious effect for Fig. 1(c) distortion, in which an Mn atom moves along the [111] direction, as shown in the column for C_{3v} in Table I.

From these calculations, we conclude that a strong Jahn-Teller effect should be observed for low concentrations in GaN (for D_{2d} and C_{2v}) but not in GaAs:Mn. Furthermore, in GaN:Mn the distortion is slightly favored for D_{2d} symmetry; however, the energies are close enough that either distortion may occur in actual systems. We note that the lowering of energy from breathing relaxation alone (0.05 eV) is smaller than the lowering of the energy (0.10 and 0.08 eV relative to breathing relaxation) for the Jahn-Teller distortion (both D_{2d} and C_{2v}). This shows clearly the importance of the Jahn-Teller effect. In addition we have analyzed the magnitudes of the atomic displacements with D_{2d} symmetry compared with T_d symmetry relaxations. Table II lists coordinates of the first-and second-nearest neighbors of a Mn substituted for a Ga atom for the two cases. It is clear that the displacements are larger for the D_{2d} Jahn-Teller distortion than for the T_d relaxation. In terms of the symmetry-adapted coordinates, the magnitude of the breathing component ΔR^B is 0.020 Å and the magnitude of the Jahn-Teller displacement is $|\Delta \mathbf{R}_i^{JT}| = 0.068$ Å, showing clearly that the Jahn-Teller effect is larger than the breathing for Mn in GaN. Furthermore, Table II shows that the displacements are much smaller for second neighbors than for first neighbors. That means that both the breathing relaxation and Jahn-Teller distortion are localized effects, which indicates that the 64-atom supercell used here is big enough to properly account for the relaxations.

We interpret as a Jahn-Teller distortion that caused by the partial occupation of the t_{2d} state which is split due to the lower D_{2d} symmetry. The Mn triplet t_{2d} of $3d$ energy level splits into singlet and doublet states at Γ point. The splitting increases approximately linearly with the magnitude of the atomic displacements, as expected. At the minimum energy position, the splitting energy $\Delta E_{t_{2d}}$ is 0.23 eV. We have studied the stability of the distorted state by varying the magnitude of the distortion in various ways.

TABLE II. The relaxed coordinates of the first- and second-nearest neighbors of a Mn substituted for a Ga atom in the 64-atom supercell for two cases: breathing relaxation maintaining T_d symmetry and the Jahn-Teller distortion with D_{2d} symmetry. The Mn atom is at the position (0.125,0.125,0.125) and all coordinates are in units of the supercell lattice constant $2a_{\text{GaN}} = 9.084$ Å.

T_d	D_{2d}
First neighbor N atoms	
−0.0021,−0.0021,−0.0021	−0.0043,−0.0043,0.0049
0.2521,0.2521,−0.0021	0.2543,0.2543,0.2549
−0.0021,0.2521,0.2521	−0.0043,0.2543,0.2451
0.2521,−0.0021,0.2521	0.2543,−0.0043,0.2451
Second neighbor Ga atoms	
0.37633,0.37633,0.12582	0.37868,0.37868,0.12654
0.37633,0.87367,0.12418	0.37868,0.87132,0.12346
0.87367,0.37633,0.12418	0.87132,0.37868,0.12346
0.87367,0.87367,0.12582	0.87132,0.87132,0.12654
0.12582,0.37633,0.37633	0.12483,0.37523,0.37090
0.12418,0.37633,0.87367	0.12517,0.37523,0.87909
0.12418,0.87367,0.37633	0.12517,0.87477,0.37090
0.12582,0.87367,0.87367	0.12483,0.87477,0.87909
0.37633,0.12582,0.37633	0.37523,0.12483,0.37090
0.37633,0.12418,0.87367	0.37523,0.12517,0.87909
0.87367,0.12418,0.37633	0.87477,0.12517,0.37090
0.87367,0.12582,0.87367	0.87477,0.12483.0.87909

We also considered large distortions in Figs. 1(b) and 1(c) that might lead to qualitative rebonding of the atoms, e.g., two N (or As) atoms forming nearest neighbors as in an AX center [like Fig. 1(b)] or large displacements of the Mn atom along the [111] direction as in a DX center [like Fig. 1(c)]. However, no configuration was found to be a stable or even metastable state in either GaAs:Mn and GaN:Mn.

Figure 2 shows the partial density of states (DOS) of the Mn $3d$ states in GaAs:Mn [Fig. 2(a)] and cubic GaN:Mn in T_d symmetry [Fig. 2(b)] and the Jahn-Teller distortion of D_{2d} symmetry [Fig. 2(c)]. The results for the undistorted cases [Figs. 2(a) and 2(b)] are very similar to those found by other groups.[29,32,34,35] In GaAs:Mn, we find that Mn $3d$ states are 2 eV below host valence band minimum (VBM) and the t_{2d} level is lower than the e_d level [see Fig. 2(a)]. On the other hand, in GaN:Mn, the Mn $3d$ state is above host VBM and the t_{2d} level is higher than e_d [see Fig. 2(b)]. The integrated weight of the peaks near the Fermi level in Fig. 2 show the amount of the state that is localized in the atomic-like $3d$ states. In each case there is one missing electron. Clearly there is larger weight in the case of GaN:Mn, which is the basis of the assignment of the state as d^5-like. For GaAs:Mn the state has only small weight on the Mn and most of the weight is in As p states, which justifies the conclusion that the state has the character of d^5+hole. Because of this difference between GaAs:Mn and GaN:Mn, there are different

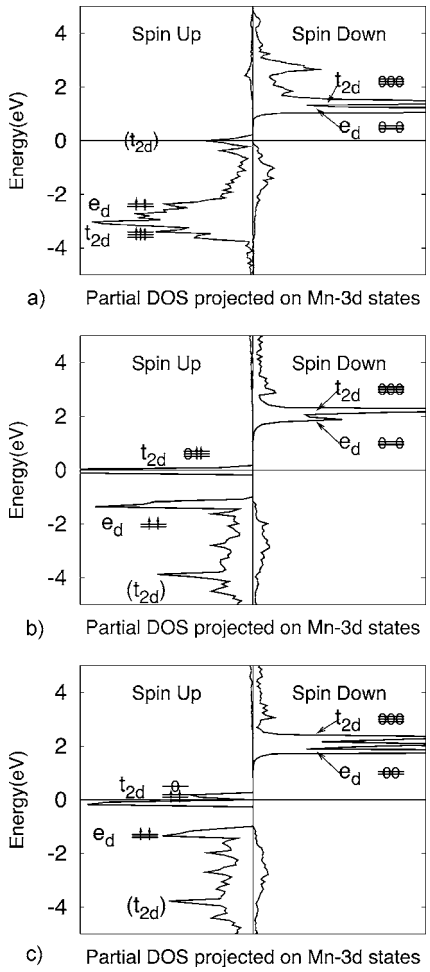

FIG. 2. The partial density of states and schematic energy level diagrams of Mn $3d$ states in (a) GaAs:Mn and (b) GaN:Mn in T_d symmetry without a Jahn-Teller distortion (no energy level splitting) and (c) with Jahn-Teller distortion of D_{2d} symmetry, which shows the splitting of the t_{2d} d states.

consequences for the Mn $3d$ states when the symmetry changed from T_d to D_{2d}: the t_{2d} energy level has no splitting (<0.01 eV) in GaAs:Mn, but a large splitting (0.23 eV maximum at Γ point) in GaN:Mn, with the Fermi level in the gap as shown in Fig. 2(c).

For the case of an isolated Mn substituted for a Ga atom in GaN, we also considered the charged state with an added electron. This charge state is expected when the system is compensated, reducing the number of holes and leading to Mn atoms in the $3d^5$ state. Since this is a symmetric closed-shell state, the Jahn-Teller distortion should disappear. Indeed, our calculations bear this out. We carried out calculations in which the atoms are constrained to have T_d symmetry (pure breathing relaxation) and other calculations in which the atom positions are relaxed starting with distorted initial positions having D_{2d} symmetry. In all cases the total energy is the same to within 0.02 eV, the splitting of t_{2d} is very small (about 0.01 eV), and the atoms relax to positions near T_d symmetry. In principle, all calculation should have the same total energy. We consider the differences to be negligible and these results can be considered as numerical tests showing the accuracy of our calculations. Clearly, this supports our conclusion that an isolated neutral Mn substituted for Ga has a Jahn-Teller distorted ground state in GaN, and that compensation can decrease the effect, causing some Mn to in the $3d^5$ state with no Jahn-Teller distortion.

Finally, we can consider the possibility of a Jahn-Teller effect for GaN:Mn in the wurtzite structure. Although we have not done any calculations on this structure, the symmetry of the states can be determined from other calculations.[30,53] Because of the lower symmetry of wurtzite, the state localized on the Mn is split into a doublet and a singlet. It turns out that the doublet is half-occupied.[53] Therefore, it follows that the energy could be lowered by a Jahn-Teller distortion that splits the doublet, leaving the Fermi level in a gap. It would be interesting to study the effect theoretically and experimentally.

IV. INTERACTIONS OF Mn-Mn PAIRS

Although we have shown that isolated Mn impurities undergo a large Jahn-Teller distortion in GaN, further studies are required to establish the effects, if any, upon the properties of GaN:Mn alloys in interesting concentration ranges for magnetic semiconductors. Since ferromagnetism is due to interactions between the Mn atoms, we must consider the effect upon Mn-Mn interactions for Mn atoms separated by typical distances found in the alloys. The Jahn-Teller effect would be expected to cause a reduction in the tendency toward ferromagnetism since it leads to a splitting of the states. The splitting will reduce the interactions between Mn pairs since hopping requires an extra energy cost. On the other hand, the interaction between the Mn atoms may be so large that it dominates over the Jahn-Teller effect.

In order to study Mn-Mn interactions, we have carried out calculations on 64-atom cells with two substitutional Mn atoms at various distances and in different spin states. For GaAs our results are very similar to published values; for example, for 2 Mn separated by $\sqrt{2}a$, the total energy difference between ferro- and antiferromagnetic spin states $\Delta E_{AF}=0.22$ eV/Mn-pair, which is comparable with 0.2 eV/Mn-pair in Ref. 29, and 114 meV/Mn (0.228 eV/Mn-pair) in Ref. 33. For GaN, we have considered different starting configurations of the atoms, in one set of calculations starting with all atoms in the ideal zinc blende positions and in a second set starting with Jahn-Teller distorted states (the atoms around the Mn-Mn pairs are placed in distorted configurations). The final positions of the atoms after relaxation are the same for the two cases, showing that checked that final configuration was independent of the starting point. Our results are $\Delta E_{AF}=0.36$ eV/Mn-pair and $\Delta E_{AF}=0.30$ eV/Mn-pair,[61] respectively, for 2 Mn atoms separated by $\sqrt{2}a/2$ and $\sqrt{2}a$. These values are very close to those found in previous work[33] that used the same GGA density functional (188 and 161 meV/Mn). The results for $\sqrt{2}a/2$ can also be compared with a calculation[30] that used the LDA, which found 156 meV/Mn.

The energy levels for the Mn $3d$ states in the gap show that the interactions between the two Mn atoms in a pair are indeed larger than the splitting caused by the Jahn-Teller

TABLE III. The total energy difference ΔE^{AF} between ferro- (FM) and antiferro- (AFM) magnetic spin states for a Mn-Mn pair in neutral and −1 charged GaN:Mn. Here $\Delta E^{AF}=E_{tot}^{AFM}-E_{tot}^{FM}$, $\sqrt{2}a/2$ and $\sqrt{2}a$ are two separations of the Mn-Mn pair, and a is lattice constant of cubic GaN.

System	Neutral GaN:Mn (−1)	Charged GaN:Mn
$\Delta E^{AF}_{\sqrt{2}a/2}$ (eV/Mn-pair)	0.36	0.30
$\Delta E^{AF}_{\sqrt{2}a}$ (eV/Mn-pair)	0.30	0.22

effect on the individual Mn atoms. In the ferromagnetic state the d energy levels are split by the Mn-Mn interactions by amounts that are much larger than the splitting due to the Jahn-Teller effect. The maximum width of the d bands in our supercell calculation is 0.4 eV for the Jahn-Teller splitting as shown in Fig. 2(c). In contrast, the maximum width of the d bands is 1.4 eV for a ferromagnetic Mn-Mn pair separated by $\sqrt{2}a/2$ with all atoms relaxed. Furthermore, the Mn-Mn interactions are present even if all atoms are in ideal positions, in which case the maximum width is only slightly changed to 1.3 eV. Similar results are found for Mn-Mn pairs separated by $\sqrt{2}a$. These results show that Jahn-Teller distortions do not have a large effect upon the magnetic interactions between Mn atoms at distances expected in actual ferromagnetic semiconductors.

It is interesting also to consider the realistic case with charge compensation, in which some of the t_{2d} levels are filled. If the states are localized near the Mn atom as in GaN:Mn, each added electron can be interpreted as a conversion of a d^4 into a d^5 state. Since a d^5 state is a spatial singlet with no degeneracy except spin, no Jahn-Teller effect will occur. We also calculated −1 charged states for an Mn pair separated with $\sqrt{2}a$ and $\sqrt{2}a/2$ GaN lattice constant. All the results as well as the neutral Mn-Mn air case are listed in Table III. We found that the total energy difference between ferro- and antiferromagnetic states are decreased in charged states, such as for $\sqrt{2}a/2$, ΔE_{AF} changes from 0.36 to 0.30 eV/Mn-pair, and for $\sqrt{2}a$ case, ΔE_{AF} changes from 0.30 to 0.22 eV/Mn-pair (see Table III). This result shows that charge compensation will decrease the tendency for ferromagnetism, as expected.

V. CONCLUSIONS

In summary, we have studied the Jahn-Teller distortion in GaAs:Mn and GaN:Mn in the cubic zinc blended structure. Our results show that a strong Jahn-Teller distortion should happen in uncompensated GaN:Mn at low concentrations where the Mn impurities are isolated. The lowering of the energy is due to the splitting of the t_{2d} states of the localized d electrons on the Mn $3d^4$ ion, leading to an energy gap. There are two possible symmetries C_{2v} and D_{2d}, with the latter having the lowest energy. In the presence of charge compensation, the Mn d states are filled, leading to filled shell spherically symmetric $3d^5$ ions and the Jahn-Teller effect disappears. These effects should be observable experimentally in cubic GaN:Mn. We also point out that the Jahn-Teller effect may occur in the wurtzite structure, based upon the results of other calculations[30,53] that found a partially occupied state at the Fermi level.

In contrast, in GaAs:Mn the Mn $3d$ states are primarily $3d^5$ with a hole in the GaAs valence band. This state is only weakly coupled to the distortions and the tendency for a Jahn-Teller distortion is a negligible effect. Although we have not done calculation on InAs:Mn, it is expected that the same conclusions hold for InAs and (InGa)As alloys.

In order to study the effects upon magnetism, we carried out calculations on Mn pairs. In agreement with other work, we find Mn-Mn interactions to lead to ferromagnetism in both GaAs and GaN, with larger interaction in GaN. The interaction between Mn-Mn pairs at realistic distances are sufficiently large that it dominates over the Jahn-Teller effect. The interactions between Mn atoms are not greatly affected by lattice relaxations and there is always a clear tendency for ferromagnetic alignment of Mn pairs. In realistic cases with charge compensation, ferromagnetism is still favored: even with 100% compensation the ferromagnetic interactions are reduced by only 20%. Finally, even though our calculations are for the cubic structure, the conclusions on magnetic interactions should carry over to the wurtzite structure since they do not depend upon detailed positions of the atoms and the ferromagnetic state persists whether or not there are distortions. Thus our results support the conclusion that GaN:Mn holds promise as a ferromagnetic semiconductor.

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