Ferromagnetism in GaN:Gd: A density functional theory study

Lei Liu[1,2], Peter Y. Yu[1,2], Zhixun Ma[1], and Samuel S. Mao[1]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA 94720

[2]Department of Physics, University of California, Berkeley, CA 94720

First principle calculations of the electronic structure and magnetic interaction of GaN:Gd have been performed within the Generalized Gradient Approximation (GGA) of the density functional theory (DFT) with the on-site Coulomb energy U taken into account (also referred to as GGA+U). The ferromagnetic *p-d* coupling is found to be over two orders of magnitude larger than the *s-d* exchange coupling. The experimental colossal magnetic moments and room temperature ferromagnetism in GaN:Gd reported recently are explained by the interaction of Gd 4*f* spins via *p-d* coupling involving holes introduced by intrinsic defects such as Ga vacancies.

75.50Pp, 71.20.Eh, 71.55.Eq, 71.70.-d

Due to their possible applications in spintronics, group III–V diluted magnetic semiconductors (DMSs) have captured much attention since ferromagnetism was reported in (Ga,Mn)As in 1996[1]. Since Mn introduces acceptors into GaAs when substituting for Ga in this ferromagnetic (FM) DMS systems free holes are believed to mediate the FM exchange between the magnetic dopants[2,3]. However, this seems not to apply to the recently discovered GaN:Gd system[4,5,6,7,8,9,10] which remains FM even at room-temperature. Teraguchi *et al.* [4] found that the Curie temperature (T_C) of their $Ga_{0.94}Gd_{0.06}N$ layer was > 400 K and is higher than that of both Gd metal (T_C =292.5 K)[11] and rocksalt-structure GdN (T_C =58 K)[12]. They proposed that ferromagnetism in $Ga_{0.94}Gd_{0.06}N$ was intrinsic and could be attributed to the Ruderman-Kittel-Kasuya-Yoshida (RKKY)-type interaction via the spin-polarized valence band of GaN[5]. Later, Dhar *et al.*[6] confirmed the room-temperature ferromagnetism of Gd-doped GaN with a Gd concentration range of 7×10^{15} to 2×10^{19} cm^{-3}. Furthermore, they found that the average magnetic moment of Gd in their GaN:Gd layers were extremely large, reaching values of 4000 μ_B, which is 500 times higher than the atomic Gd moment.[6] They have correlated this colossal magnetic moment of Gd in GaN to defects since in Gd-implanted and unannealed GaN layers (which were expected to contain a large amount of intrinsic defects) the magnetic moment per Gd atom became an order of magnitude larger than that of epitaxially grown layers doped with the same Gd concentration.[8]

So far the microscopic nature of ferromagnetism in the Gd doped GaN has remained controversial. Dhar *et al.*[6] pointed out that the FM coupling in the GaN:Gd system cannot be explained simply in terms of direct, double, or super-exchange between Gd atoms since the average Gd-Gd distance is too large. In addition, as all their samples

are highly resistive, they also ruled out free-carrier mediated RKKY-type of long range coupling. [6] Based on subsequent experiments, they concluded that defects have to play an important role in the ferromagnetism in GaN:Gd. The electronic and magnetic properties of GdGaN alloy have been studied by Dalpian *et al.* [13] using the General Potential Linearized Augmented Plane Wave (LAPW) method within the spin-polarized DFT and the Local Density Approximation (LDA). They found that FM phases can exist in n-type GaN:Gd samples originating from the coupling between the Gd *f* and the host *s* states. However, this model cannot explain the FM phase in insulating GaN:Gd nor the role for intrinsic defects in enhancing the magnetic moment of Gd in GaN. In addition, according to x-ray photoemission spectroscopy (XPS) observations,[14] the 4*f* states of Gd in compounds usually stay relatively far from the Fermi energy level so any *s*-*f* coupling of conduction electrons in GaN should be weak. Moreover, theoretical studies on semiconducting GdN[15] and metallic Gd[16] have both indicated that going beyond the standard LDA is desirable for calculating the electronic and magnetic behaviors of the 4*f* Gd systems. In this Letter we present a new first-principle calculation of the electronic and magnetic structure of GaN:Gd based on the GGA+U formalism. In particular, intrinsic defects such as vacancies are included explicitly in the model. We found that Ga vacancies can introduce localized holes which are strongly hybridized with the Gd 5*d* orbitals. This strong *p*-*d* coupling can explain both the huge magnetic moment of Gd ions and the high T_c of GaN:Gd. In addition to intrinsic vacancies we have also considered the effect of donors, such as oxygen substituting nitrogen, on the FM phases of GaN:Gd.

The electronic structures of GaN:Gd systems are calculated based on a spin-polarized DFT using the Full-potential Linearized Augmented Plane Wave (FLAPW)

method as implemented by the software Wien2K.[17] The GGA within the PBE (Perdew, Burke and Ernzerhof) scheme[18] is used to obtain the exchange-correlation potential. The LDA+U method[19,20] is employed to calculate the onsite Coulomb correlation for the Gd 4*f* electrons, where the Coulomb repulsion energy U and the exchange energy *J* are chosen to be 6.7 and 0.7 eV respectively[13,14]. For controlling the size of basis set for the wave functions, the value of $R_{MT}K_{MAX}$ (the product of the smallest muffin-tin radius and the largest reciprocal space vector in the plane wave expansion) is set to 8.0. Sampling of k-points in the Brillouin zone is varied until a convergence of better than 1 meV in total energy is obtained. All our model structures were optimized with the help of the projector-augmented-wave (PAW)[21] calculations which are found to approach the energy minimum of the LAPW results quite well.

In this study, both zincblende and wurtzite GaN structures doped with Gd are examined by supercell models where the Gd atoms are separated by three atom layers to simulate their long rang interaction in real crystals. For simplicity, only the calculated results of cubic supercells are presented, although the results for the hexagonal supercells are qualitatively similar. Two examples of supercells, with the unit cell formula of $GdGa_7N_8$, to model both zincblende and wurtzite GaN containing a Gd_{Ga} are shown in Fig.1. Since Gd_{Ga} is an isovalent impurity in GaN, GaN:Gd remains semiconducting. From the band structures of $GdGa_7N_8$ calculated in the FM configuration and plotted in Fig.2 (a) and (b), we find that the spin-up (majority spin) and spin-down (minority spin) branches of the Gd 4*f* orbitals are separated from the valance band maximum (VBM) and conduction band minimum (CBM) by about 5 eV. As a result, the coupling between the 4*f* orbitals and free carriers, whether n- or p-type, should be weak. Unlike other DMS

systems, Gd in GaN has both partly filled 5*d* shell and 4*f* shell. Since both 5*d* and 4*f* electrons can contribute to the magnetic moment of Gd system, it is important to clarify their roles in the ferromagnetism of GaN:Gd. In GaN matrix, the fivefold-degenerate 5*d* orbitals of Gd will be split into two e_g orbitals and three t_{2g} orbitals by the tetrahedral crystal field from the surrounding N anions. The calculated density-of-states (DOS) of the Gd 5*d* orbitals of both symmetries are plotted in Fig.2 (c). In both cases the DOS are significant only about 2.5 eV or more above the CBM. As the lowest conduction band of GaN is mainly s-like and has very little *d* character any *s*-*d* exchange coupling should be weak as long as the Gd local environment has T_d symmetry. In real wurtzite samples, defects and the hexagonal local symmetry may produce *s*-*d* coupling. This effect will be discussed later. In contrast to the conduction band states, the relatively flat Gd 5*d* orbitals with t_{2g} symmetry occur just around the *p*-like VBM of GaN. Since the Gd 5*d* t_{2g} levels have the same symmetry as the GaN VBM at zone center, the *p*-*d* hybridization between them should be very strong just as in the case of the Mn-doped GaAs. However, we found the energy difference ΔE_{FM-AFM} between FM and antiferromagnetic (AFM) configurations of our $GdGa_7N_8$ model structure to be essentially zero. We, therefore, conclude that GaN:Gd would be paramagnetic instead of ferromagnetic if there are no other defects in GaN:Gd in agreement with the experimental results.[8]

Although experimental results strongly suggest that defects are important for enhancing the magnetic moment of Gd ions, there has been no identification of these defects. The fact that strain is exerted on the GaN epilayer by the lattice mis-matched substrate and that the ion radii of Gd is much larger than that of the host Ga ion strongly suggests the existence of a high density of vacancies. In this study, we have considered

the effect of both N vacancies (V_N) and Ga vacancies (V_{Ga}) on ferromagnetism of GaN:Gd. As an example, we consider the model structure based on the supercell:$GdGa_7N_7$ which contains one V_N. Its band structure, calculated again in the FM configuration, is shown in Fig. 3. In this case, removal of one N atom introduces three conduction electrons to the system and causes the Fermi level to shift well above the VBM. Since the local symmetry now allows strong *s*-*d* coupling, the lowest conduction bands will contain significant *d* character. This can be seen from the DOS of the *d* states shown in Fig. 3(c). The main difference between these DOS and those depicted in Fig. 2(c) is the significant amount of DOS occurring at the Fermi level. For such Gd_{Ga}-V_N complex, the energy difference ΔE_{FM-AFM} equals 3.9 meV/Gd atom. This indicates that *s*-*d* exchange coupling is still rather weak and possibly AFM in nature. For $GdGa_7N_7$ supercell with wurtzite structure, the magnitude of ΔE_{FM-AFM} is even smaller being of -0.7 meV/Gd atom. Contrary to the conclusion of Dalpian and Wei, we believe that n-type carriers will not contribute to the colossal magnetic moments of Gd nor to the ferromagnetism observed in GaN:Gd. Such prediction is confirmed by the recent experimental observation that n-type zincblende GaN films exhibit a paramagnetic-like behaviors[10] rather than a ferromagnetic one.

As an alternative, we consider the FM configuration of the band structure based on the supercell: $GdGa_6N_8$ which contains a V_{Ga}. In this case each missing Ga atom contributes three holes to the sample. The resulting band structures and DOS of the *d* states are shown in Fig. 4. We notice that the *d* band DOS near the Fermi level shows noticeable difference between the spin-up and spin-down states. The calculated energy difference ΔE_{FM-AFM} is equal to -697.1 meV/Gd. Thus we found a strong FM *p*-*d*

exchange coupling between the *p*-like top GaN valence bands and Gd 5*d* orbitals. Compared with the magnitude of AFM *s*-*d* coupling in $GdGa_7N_7$, the FM *p*-*d* exchange in $GdGa_6N_8$ is almost 180 times stronger. The *p*-*d* coupling is so strong that the three unoccupied spin-down valence bands from GaN matrix are pushed above the VBM of the spin-up state. This is also true for Gd_{Ga}-V_{Ga} complex in the wurtzite structure, where the calculated ΔE_{FM-AFM} is -326.1 meV/Gd for the supercell unit of $GdGa_6N_8$ and -386.6 meV/Gd for the suprecell unit of $GdGa_{14}N_{16}$. Moreover, the calculated total magnetic moment per Gd atom for all the three models is 10 μ_B which is equal to the sum of the magnetic moments of the Gd *f* orbitals plus that of the holes introduced by the vacancies. This strong coupling persists even for model structures with multiple defects. For examples, for the case of the supercell:$GdGa_6N_6O_2$, where two nitrogen atoms are replaced by oxygen donors (with the result that two of the holes from the V_{Ga} are compensated by the electrons from the donor) we found that the total moment per Gd atom is reduced to 8 μ_B but the energy difference E_{FM-AFM} remains at a rather large value of -159.5 meV. This result suggests that the sample remains FM with a T_c higher than room temperature. When the effect of holes introduced by defects like vacancies are included, one can understand the experimental observation that intrinsic defects increase the magnetic moments of Gd ions in GaN:Gd. [8] The reported magnitude of the effective magnetic moment per Gd atom suggests the density of such holes can be orders of magnitude higher than that of the Gd atoms. That samples exhibiting colossal magnetic moments are found to be insulating can be explained by the fact that the high density of intrinsic defects in those samples also results in strong scattering and localization of any carriers introduced by the defects. We note that the samples ion-implanted with Gd

should be essentially amorphous and yet exhibit the largest magnetic moment. Finally, we suggest that the effect of temperature on the magnetic moment of Gd in GaN should be quite interesting. On one hand, thermal agitation will weaken the FM ordering. On the other hand, higher temperature will excite more mobile carriers which can enhance the FM interaction between the Gd ions and hence increase T_C . The competition of these two opposing effects may explain the reported temperature dependence of magnetization of GaN:Gd, which does not show significant decay above 400K! [4,6]

In conclusion, we found that the FM *p-d* exchange coupling in GaN:Gd (whether with zincblende or wurtzite structure) is over two orders of magnitude stronger than the AFM *s-d* exchange. Hence, holes are more effective than electrons in contributing to the observed colossal magnetic moment of Gd ions. Since each Gd atom replacing a Ga atom in GaN:Gd can supply at most 7 μ_B from its 4*f* electrons, most of the measured magnetic moment must come from holes present in the GaN host. Intrinsic defects, such as Ga vacancies, are effective sources of these holes.

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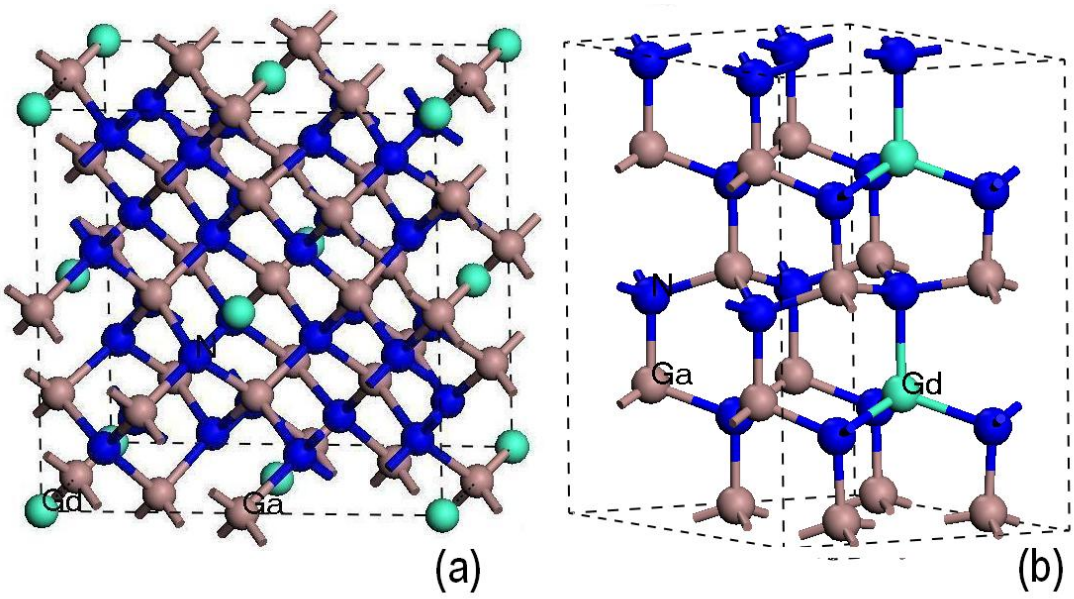

Fig. 1. $GdGa_7N_8$ supercells of Gd-doped GaN with the (a) zincblende and (b)wurtzite structures. The blue balls represent N atoms, the mauve balls represent Ga atoms while the turquoise balls represent Gd atoms.

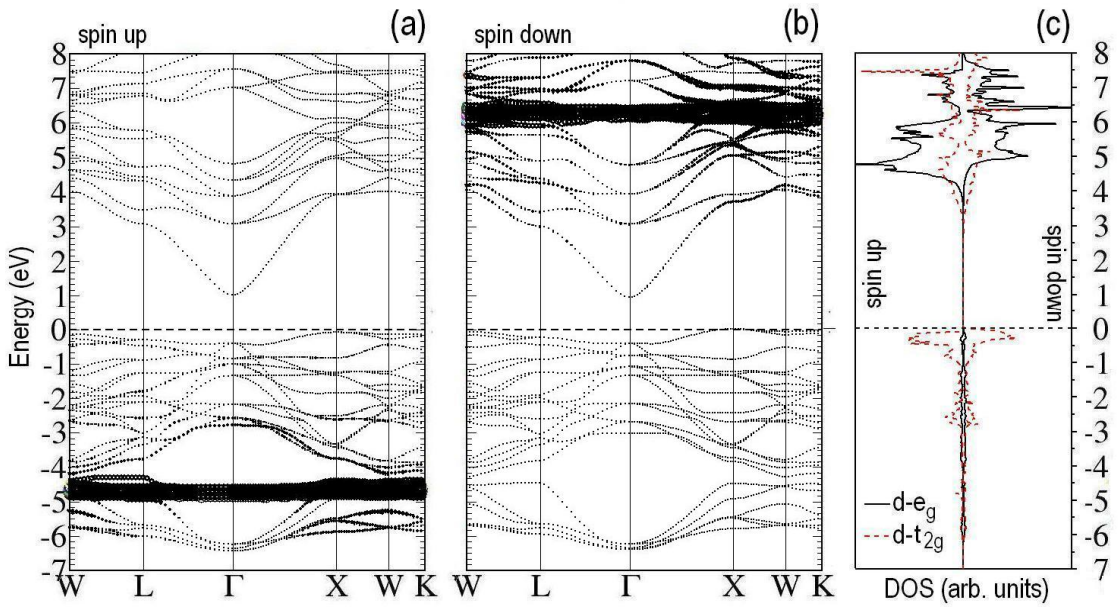

Fig. 2. Calculated band structures ((a) and (b)) and *d* orbital DOS (c) of the $GdGa_7N_8$ supercell in the FM configuration. The circle size of each state in the band structures has been chosen to be proportional to the strength of the Gd 4*f* orbitals (said to be band-character plotted in some literature). The energy of the VBM is taken to be zero.

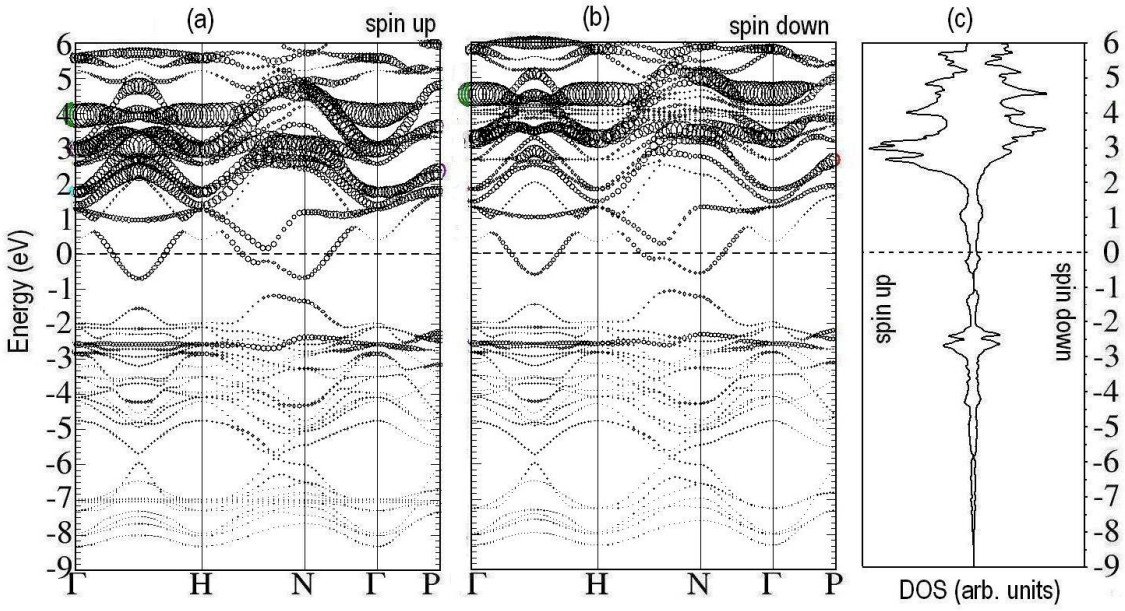

Fig. 3. Calculated band structure ((a) and (b)) and *d* orbital DOS (c) of $GdGa_7N_7$ supercell in the FM configuration. The Gd *d* orbitals are now band-character plotted in the band structures while the Fermi level is now taken to be zero.

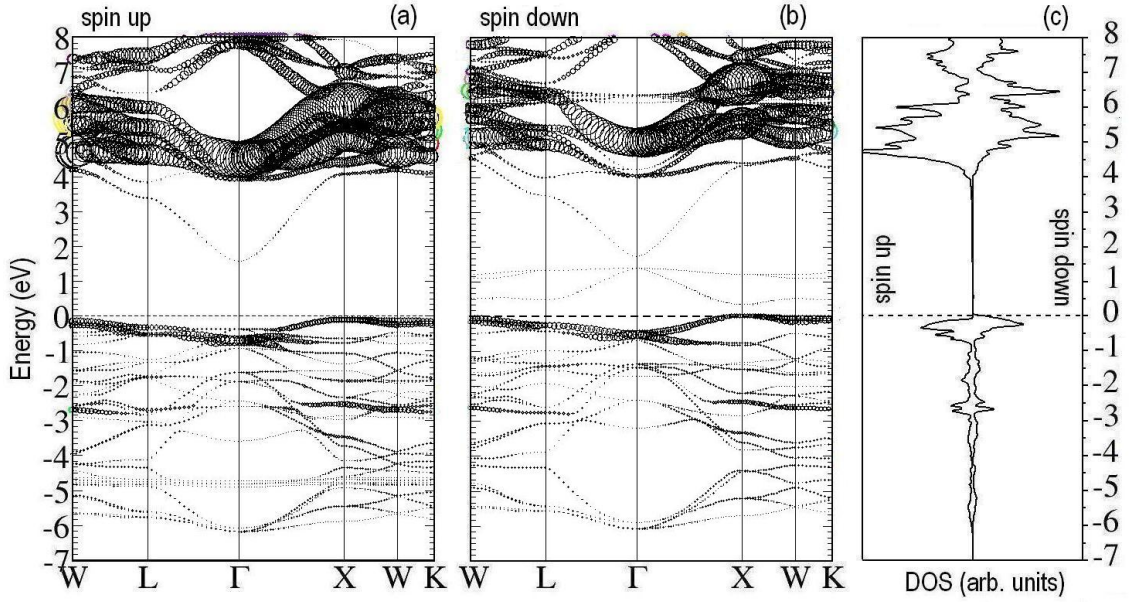

Fig. 4. Calculated band structures ((a) and (b)) and *d* orbital DOS (c) of $GdGa_6N_8$ in the FM configuration. The Gd *d* orbitals are again band-character plotted in the band structures. The Fermi level is again taken to be zero.

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