PHYSICAL REVIEW B **78**, 161201(R) (2008)

Intrinsic ferromagnetism due to cation vacancies in Gd-doped GaN: First-principles calculations

Y. Gohda* and Atsushi Oshiyama
Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan
and CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan
(Received 27 August 2008; published 14 October 2008)

We report total-energy electronic-structure calculations based on density-functional theory that clarify magnetism of Gd-doped GaN. We find that Ga vacancies with the magnetic moment of $3\mu_B$ formed upon Gd doping interact ferromagnetically with each other and thus cause gigantic magnetic moments per Gd atom. Our detailed analyses are indicative of intrinsic ferromagnetism due to cation vacancies rather than magnetic dopants in nitride semiconductors.

DOI: 10.1103/PhysRevB.78.161201 PACS number(s): 71.55.Eq, 61.72.jd, 75.50.Pp

Adding magnetic functionality to nonmagnetic semiconductors at room temperature is a principal target to realize emerging spintronics. Syntheses of diluted magnetic semiconductors (DMSs) in which magnetic impurities are doped in II-VI (Ref. 1) and lately III-V (Ref. 2) semiconductors have been pursued for this purpose. However, the coupling among magnetic impurities is occasionally antiferromagnetic (AFM) and even when it is ferromagnetic (FM), the Curie temperature is extremely low. For Mn-doped CdTe it is below 2 K,[3] and for the more successful case, Mn-doped GaAs, it is about 100 K at most.[2,4] The observed ferromagnetic behaviors are speculated to be due to Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions[5] since doped Mn induces holes in the valence bands.

Nitride semiconductors such as GaN and InN have emerged as new materials for blue light-emitting and laser diodes[6] and now prevailed as most important semiconductors in optoelectronics. Recently, ferromagnetic behaviors at well above room temperature have been reported for GaN,[7–12] offering a new stage for interactions among charge, spin, and light. A Curie temperature higher than 400 K has been indeed reported for gadolinium-doped GaN.[7] More surprisingly, the colossal magnetic moment of $4000\mu_B$ per Gd atom has been observed in epitaxial Gd-doped GaN.[9] These magnetic behaviors are quite different in quality from the previous II-VI and III-V DMSs so that the clarification of the microscopic origins for the ferromagnetic state in GaN is imperative.

The colossal magnetic moment may be correlated with intrinsic defects introduced upon Gd doping since Gd-implanted samples show magnetic moments even larger than $4000\mu_B$.[10] This speculation is partly substantiated by recent calculations based on density-functional theory (DFT) for a small $GdGa_7N_8$ periodic unit, in which a complex of Gd and a Ga vacancy (V_{Ga}) shows the magnetic moment of $10\mu_B$.[13] Indeed, Ga monovacancies, one of the common intrinsic defects in GaN, have recently been found to exhibit spontaneous spin polarization having the magnetic moment of $3\mu_B$ in the neutral charge state.[14–17] The spin polarization around the vacancy itself is surprising since neighboring atoms usually form rebonds, and net spin becomes minimum in covalent semiconductors. Further, neither the ground-state spin configuration of Ga vacancies with a Gd atom nor the characteristics of interactions among V_{Ga} and Gd spins has not been clarified yet.

In this work, we report total-energy electronic-structure calculations based on DFT for a variety of spin and geometrical configurations for a Gd atom and Ga vacancies in GaN. We have found that the Ga vacancies interact with each other ferromagnetically with the presence of the Gd atom and that the magnetic moment increases linearly with increasing the number of Ga vacancies. We have obtained the magnetic moment of $\mu=220\mu_B$ for 71 Ga vacancies per one Gd atom. We thus argue that the colossal magnetic moment observed is attributed to the ferromagnetic interactions among cation-vacancy spins in GaN. The results also indicate an unprecedented magnetism due to atom vacancies in covalent semiconductors.

First-principles total-energy calculations have been performed on the basis of DFT (Refs. 18 and 19) within the generalized gradient approximation (GGA) (Ref. 20) using the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE).[21] The core electrons are treated by the projector-augmented wave method[22] as implemented in the VASP code.[23–25] Thirteen electrons of Ga including closed-shell $3d$ states are calculated explicitly as valence electrons as well as 18 electrons in the Gd $5s$, $5p$, $4f$, $5d$, and $6s$ states. For Gd $4f$ electrons, the DFT+U method[26] is adopted to incorporate on-site Coulomb repulsion among localized f electrons sufficiently, where the Hubbard U (6.7 eV) and the exchange J (0.7 eV) have been obtained in the local spin density approximation and describe spectroscopic and magnetic experiments satisfactorily.[27] Electronic wave functions are expanded using the plane-wave basis set with a cutoff energy of 400 eV. The wurzite atomic structure of the $Gd_xGa_{1-x}N$ system is fully optimized using the $2\sqrt{3}\times2\sqrt{3}\times2$ supercell containing 96 sites and the $6\times6\times4$ supercell with 576 sites, where each supercell contains one Gd atom (corresponding to $x=0.02$ and 0.003, respectively) unless otherwise stated. The electronic-state sampling is made using $4\times4\times4$ and $2\times2\times2$ grids of $\boldsymbol{k}$ points over the first Brillouin zone for the 96-site and 576-site supercells, respectively.

We begin with two Ga vacancies around a Gd atom. We have first explored possible spin configurations of the Gd and two V_{Ga}, and found that the ferromagnetic configuration is most stable having energy differences of 10–50 meV compared with the configurations containing antiferromagnetic arrangements. Figure 1(a) shows optimized atomic structure of the ferromagnetic configuration in the 96-site wurzite su-

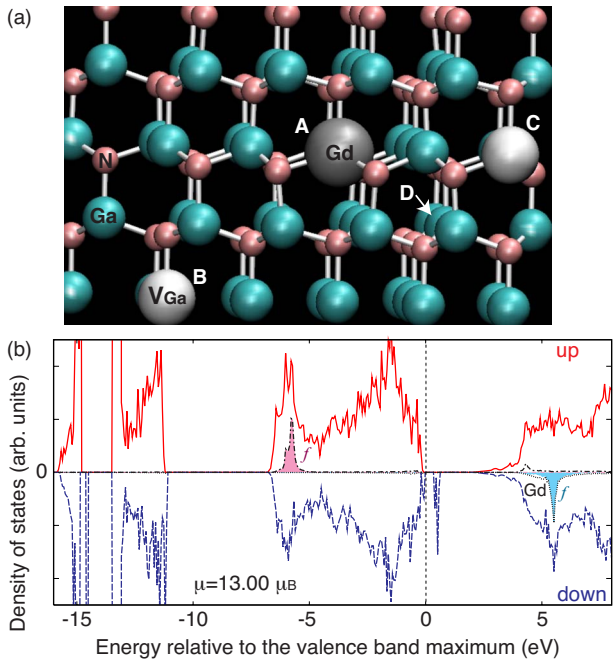

FIG. 1. (Color online) (a) Optimized atomic structure of GaN:Gd with two Ga vacancies using the 96-site wurtzite supercell. (b) Density of states for the most stable electronic structure of the atomic configuration shown in (a) which is ferromagnetic. The local density of states for Gd and its f component are also shown. Majority and minority spins are denoted as "up" and "down," respectively.

percell. Both Gd and V_{Ga} induce outward breathing relaxation of the first-neighbor nitrogen atoms. This relaxation pattern is common to all the spin configurations and is in contrast to Jahn-Teller relaxation commonly observed in covalent semiconductors. This unusual relaxation pattern is found to be a consequence of small atomic radius of nitrogen in nitride semiconductors.[17] The density of states for the ferromagnetic configuration is shown in Fig. 1(b). The local density of states indicates that the Gd f shell is half filled by electrons with the majority spin. For the case without V_{Ga}, the magnetic moment comes only from the half-filled Gd $4f$ electrons resulting in $\mu=7.00\mu_B$. It should be noted that the Gd $5d$ electron in GaN:Gd is involved in the chemical bondings with N and thus does not contribute to the net magnetic moment, resulting in smaller magnetization of Gd in GaN than in metallic hcp Gd. Since all the Gd valence electrons except for the localized $4f$ electrons contribute to the chemical bondings with the valence of three, the defect-free GaN:Gd remains semiconducting.

The two V_{Ga} induce defect levels which are located in the lower part of the band gap. In the neutral charge state, the six levels in the gap with the minority spin [Fig. 1(b)] are unoccupied whereas the counterparts with the majority spin are resonant in the valence band.[28] Consequently, the two V_{Ga} generate six holes in the band gap and then contribute to the magnetic moment of $6\mu_B$. Spins induced by these two V_{Ga} interact with the Gd spin ferromagnetically and the total magnetic moment becomes $\mu=13\mu_B$ in GaN:Gd with two Ga vacancies.

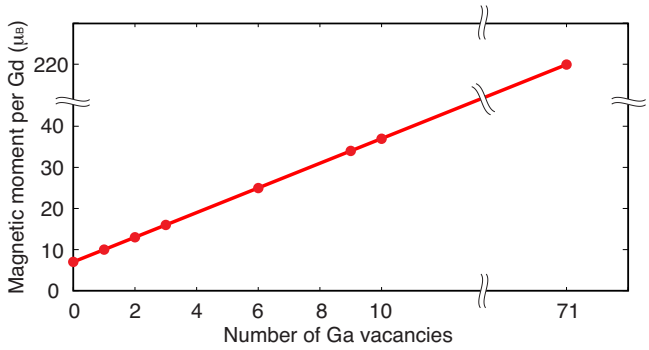

FIG. 2. (Color online) Magnetic moment per Gd atom with respect to the number of V_{Ga}.

We next increase the number of V_{Ga} around the Gd atom and calculate the magnetic moment μ as shown in Fig. 2. For all the cases, the ferromagnetic spin polarization is obtained. As the number of V_{Ga} increases, the magnetic moment increases linearly by $3\mu_B$ per V_{Ga} due to three holes arising from the vacancy with the minority spin. We have found that the magnetic moment reaches $220\mu_B$ per Gd atom with 71 V_{Ga}. Therefore, the huge magnetic moment of $4000\mu_B$ in $Gd_xGa_{1-x}N$ reported in experiments[9] is highly attributable to the magnetism due to Ga vacancies.

To verify that the ferromagnetic configuration is stable when the number of the Ga vacancies is large enough, we compare total energies of various spin configurations of GaN:Gd with ten Ga vacancies. Figure 3 shows calculated total energies for seven spin configurations, each of which has a particular magnetic moment. The ferromagnetic configuration with $\mu=37\mu_B$ is most stable, whereas an antiferromagnetic configuration among ten Ga vacancies with $\mu=7\mu_B$ is the least. The configuration where Gd ($7\mu_B$) interacts antiferromagnetically with ferromagnetically ordered Ga vacancies ($-30\mu_B$) is also less stable than the ferromagnetic configuration by 0.09 eV. We have also examined the energy difference without the Gd atom. We have found that the ferromagnetic configuration ($\mu=30\mu_B$) is lower in total energy than the antiferromagnetic configuration ($\mu=0\mu_B$) by 1.12 eV, which is again indicative of intrinsic ferromagnetism due to Ga vacancies.

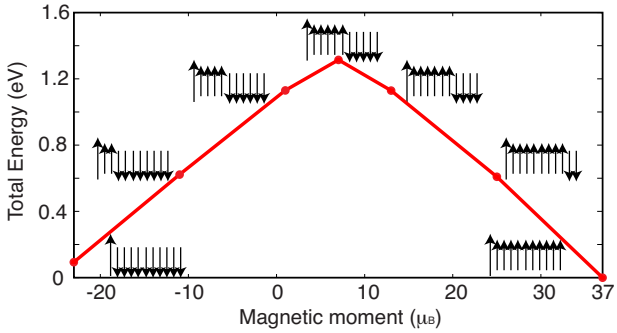

FIG. 3. (Color online) Total energies of various spin configurations for ten V_{Ga} in $Gd_{0.02}Ga_{0.98}N$ as a function of the magnetic moment per Gd atom. Energies are relative to that of the most stable ferromagnetic configuration. The long arrows represent the spin of Gd schematically, whereas the short ones are for Ga vacancies.

TABLE I. Total energy E of two Gd atoms and two V_{Ga} in $Gd_{0.04}Ga_{0.96}N$ for each spin configuration together with the corresponding magnetic moment μ per Gd atom. Energies are relative to that of the most stable ferromagnetic configuration. The distance between two Gd atoms is 8.30 Å.

Spin configuration	E (meV)	μ (μ_B)
$Gd^{\uparrow}Gd^{\uparrow}V_{Ga}^{\uparrow}V_{Ga}^{\uparrow}$	0	10.00
$Gd^{\uparrow}Gd^{\uparrow}V_{Ga}^{\uparrow}V_{Ga}^{\downarrow}$	272	7.00
$Gd^{\uparrow}Gd^{\downarrow}V_{Ga}^{\uparrow}V_{Ga}^{\uparrow}$	41	3.00
$Gd^{\uparrow}Gd^{\downarrow}V_{Ga}^{\uparrow}V_{Ga}^{\downarrow}$	233	0.00

In order to examine the magnetic interaction between Gd atoms with the presence of Ga vacancies, we have considered the case where two Gd atoms interacting with each other with the presence of two Ga vacancies. In Table I, we show the total energies of several spin configurations and the corresponding magnetic moment μ per Gd atom. The distances between Gd and V_{Ga} examined here are 6.43 and 8.30 Å. Our calculated results clearly demonstrate that Gd atoms interact ferromagnetically with the presence of Ga vacancies nearby.

To obtain further insights as to the stable spin configurations, we have examined two-body interactions between V_{Ga}-V_{Ga}, Gd-Gd, and Gd-V_{Ga} pairs in various geometrical arrangements. Table II shows the energy difference between AFM and FM configurations $\Delta E = E_{AFM} - E_{FM}$ for the various pairing geometries along with the distance d between the two spin sites and the calculated magnetic moment μ. The positions of the spin sites A, B, C, and D are depicted in Fig. 1(a). Here all the cation sites except for the spin sites we consider are occupied by Ga atoms. For the "V_{Ga}@A-V_{Ga}@$A_{\perp}$" configuration, we used a 192-site supercell, where two 96-site cells stack in the c direction, while the stacking direction is parallel to the (0001) plane for the "V_{Ga}@A-V_{Ga}@$A_{\parallel}$" configuration. As for the "V_{Ga}-V_{Ga} (zinc-blende)" configuration, we used a 128-site zinc-blende supercell, where the cubic 64-site cell is doubled.

TABLE II. Energy difference between AFM and FM states $\Delta E = E_{AFM} - E_{FM}$ for various spin pairs together with the distance between the two spin sites d and the corresponding magnetic moment μ. The positions of the cation sites A, B, C, and D are indicated in Fig. 1(a). Note that configurations of the AB and the BC sites are equivalent considering the periodicity of the supercell. For the V_{Ga}@A-V_{Ga}@$A_{\perp}$ and V_{Ga}@A-V_{Ga}@$A_{\parallel}$ configurations, we used 192-site wurtzite supercells, while a 128-site zinc-blende supercell is used for the V_{Ga}-V_{Ga} (zinc-blende) configuration.

Site arrangement	d (Å)	ΔE (meV)	μ_{FM} (μ_B)	μ_{AFM} (μ_B)
V_{Ga}@A-V_{Ga}@B	8.30	9	6.00	0.00
V_{Ga}@A-V_{Ga}@C	6.43	−18	6.00	0.00
V_{Ga}@A-V_{Ga}@D	4.53	19	6.00	0.00
V_{Ga}@A-V_{Ga}@$A_{\perp}$	10.48	2	6.00	0.00
V_{Ga}@A-V_{Ga}@$A_{\parallel}$	11.14	1	6.00	0.00
V_{Ga}-V_{Ga} (zinc-blende)	9.09	−33	6.00	0.00
Gd@A-Gd@B	8.30	0.0	14.00	0.00
Gd@A-V_{Ga}@B	8.30	1	10.00	4.00
Gd@A-V_{Ga}@C	6.43	38	10.00	4.00
Gd@A-V_{Ga}@D	4.53	1	10.00	4.00

As for V_{Ga}-V_{Ga} interaction, the ferromagnetic coupling is found to be energetically favorable in most cases for the wurtzite structure, although the spatial arrangement of the two spin sites certainly affects the coupling. The total-energy difference ΔE is of the order of 10 meV when the distance d is less than 10 Å, whereas it decreases and essentially vanishes for $d > 10$ Å. We have also found that the antiferromagnetic coupling is favorable in some arrangements: the arrangement of the V_{Ga}@A-V_{Ga}@C in a plane perpendicular to the c axis in the wurzite structure and also the arrangement in the zinc-blende structure. The latter is consistent with previous calculations,[16] in which two V_{Ga} show antiferromagnetic coupling in zinc-blende GaN giving the energy difference of $\Delta E = -27$ meV within the GGA using the same geometry with ours. Our results thus infer that the topology of the bond network is decisive in occurrence of magnetism in GaN, which is in accord with the experimental observation of superparamagnetism rather than ferromagnetism in zinc-blende Gd-doped GaN.[12]

On the other hand, spin interaction between two Gd atoms is negligibly small. Note that cases with short separations are not considered here because it has been concluded experimentally that Gd atoms distribute more or less uniformly without clusterization.[8,9] We have not obtained sizable energy difference between ferromagnetic and antiferromagnetic couplings between two Gd atoms as in Table II. This is a consequence that the electronic state responsible for the Gd spin is the $4f$ state localized at the atomic site. It is noteworthy that the coupling becomes ferromagnetic with the presence of V_{Ga} nearby (Table I). In addition, Gd and V_{Ga} always couple ferromagnetically as far as we have explored, although the anisotropy of the wurtzite structure strongly affects the Gd-V_{Ga} interaction.

We are now in a position to discuss the observed colossal magnetic moment: Gd incorporation is likely to cause Ga vacancies; formation of defect complexes of the Gd atom and the Ga vacancies is energetically favorable; this is indeed confirmed by our calculations showing that the binding energy of Gd-V_{Ga} is ~0.3 eV; then the coupling between Gd and V_{Ga} is ferromagnetic as shown in Table II; in this situation, the coupling among V_{Ga} is also ferromagnetic as discussed above.

The present DFT+U calculations have clarified occurrence of ferromagnetism due to Ga vacancies in wurtzite GaN. The carrier mediated mechanism such as RKKY or Zener-type interaction which has been speculated to be the mechanism of ferromagnetism of Mn-doped GaAs and InAs (Ref. 5) is irrelevant to the present ferromagnetic state because no free carriers exist. Double exchange mechanism with multiple orbitals is also unlikely. We provisionally conclude that the wave functions of the defect states due to V_{Ga} exhibiting characteristic extension according to the bond network in the wurtzite structure, especially via nitrogen sites, result in ferromagnetic superexchangelike couplings.

In conclusion, we have performed first-principles calculations on the spin polarization of Ga vacancies in Gd-doped GaN focusing on the interaction among Ga vacancies and the Gd atom. We have found that the ferromagnetic configuration among spins of Ga vacancies and the Gd atom is energetically most stable and that the magnetic moment increases monotonically with the increasing number of Ga vacancies. The present results are indicative of intrinsic ferromagnetism due to cation vacancies in nitride semiconductors.

Parts of the numerical calculations were performed at RCCS-NINS, Okazaki, at ISSP, The University of Tokyo, and at the Cyberscience Center, Tohoku University. This work has been partly supported by the Grant-in-Aid for Scientific Research in Priority Areas through Contracts No. 17064002 and No. 18069001 from MEXT, Japan.

*Present address: Department of Physics, The University of Tokyo, Tokyo 113-0033, Japan; gohda@phys.s.u-tokyo.ac.jp

[1] For a review, J. K. Furdyna and J. Kossut, in *Diluted Magnetic Semiconductors*, Semiconductor and Semimetals, Vol. 25 (Academic, New York, 1988).

[2] For a review, H. Ohno, Science **281**, 951 (1998).

[3] A. Haury, A. Wasiela, A. Arnoult, J. Cibert, S. Tatarenko, T. Dietl, and Y. M. d'Aubigne, Phys. Rev. Lett. **79**, 511 (1997).

[4] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).

[5] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).

[6] For a review, S. Nakamura, Science **281**, 956 (1998).

[7] N. Teraguchi, A. Suzuki, Y. Nanishi, Y. K. Zhou, M. Hashimoto, and H. Asahi, Solid State Commun. **122**, 651 (2002).

[8] H. Asahi, Y. K. Zhou, M. Hashimoto, M. S. Kim, X. J. Li, S. Emura, and S. Hasegawa, J. Phys.: Condens. Matter **16**, S5555 (2004).

[9] S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, Phys. Rev. Lett. **94**, 037205 (2005).

[10] S. Dhar, T. Kammermeier, A. Ney, L. Pérez, K. H. Ploog, A. Melnikov, and A. D. Wieck, Appl. Phys. Lett. **89**, 062503 (2006).

[11] A. Ney, T. Kammermeier, E. Manuel, V. Ney, S. Dhar, K. H. Ploog, F. Wilhelm, and A. Rogalev, Appl. Phys. Lett. **90**, 252515 (2007).

[12] F. Y. Lo, A. Melnikov, D. Reuter, A. D. Wieck, V. Ney, T. Kammermeier, A. Ney, J. Schörmann, S. Potthast, D. J. As, and K. Lischka, Appl. Phys. Lett. **90**, 262505 (2007).

[13] L. Liu, P. Y. Yu, Z. Ma, and S. S. Mao, Phys. Rev. Lett. **100**, 127203 (2008).

[14] P. Mahadevan and S. Mahalakshmi, Phys. Rev. B **73**, 153201 (2006).

[15] P. Larson and S. Satpathy, Phys. Rev. B **76**, 245205 (2007).

[16] P. Dev, Y. Xue, and P. Zhang, Phys. Rev. Lett. **100**, 117204 (2008).

[17] The high spin state with the magnetic moment of $3\mu_B$ is found to be energetically most stable among possible spin configurations for V_{Ga} in GaN: Y. Gohda and A. Oshiyama (unpublished).

[18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[19] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[20] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[23] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[24] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[25] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[26] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[27] B. N. Harmon, V. P. Antropov, A. I. Liechtenstein, I. V. Solovyev, and V. I. Anisimov, J. Phys. Chem. Solids **56**, 1521 (1995), and references therein.

[28] Our level structure for two V_{Ga} is an extension to a spin-polarized defect-complex case of the level structure for single spin-unpolarized V_{Ga} obtained in the past: S. Limpijumnong and C. G. Van de Walle, Phys. Rev. B **69**, 035207 (2004), and references therein.