PHYSICAL REVIEW B **86**, 180401(R) (2012)

# Superparamagnetism in Gd-doped GaN induced by Ga-vacancy clustering

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(Received 19 March 2012; published 2 November 2012)

On the basis of the energetics and magnetic exchange interactions obtained from large-scale first-principles electronic structure calculations, a gallium-vacancy clustering model is proposed for the origin of colossal magnetic moments and high-temperature magnetism in gadolinium-doped gallium nitride. Monte Carlo simulations of the growth coupled to simulations of the magnetic moments show that the clustered geometry of vacancies plays a crucial role in establishing the existence of two distinct temperature regimes, observed experimentally and corresponding respectively to alignment of moments only within each cluster at high temperatures and globally at low temperatures.

DOI: 10.1103/PhysRevB.86.180401 PACS number(s): 75.50.Pp, 31.15.E−, 75.30.Hx

The decades-old search for above-room-temperature dilute ferromagnetic semiconductors (DMS) is motivated by their potential in spintronic applications. Among the many proposed DMS material combinations, Gd-doped GaN[1,2] is one of the most puzzling and controversial. In contrast with most transition-metal-doped magnetic semiconductors, which require doping of the order of a few percent of the magnetic dopant, Gd-doped GaN was reported to maintain magnetization above room temperature even for extremely dilute concentrations of parts per million of the dopant. Furthermore the reported magnetic moments were termed "colossal": they are of order 4000 $\mu_B$ per Gd for concentrations of order $10^{15}$ cm$^{-3}$ Ref. 2.

It soon became clear that this magnetism finds its origins in defects. Evidence for this arises from the fact that implantation as opposed to incorporation during growth leads to an enhancement of these magnetic phenomena, while annealing reduces them.[3] Furthermore, x-ray magnetic circular dichroism (XMCD) studies revealed that the Gd magnetic moments (7 $\mu_B$ per $Gd^{3+}$) did not follow the overall ferromagnetic hysteresis but behaved paramagnetically.[4] Thus the Gd-doped GaN magnetism appears to be part of a more general type of defect-induced possibly $d^0$ magnetism,[5] as observed in various other systems (e.g., ZnO, $Hf_2O$[6,7]).

Nonetheless the nature of the responsible defects has remained elusive. An early model by Dalpian and Wei[8] based on conduction band splitting due to $sf$ coupling and $n$-type doping via substitutional oxygen was refuted by Mitra *et al.*[9] Based on first-principles computational studies, two types of native defects have been proposed to be responsible for the magnetism: N or O interstitials[9] and gallium vacancies ($V_{Ga}$).[5,10,11] Currently it is still unclear which kind of defects are finally responsible for the unusual magnetism in GaN:Gd. A positron annihilation study[12] found no correlation between Ga vacancies and ferromagnetism but a weak correlation with O, which possibly supports the interstitial O model. Further evidence against the vacancy model is the fact that Ga vacancies are among the energetically most costly native defects to form in GaN.[13] In addition, they only carry a maximum magnetic moment of 3 $\mu_B$ in their neutral charge state, which is only stable for Fermi levels near the valence band maximum, that is, in p-type GaN, whereas GaN:Gd is found to be mostly semi-insulating, suggesting a midgap Fermi level.

On the other hand, a systematic study of the exchange interactions among interstitials, vacancies, and Gd, which could provide crucial insight on the observed magnetic phenomena such as high Curie temperatures, is still missing. As part of this study, we investigated by first-principles theory the magnetic interaction between O and N interstitials and found both ferro- and antiferromagnetic coupling that are strictly short range. From these results we expect no long-range ferromagnetic ordering, which excludes interstitials as the main origin of the ferromagnetism in GaN:Gd.[14]

In this paper we thus revisit the vacancy model but make an attempt to overcome the objections stated earlier. We believe that the key to explaining the occurrence of a large concentration of vacancies lies in the inhomogeneous nanostructure. While a model of homogeneously distributed individual vacancies is indeed thermodynamically unfavorable, clustering of vacancies during growth will be shown to occur naturally within a plausible growth model. Second, once vacancies or voids occur as extended defects, it is clear that they can locally pin the Fermi level and thus keep the vacancies in the (maximum magnetic moment carrying) neutral charge state. This overcomes the second objection. The role of the Gd in this whole process is then simply of perturbing the crystal growth.

Based on large-scale *ab initio* calculations we extract parameters for simplified models of the growth and the temperature dependency of the magnetic properties. Inserting these into a Monte Carlo growth simulation, we find that *clustering of vacancies* is preferential during growth. Using subsequent Monte Carlo simulations of the magnetic moments using our calculated exchange interations we find that these models possess magnetic properties that agree closely with the experiments. In particular, they can explain the observed existence of two distinct temperature regimes, which we find to correspond to global (at low $T$) versus only locally ordered magnetic moments (at higher $T$).

 

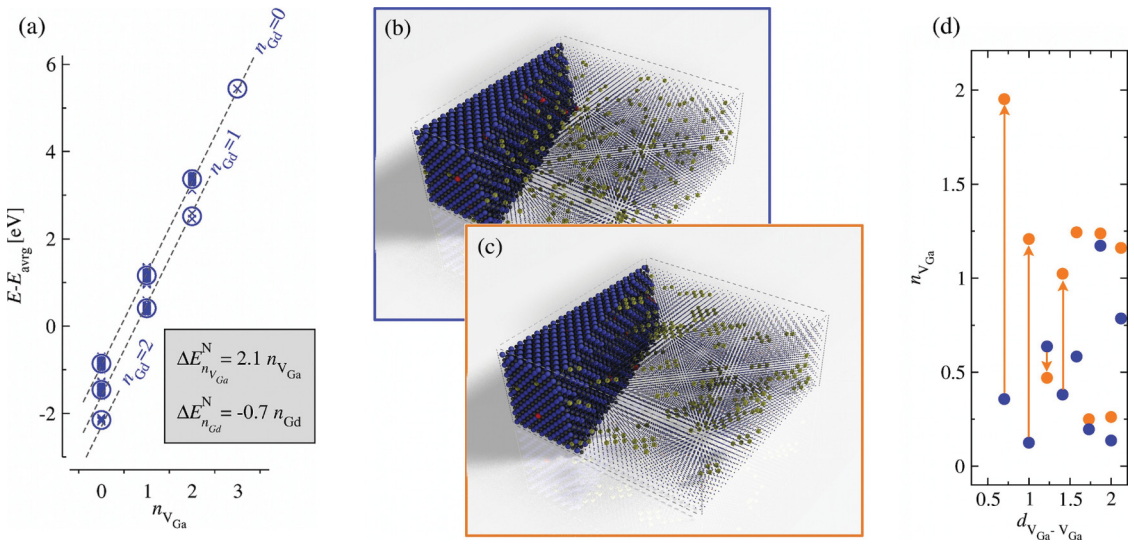


FIG. 1. (Color online) (a) Energy contribution $E$ per N site in $Ga_{208}N_{256}Gd_{16}$ as obtained from *ab initio* calculations relative to the average energy contribution $E_{avrg}$ among N atoms as a function of the number of nearest neighboring $V_{Ga}$'s and Gd atoms ($n_{V_{Ga}}$ and $n_{Gd}$). The inset specifies the parameter which give the functional dependency shown as dashed lines. Panels (b) and (c) illustrate a real space representation of 15 layers of zinc-blende GaN:Gd with overall 24 000 Gd (red [gray]), Ga (blue [dark gray]), $V_{Ga}$ (yellow [light gray]), and N (not shown) sites and a concentration of 1% Gd and 3% $V_{Ga}$ on the Ga lattice. In the right part of the figures exclusively $V_{Ga}$ are illustrated. In panel (b) random growth (RGr) is assumed, and in panel (c) the atom-by-atom kinetic Monte Carlo growth model (kMCG) is applied using a temperature of 600 K and 800 steps for each movable atom on the incomplete surface (for further details see text). Panel (d) depicts the enhanced clustering of $V_{Ga}$'s by considering the average number of neighboring $V_{Ga}$ at a given distance, which is observed during the kMCG (orange [light gray]) in contrast to the RGr (blue [dark gray]). Arrows indicate the impact of the kMCG for the shorter distances, which come along with magnetic coupling.

For the first-principles density functional calculations we use the all-electron full-potential method KKRnano,[15] which is based on the Korringa-Kohn-Rostoker (KKR) Green's function method. An important functionality for our work is that within this method the pairwise magnetic exchange coupling parameters $J_{ij}$ between sites of local magnetic moments $i$ and $j$ entering a Heisenberg model can be calculated directly by means of the Liechtenstein formula.[16] The calculations are performed in the LSDA + U (local spin density approximation with Hubbard-U corrections) method.[17]

In the studied supercells we obtain a reliable statistical model of the magnetic moment distributions. We find the following patterns of the spin polarizations: (1) Gd carries the expected spin of 7 $\mu_B$, (2) N atoms near vacancies carry different magnetic moments depending on how many vacancies they are a close neighbor to: 0.0, 0.5, 1.2, and 1.8 $\mu_B$ for the number of adjacent vacancies, $n_{V_{Ga}} = 0,1,2,3$. Since no significant spin polarization is present on N atoms without adjacent vacancies ($n_{V_{Ga}} = 0$), we find that magnetic interactions between them are negligible small. While the individual magnetic coupling constants $J_{ij}$ show significant fluctuations, we find that the $J_{ij}$'s averaged over all defect configurations have clear trends.

The calculations show that the $J_{ij}^{N-N}$ of two N atoms are only important, when they are located at neighboring sites. Here two different $J_{ij}^{N-N}$'s occur: One between N-N neighbors belonging to the same vacancy, $J_{ij}^{N-N} = 7.5$ meV, and one for N-N neighbors adjacent to two different vacancies, $J_{ij}^{N-N} = 2.3$ meV, thus mediating the coupling between vacancies. Moreover N atoms interact with neighboring Gd atoms by $J_{ij}^{Gd-N} = 4.5$ meV. The parallel spin alignment of N atoms around vacancy complexes is further stabilized by the interaction between N atoms and the small moment on the vacant sites by $J_{ij}^{N-V_{Ga}} = 2.1$ meV.[18] Longer ranged interactions as well as Gd-Gd interactions are negligible.

Next, we analyze the onset of the macroscopic magnetization, that is, the percolation limit. While for substitutional impurities with nearest neighbor interaction the percolation threshhold is 20%,[19] for Ga vacancies we obtain $c_V = 4.8\%$, a value which is strongly reduced since the interaction is mediated by the nearest neighbor N atoms. In other words, to find a coupled magnetic state satisfying the percolation limit we would need at least a 4.8% vacancy concentration, which seems implausible given the high energy of formation of vacancies in bulk. However, the formation of large magnetic $V_{Ga}$ clusters in the concentration range below 4.8% is possible if the migration barrier is not too high.

Since the migration barriers at surfaces are much lower than in bulk, one might expect the formation of $V_{Ga}$ clusters during the deposition process, which we simulate by a kinetic Monte Carlo growth model (kMCG). We consider atom-by-atom layerwise growth on a GaN substrate with fixed concentrations of Gd and $V_{Ga}$ per layer of 1% Gd and 3% $V_{Ga}$. An atom arrives on a random site and is allowed to hop only via vacant neighboring sites, where exchange of two atoms is forbidden due to the large energy barriers. The energies of initial and final local structures before and after hopping are calculated based on our *ab initio* results and are used in a kinetic Monte Carlo approach.[17]

Compared to the random growth (RGr) model the kinetic Monte Carlo growth model (kMCG) shows a clear segregation behavior in relatively vacancy-poor and vacancy-rich regions, that is, the formation of vacancy clusters. Figure 1(d) shows that the average number of neighboring vacancies increase for short distances by a factor of 4, when using on average $3.2 \times 10^5$ Monte Carlo steps per atom. The origin for this effect is simple: During the hopping, Ga atoms prefer a Ga-rich region without vacancies, leaving behind vacancy-rich regions. An important second question regards the role of Gd, where two counteracting effects are occuring: Gd prefers vacancy-rich regions while Ga clearly prefers Gd atoms on neighboring sites. At the present doping concentration, the second contribution is decisive and we find that Gd atoms are preferentially completely surrounded by Ga atoms and thereby decoupled from the vacancy clusters.

The growth analysis within this kMCG model leads to typical vacancy clusters combining on the order of 50 spin-polarized N sites to one complex. Since our kMCG model assumes a fixed concentration of 3% $V_{\mathrm{Ga}}$, it does not explain the occurrence of vacancies *per se* but establishes their tendency to cluster. Our results therefore suggest the following scenario: Gd strongly perturbs the growth of GaN crystals. This may be in part due to its large size and one way to compensate the large tensile strain induced by Gd would be to incorporate vacancies in the growth. Our simulations show that such vacancies will have a tendency to cluster under quite plausible rules. It suggests that large internal surfaces of voids occur in GaN:Gd with N dangling bonds, which can carry a sizable magnetic moment.

Next, we studied the thermal magnetic behavior of such clusters by setting up a model, which is based on the following assumptions: First, all N atoms adjacent to at least one vacancy are uniformly spin polarized with 0.5 $\mu_{\mathrm{B}}$. Second, the $J_{ij}^{\mathrm{N-N}}$ and $J_{ij}^{\mathrm{N-}V_{\mathrm{Ga}}}$ are all chosen to be equal to the average ones as obtained from the *ab initio* calculations and introduced above, while the weaker interactions from N to Gd as well as Gd to Gd are neglected for the sake of simplicity.

Our Monte Carlo studies on the magnetic fluctuations within the Heisenberg model show that the magnetic ordering is crucially different for clustered (kMCG) and randomly grown (RGr) samples. Figure 2(a) reveals that the FC magnetization curve can be conceptually split into low- and high-temperature regimes. In the former the magnetization of kMCG appears to be more resistant to temperature fluctuations by a factor of 2 than the magnetization of RGr. Further for RGr the magnetization of the second phase is hardly distinguishable from the background fluctuations. This picture changes for kMCG: Here, a significant magnetization is observed up to about 100 K, which shows a clearly reduced decay with temperature.

The low-temperature phase represents the case where a strong correlation of the spins of all clusters[20] is present due to the initial FC configuration, which is maintained by the magnetic coupling. The inset of Fig. 2(a) clearly reveals that this phase does not exist for an initial ZFC configuration, where the simulation is started from a random distribution of spins. In the high-temperature phase this strong correlation of magnetic moments for the global sample is lost due to rotations

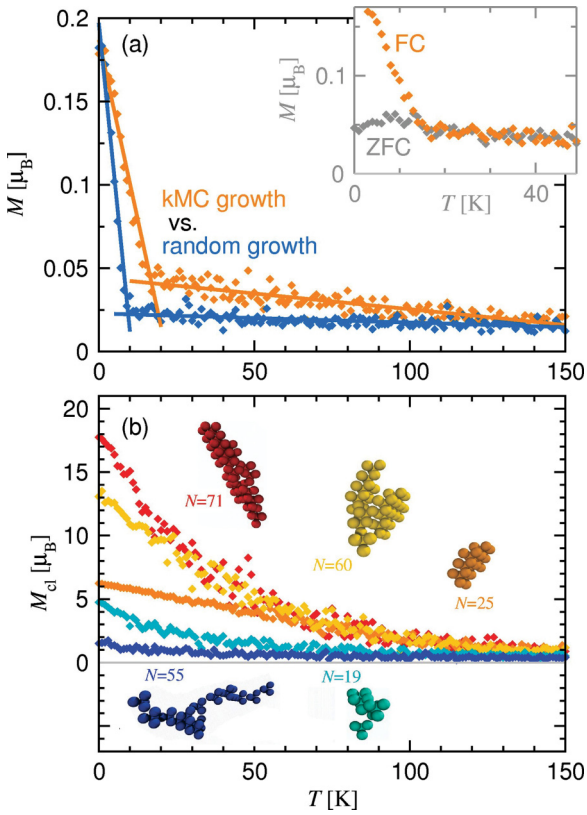


FIG. 2. (Color online) Monte-Carlo (MC) simulations of randomly grown (RGr) sample (blue [dark gray]) and sample grown by means of the kinetic Monte Carlo growth model (kMCG, orange [light gray]). Exclusively nearest neighbor exchange interactions among spin-polarized N atoms and from those to $V_{\mathrm{Ga}}$ are considered. (a) Magnetization $M$ per spin-polarized N atom as a function of temperature. Straight lines are fits to the data points of the two different magnetic phases observed. The inset shows the temperature dependency for the standard field-cooled (FC) case and the zero-field-cooled (ZFC) case. (b) Absolute magnetization per cluster $M_{\mathrm{cl}}$ as a function of temperature for two and three different clusters of sample RGr and kMCG, respectively. The arrangement of cluster atoms is illustrated in corresponding color coding. Note that for all results shown the average magnetizations of 10 MC runs are presented.

of many of the individual cluster magnetization vectors, $\vec{M}_{\mathrm{cl}}$. However, the magnetic moments within a distinctive cluster keep preferentially aligned, where the coupling strength is determined by the shape of the clusters: Compact clusters as mostly present in the kMCG sample (e.g., $N = 25$, orange [light gray]) appear to be strongly coupled up to a blocking temperatures around 100 K. In contrast more extended clusters existing in the RGr sample with only a single interaction link (e.g., $N = 55$, blue [dark gray]) are loosing their magnetization already at low temperatures of only 10 to 20 K. Overall in this high-temperature phase a significant net magnetization is maintained for the kMCG sample, which we find to be primarily determined by the larger clusters of the sample. In fact, the individual $\vec{M}_{\mathrm{cl}}$ rotates independently in a superparamagnetic state. Owing to several simplifications made in our model, such as neglecting relaxations and considering only nearest neighbor $J_{ij}$'s, it is not the aim of this work to precisely predict transition temperatures

but rather to provide a qualitative explanation for the magnetic phenomena. Our simulations provide new insights considering Fig. 2(c) of the experiments published by Dhar *et al.*,[2] which show striking qualitative similarities including the presence of two magnetic phases. However, our calculations do not yet consider the experimentally observed difference of the FC and ZFC curves, an effect which can be caused by a pinning of the magnetic clusters to Gd spins or further defects.

From our analysis we conclude that a random distribution of vacancies cannot create the experimentally observed magnetic properties, while vacancy clustering as we obtained from our kMCG model leads to strikingly similar magnetic properties with the experimentally observed ones. The occurrence of such large open volumes rather than isolated Ga vacancies is supported by positron annihilation spectroscopy,[12] although these authors concluded that there was no clear correlation of these clusters with the magnetism persisting to room temperature in some samples. This indicates that besides the mechanism proposed here, there may still be an as-yet-unknown magnetic phase or contamination in certain samples persistent to even higher temperatures.

The fact that Roever *et al.*[12] observed a slight enhancement of magnetism with O concentration is consistent with our model. In fact, O in GaN predominantly occurs substitutional on N sites and leads to *n*-type doping. The latter can easily be simulated in our calculations by shifting the Fermi level up and was found to give a slight increase in exchange interactions.[17] Relatedly, Davies *et al.*[21] found an increase in magnetic effects with Si codoping, which also is an *n*-type dopant. Thus, rather than viewing the O effects as an indication for O interstitial participation in the magnetism,[9,22] we view it as arising from a strengthening of the exchange interactions by *n*-type doping.

We caution that the details of our growth model, which is for (001) growth of zinc-blende GaN, whereas the actual samples are (0001) grown wurtzite GaN, do not matter for the final conclusions. In fact, the key point of our model is that the magnetic properties arise from some type of extended defects involving Ga vacancies. Our growth model is one way of generating these but it is not necessarily the actual way these form in the samples. Hollow core dislocations or grain boundaries could be another source of such extended Ga vacancies. Very recently,[23] the high-temperature magnetic phase in Gd-doped GaN was shown under certain growth conditions to be quite anisotropic with magnetization preferentially along the growth direction. This happens to coincide with the direction of a dense dislocation network observed in the same samples, which we surmise could well be the location of N-dangling bond magnetic moments similar to the ones found near the vacancy clusters studied here.

The authors thank Ph. Mavropoulos and M. Ležaić for fruitful discussions. A.T. gratefully acknowledges financial support from the DAAD and W.R.L. is thankful for support of US-NSF Grant No. DMR-1104595. Computing resources were provided by the Jülich Supercomputing Centre.

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[1] N. Teraguchi, Solid State Commun. **122**, 651 (2002).
[2] S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, Phys. Rev. Lett. **94**, 037205 (2005).
[3] M. A. Khaderbad *et al.*, Appl. Phys. Lett. **91**, 072514 (2007).
[4] A. Ney *et al.*, Phys. Rev. B **77**, 233308 (2008).
[5] P. Dev, Y. Xue, and P. Zhang, Phys. Rev. Lett. **100**, 117204 (2008).
[6] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[7] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **93**, 177206 (2004).
[8] G. M. Dalpian and S. H. Wei, Phys. Rev. B **72**, 115201 (2005).
[9] C. Mitra and W. R. L. Lambrecht, Phys. Rev. B **80**, 081202 (2009).
[10] L. Liu, P. Y. Yu, Z. Ma, and S. S. Mao, Phys. Rev. Lett. **100**, 127203 (2008).
[11] Y. Gohda and A. Oshiyama, Phys. Rev. B **78**, 161201 (2008).
[12] M. Roever, J. Malindretos, A. Bedoya-Pinto, A. Rizzi, C. Rauch, and F. Tuomisto, Phys. Rev. B **84**, 081201 (2011).
[13] S. Limpijumnong and C. G. Van de Walle, Phys. Rev. B **69**, 035207 (2004).
[14] A. Thiess, Ph.D. thesis, RWTH Aachen University, 2011.
[15] A. Thiess, R. Zeller, M. Bolten, P. H. Dederichs, and S. Blugel, Phys. Rev. B **85**, 235103 (2012).
[16] A. I. Liechtenstein *et al.*, J. Magn. Magn. Mater. **67**, 65 (1987).
[17] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.86.180401 for details related to the performed density-functional calculations. Further, we briefly discuss the potential effect of *n*-doping by analyzing the integrated magnetic exchange interaction. In addition, more details on the applied GaN:Gd growth model are provided.
[18] This additional contribution enters because of the necessary introduction of empty scattering sites on Ga vacancy sites in the KKR formalism and can be related to the interaction of adjacent N sites.
[19] K. Sato *et al.*, Rev. Mod. Phys. **82**, 1633 (2010).
[20] All spins which are magnetically coupled within the simplified model are accounted for as one cluster.
[21] R. P. Davies *et al.*, Appl. Phys. Lett. **96**, 212502 (2010).
[22] Z. Liu *et al.*, Appl. Phys. Lett. **100**, 232408 (2012).
[23] T. F. Kent *et al.*, Appl. Phys. Lett. **100**, 152111 (2012).