Palladium in GaN: A 4*d* metal ordering ferromagnetically in a semiconductor

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It is shown that a 4*d* metal (palladium) orders ferromagnetically in GaN, forming a dilute magnetic semiconductor. The ferromagnetic ordering occurs despite Pd being nonmagnetic in its natural phase. $Pd_{0.0625}Ga_{0.9375}N$ is shown to possess a magnetic moment of 1.3 μ_B per supercell, with a spin-polarized impurity band in the GaN band gap and the Fermi level lying within this band. The impurity band is shown to arise from the hybridization of the Pd 4*d* level with N 2*p* states. Though the largest experimental and theoretical focus up to now has been on 3*d* metals such as Mn in III–V and II–VI semiconductors, the results presented here show that 4*d* metals such as palladium, may also be considered as candidates for ferromagnetic dopants in semiconductors. This broadens the range of dopants which may be taken into account in attempts to overcome technological and other barriers related to the dopants used presently to obtain magnetically ordered semiconductors for potential spintronic applications.

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I. INTRODUCTION

Ferromagnetic ordering of dopants in semiconductors has attracted considerable interest, due to their relevance to "spintronic" applications. These spintronic applications hold the prospect of greatly increasing the functionality of semiconductors by not only using the charge of the electron, but also its spin. Such applications do, however, still need to overcome important barriers, such as the ability to support spin polarized charge transport, while simultaneously achieving a sufficiently high Curie temperature[1] to allow ferromagnetic properties to persist at room temperature.

Considerable effort has gone so far into the study of 3*d* transition metals, such as manganese[2] and chromium,[3,4] as dopants in III–V and II–VI semiconductors.[1,2,5] As far as 4*d* metals are concerned, only the optical spectra of niobium and molybdenum impurities in GaN have been considered thus far.[6] This is most likely due to 4*d* metals not being ferromagnetic in their natural phases. Only recently have the 4*d* transition metals Zr, Tc, Ru, and Nb been proposed as dopants for a class of transition-metal doped I_2–VI semiconductors.[7–9] However, it has previously been shown that palladium (a 4*d* metal), which is nonmagnetic in its fcc ground state, does exhibit ferromagnetic order when in a hcp or double-hcp (dhcp) phase.[10] A Pd atom in these phases experiences an environment of similar symmetry as in a wurtzite semiconductor such as gallium nitride (GaN). Similarly, Pd clusters[11,12] have experimentally been found to be ferromagnetically ordered. First principle calculations showed that ferromagnetic order in small Pd clusters occurs because they stabilize in a structure which breaks the fourfold symmetry of the natural fcc phase, while Pd clusters in the fcc phase are found to be nonferromagnetic.[13,14] Recently, ferromagnetic order in Pd clusters was found to be directly related to the density of stacking faults existing in fcc Pd particles.[15] Since the occurrence of a stacking fault locally breaks the fourfold symmetry of the fcc lattice, the experimental data of Sampedro *et al.*[15] show that ferromagnetically ordered atoms lie in clusters which exhibit a close-packed structure characterized by a lack of fourfold symmetry.

Considering that the creation of ferromagnetic semiconductors is still at an early stage and technological limitations still need to be overcome before magnetically ordered semiconductors suitable for spintronic applications can be realized, it is important that alternative dopants are available for consideration during attempts to overcome these limitations. It is therefore of interest to establish whether the 4*d* transition metal palladium, when incorporated in semiconductors (such as GaN), orders ferromagnetically, giving rise to dilute magnetic semiconductors, in the same way as has been found for 3*d* dopants such as manganese[2] in GaN.

II. METHOD

Ab initio all electron density functional theory (DFT) calculations have been performed for substitutional Pd in GaN, using the generalized gradient (GGA) approximation of Perdew-Burke-Ernzerhof[16] and subsequently the linear spin density approximation (LSDA) to the exchange-correlation potential. The motivation for this choice of the exchange-correlation potentials is given below.

The L(S)DA approximation with or without gradient corrections has been successfully used so far to calculate the electronic structure and magnetic order in 3*d*-metal-doped III–V and II–VI semiconductors[2–4,17–21] and, recently, in a class of anti-CaF_2 I_2–VI semiconductors doped with 4*d* metals.[7–9] It should be mentioned that L(S)DA underestimates the lattice constants of transition metals.[22] Gradient corrections, on the other hand, dramatically reduce the error[22–24] and also give the correct natural phase stability,[25] but they tend to overestimate the magnetic moment.[22,28] This is confirmed by our spin-polarized, GGA calculation of the magnetic moment of Pd metal atoms in the fcc phase at the optimum lattice constant. It produced a nonvanishing magnetic moment, leading to the conclusion that fcc Pd is ferromagnetically ordered, in contrast to experimental

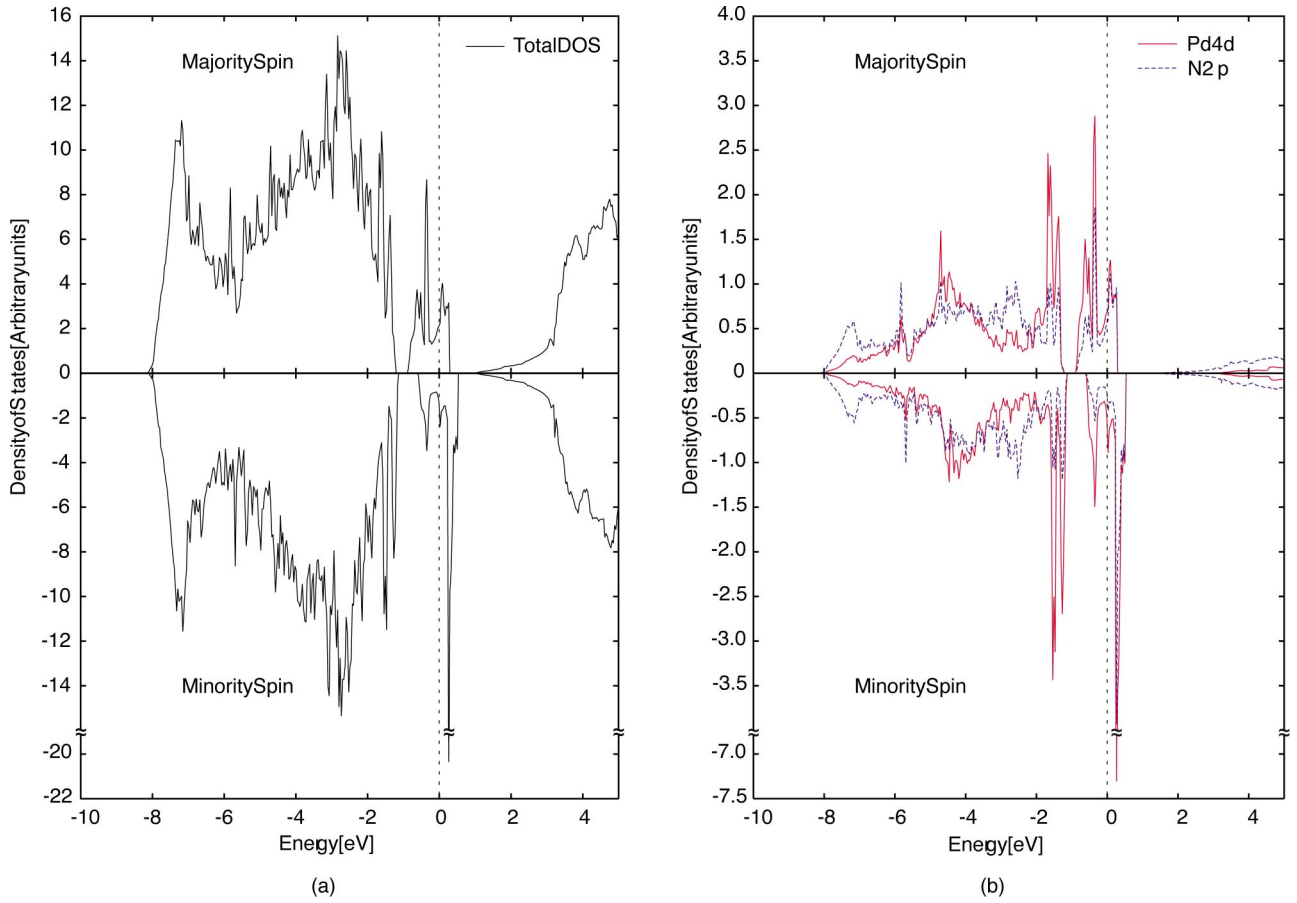

FIG. 1. (Color online) (a) Total density of states of wurtzite $Pd_{0.0625}Ga_{0.9375}N$ and (b) partial density of states corresponding to Pd and the contribution from the N neighbors of Pd combined. All energies are relative to the Fermi energy.

observations.[10] On the other hand, the LSDA approximation gives the magnetic moment of hcp Pd in excellent agreement with the value obtained in ARUPS measurements.[10] We have therefore also carried out a LSDA calculation for Pd-doped GaN to check whether the obtained magnetic order is not an artifact of the GGA approximation.

An augmented plane waves with local orbitals (APW+lo) basis set was employed in the calculations using the full potential periodic formalism with the relativistic treatment of the core electrons, as implemented in the WIEN2K code.[29] Blöchl's modified tetrahedron method[30] was used for integration over the Brillouin zone. In APW+lo (see Ref. 33) calculations the value of $R_{mt} \cdot k_{max}$ (smallest muffin tin radius multiplied by the maximum k value in the expansion of plane waves in the basis set) determines the accuracy of the basis set used; $R_{mt} \cdot k_{max} = 5.5$ was used together with a $10 \times 10 \times 5$ k-point mesh for the integration over the Brillouin zone (58 k points in the irreducible wedge of the Brillouin zone). The following initial atomic configurations were employed: $4d^8 5s^2$ (Pd), $3d^{10} 4s^2 4p$ (Ga), and $2s^2 2p^3$ (N). Experimentally determined lattice constants of GaN in the wurtzite structure were used in the calculations,[34] with $a = 3.190$ Å, $c = 5.189$ Å, and $u = 0.3821$; the c/a ratio of GaN is slightly smaller than that of the ideal wurtzite structure.

All the $Pd_xGa_{1-x}N$ calculations were performed using a 32-atom supercell created from $2 \times 2 \times 2$ wurtzite unit cells. A gallium atom in the supercell was replaced by palladium, since it is expected that Pd, similarly as Mn[32], when incorporated into the GaN lattice, will replace Ga. This is justified by the similarities between the electron affinities, electronegativities and atomic radii of Pd and Mn[31] and the experimental observation that Mn replaces Ga in GaN.[32] As the c/a ratio of GaN deviates slightly from that of the ideal wurtzite structure, one of the four N neighbors of the Pd impurity is unique, resulting in C_{3v} symmetry about the axis joining the Pd and unique N atom. Geometry optimization was performed allowing all the atoms in the supercell to relax, constrained to C_{3v} symmetry. Geometry optimization was continued until all the forces were less than 2.0 mRy $bohr^{-1}$. To ensure that the most stable geometry was found, a geometry optimization was subsequently performed with the Pd atom initially distorted away from C_{3v} symmetry in a random direction.

Since a single Ga atom is replaced by Pd in an infinite periodic supercell, the resulting $Pd_xGa_{1-x}N$ ($x = 0.0625$) structure would be ordered and ferromagnetic by definition, if the material exhibits spin polarization. Effects such as disorder or dopant clustering are therefore neglected. These effects would serve to reduce any magnetic ordering in a material, if such order is present. This approximation is sufficient for establishing whether spin polarization exists, as well as establishing theoretical limits to spin polar-

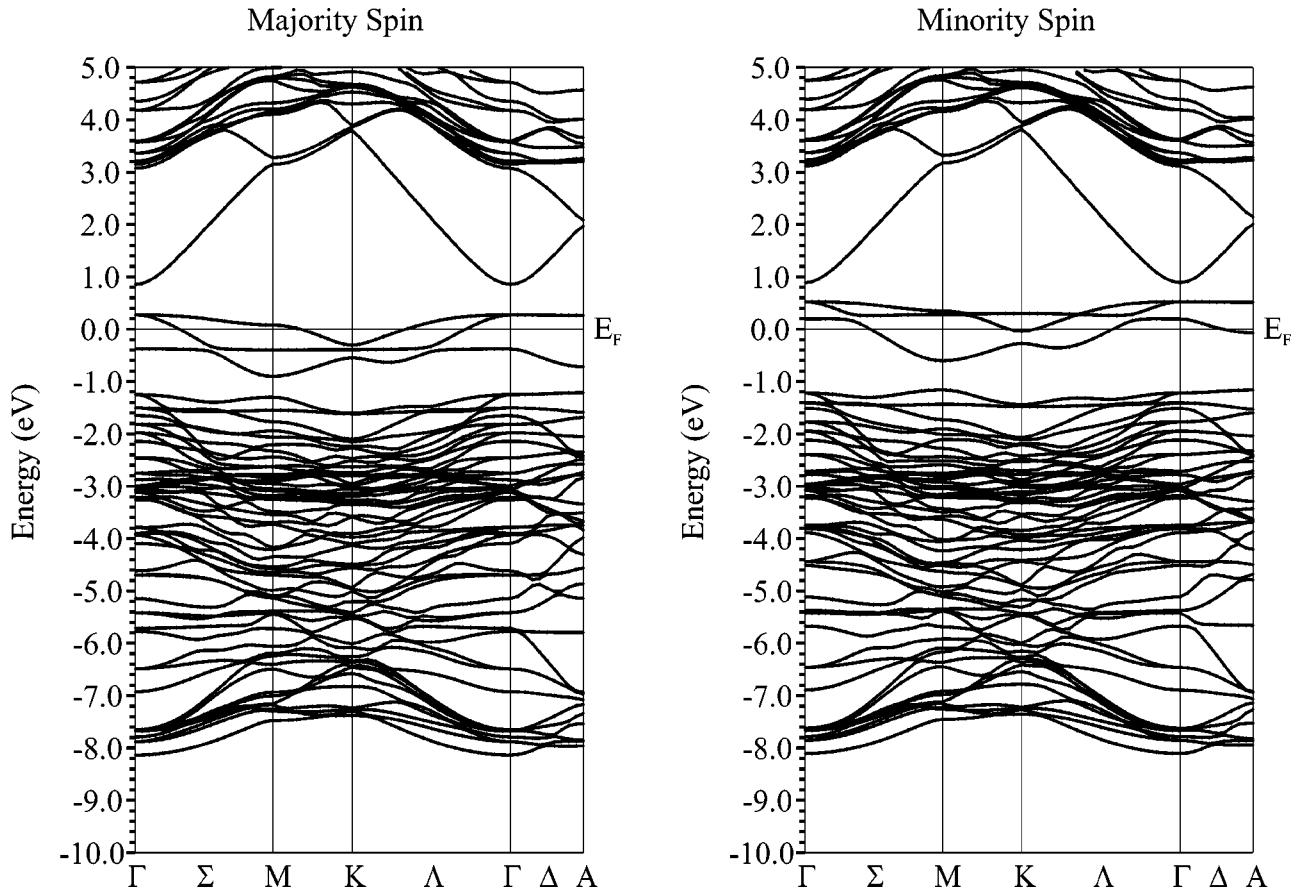

FIG. 2. Band structure diagram of wurtzite $Pd_{0.0625}Ga_{0.9375}N$. Path in Brillouin zone as for an hcp structure. All energies are relative to the Fermi energy.

ization in $Pd_xGa_{1-x}N$, similar to what was the case for previous calculations of Mn in GaN (Ref. 2).

III. RESULTS AND DISCUSSION

After geometry optimization the unique Pd-N bond was found to elongate by 7.3% to 2.10 Å, while the remaining Pd-N bonds elongated by 5.7% to 2.06 Å. The center has C_{3v} symmetry about the axis joining the Pd and unique N atoms. When the Pd atom was slightly distorted away from this structure in a random direction, it was found to relax back to within 0.06 Å of the above geometry.

We find a global magnetic moment of 1.3 μ_B per supercell, demonstrating that palladium orders ferromagnetically in GaN, which becomes a ferromagnetic semiconductor. The existence of the ferromagnetic order is confirmed by a LSDA calculation which yields 1.2 μ_B per supercell. As expected, the palladium dopant atom is found to be the main contributor to the magnetic moment, with a localized magnetic moment of 0.57 μ_B per atom. The unique nitrogen neighbor of Pd makes a small contribution of 0.15 μ_B to the magnetic moment, with the three remaining N neighbors of Pd combined making a similar contribution (0.18 μ_B). The gallium second nearest neighbors of Pd contribute less than 0.006 μ_B per atom.

The density of states (DOS) of $Pd_xGa_{1-x}N$ is illustrated in Fig. 1. It is seen that the introduction of palladium introduces an impurity gap state, with both the majority and minority-spin components retaining a band gap. The introduction of Pd therefore maintains the semiconducting nature of GaN. Importantly, the Pd impurity related band is spin polarized, with a spin polarization of 0.24–0.31 eV and the Fermi level lying within this band; charge carriers traveling through a $Pd_xGa_{1-x}N$ layer will therefore be spin polarized. Individual impurity levels close to the Fermi level were spin polarized by 0.25–0.68 eV.

It is evident from the partial DOS [Fig. 1(b)] that the impurity band is formed by the Pd 4*d* level hybridizing with the 2*p* levels of the N neighbors of Pd. This is similar to previous results of Mn in GaN, where Mn 3*d* levels hybridized with N 2*p* states.[2]

We find that the palladium related impurity band width is 1.22 eV for the majority-spin and 1.16 eV for the minority-spin component. The impurity band is 0.27 eV above the valence band maximum for the majority spin, while it is 0.34 eV below the conduction band minimum for the minority-spin component.

The impurity bandwidth of ~1.2 eV is slightly smaller than what was found for Mn in GaN, but considerably larger than for Mn in GaAs (Ref. 2). In situations where "Fermi-level engineering" is required to bring the Fermi level within the impurity band (for example in samples where residual impurities or unintentional doping are an issue), this has im-

portant implications, since a wider impurity band provides greater flexibility in achieving this aim.

The calculated width of the band gap of 2.0 eV in the impurity supercell $Pd_xGa_{1-x}N$ is close to that of pure GaN (1.9 eV) and similar to previous theoretical calculations of the GaN band gap[2] of 2.4 eV. These values are smaller than the experimental[35] GaN band gap of 3.47 eV, which is expected since density functional theory is well known to underestimate band gaps.[36] We find that the valence band and conduction bands of the impurity supercell are only slightly spin polarized by the introduction of Pd; the valence band is spin polarized by 0.07 eV and the conduction band by 0.03 eV. This is in contrast to previous results[2] for Mn in GaN, where the conduction band exhibited large spin polarization. This difference is ascribed to the fact that the minority-spin impurity-band states were found to lie close to the conduction band minimum for Mn in GaN (Ref. 2) and in resonance with this band, leading to its broadening for the minority spins, while for Pd in GaN the impurity band lies within the band gap for both spin states and does not impact on the conduction or valence bands.

It has been pointed out[2] that the presence of a spin-polarized band is in itself not a sufficient condition for efficient spin-polarized carrier transport and subsequent spin-polarized charge injection. It is also required that charge carriers within the spin-polarized band should be sufficiently mobile. We assess this by referring to the calculated band structure of $Pd_{0.0625}Ga_{0.9375}N$, illustrated in Fig. 2.

From the band structure of $Pd_{0.0625}Ga_{0.9375}N$ it is seen that a spin-polarized impurity band is present both for majority and minority-spin states. The Fermi level passes through this band in both spin states and therefore a Fermi surface exists for each of them. Thus, it should be stressed that the system is metallic in contrast to Mn-doped GaN, which is semimetallic. This may be a disadvantage for some spintronic applications.

The impurity bands exhibit the greatest degree of dispersion in directions parallel to the hexagonal plane, such as between points Γ and K, and Γ and M. Considerably less dispersion exists along directions parallel to the c axis, such as between points Γ and A, both in the majority and minority-spin states. This is a consequence of the details of the construction of the $Pd_{0.0625}Ga_{0.9375}N$ supercell, where the Pd-Pd distance is greater in the c direction (10.38 Å) than within the hexagonal plane (6.38 Å). It is therefore evident that a Pd-Pd separation of $\sim$6.4 Å produces significant hybridization, while a separation of $\sim$10.4 Å does not. This provides a lower and upper bound, respectively, for the minimal Pd-Pd distance needed to obtain the necessary impurity band dispersion. These lower and upper bounds for the minimal Pd-Pd distance are very similar to those found previously for the minimal Mn-Mn distance[2] in GaN. $Pd_xGa_{1-x}N$ is therefore expected to support effective mass transport, provided the minimal Pd-Pd distance is satisfied.

The ferromagnetic ordering of palladium in GaN occurs despite the fact that this 4*d* metal is nonmagnetic in its natural phase. A Pd atom in a wurtzite semiconductor such as GaN experiences an environment with similar lack of fourfold symmetry as in a hcp or dhcp phase.[10] Although the DOS in pure 4*d* metals is reduced by the stronger interaction of 4*d* wave functions compared to 3*d* wave functions, this change of crystal symmetry raises the DOS at the Fermi level sufficiently to fulfill the Stoner criterion for ferromagnetism.

IV. CONCLUSIONS

We have shown that substitutional Pd impurities in GaN order ferromagnetically, leading to a dilute magnetically ordered semiconductor. This ferromagnetic ordering is shown to occur despite the fact that 4*d* metals are nonmagnetic in their natural phases. This is ascribed to the similarity between the symmetry of the environment experienced by Pd in GaN and the hcp phase of Pd, which has previously been shown to be ferromagnetic.

We have also demonstrated that $Pd_xGa_{1-x}N$ with a realistic Pd content of $x=0.0625$, possesses a magnetic moment of 1.3 μ_B per supercell. A spin-polarized impurity band is induced in the GaN band gap, with the Fermi level lying within the band (the system is metallic in contrast to Mn-doped GaN which is semimetallic). The impurity band has a width of $\sim$1.2 eV, which is slightly smaller than for Mn in GaN, but considerably larger than that found for Mn in GaAs (Ref. 2). This band was found to be primarily due to the hybridization of the Pd 4*d* level with N 2*p* states. The band was also shown to be capable of supporting effective mass transport.

Neither the conduction nor the valence band of Pd in GaN are significantly spin polarized. This is in contrast to Mn, which induces a significantly spin-polarized conduction band in GaN, and a spin-polarized valence band in GaAs (Ref. 2).

While the largest experimental and theoretical focus up to now has been on Mn in III–V and II–VI semiconductors such as GaN and GaAs, we have shown that it is also worthwhile to consider 4*d* metals, such as palladium, as ferromagnetic dopants in semiconductors. This broadens the range of dopants which may usefully be considered when attempting to overcome the technological limitations faced in the production of magnetically ordered semiconductors for spintronic applications.

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