Magnetic Metastability in Tetrahedrally Bonded Magnetic III-Nitride Semiconductors

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Results of density-functional calculations for isolated transition metal (TM = V, Cr, Mn, Fe, Co, Ni on cation sites) doped GaN demonstrate a novel magnetic metastability in dilute magnetic semiconductors. In addition to the expected high spin ground states ($4\mu_B$/Mn and $5\mu_B$/Fe), there are also metastable low spin states ($0\mu_B$/Mn and $1\mu_B$/Fe)—a phenomenon that can be explained in simple terms on the basis of the ligand field theory. The transition between the high spin and low spin states corresponds to an intraionic transfer of two electrons between the t_2 and e orbitals, accompanied by a spin-flip process. The results suggest that TM-doped wideband semiconductors (such as GaN and AlN) may present a new type of light-induced spin-crossover material.

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Transition metal (TM)-doped dilute magnetic semiconductors (DMS) currently attract intense scientific interest because of their potential use in spintronic devices [1]. From a fundamental standpoint, DMS also present a unique type of system which offers the possibility of studying the interaction between the delocalized electrons of the host semiconductor and the localized *d*-band electrons of the magnetic ions and, consequently, the magnetic phenomena, with a relatively simple band structure. One characteristic feature associated with TM-doped III-V semiconductors is that the host band gap serves as the "arena" for the localized TM-*d*-band electrons, in which the Fermi level is typically located. This, in principle, facilitates the possibility to tune the magnetic behavior by external perturbations. Indeed, control of the magnetic state in InAs-based DMS by light irradiation [2] or by external electric fields [3] has been demonstrated.

Moreover, besides the ground state, the presence of a magnetic metastable (or "metamagnetic") state is the key underlying conceptual mechanism for storage, memory, and display device applications. Examples of such novel materials include some bulk transition metals [4], nanoscale magnetic thin films and nanoparticles [5–7], and molecular magnets [8]—that can be engineered to display different stable magnetized states. In particular, the so-called spin-crossover (SCO) phenomenon originates from the existence of two or more electronic configurations for the metal ions, corresponding to different spin states. Studies of this novel property have been strongly stimulated by industrial and technological interest [9,10]. So far, the majority of SCO materials involve octahedral TM complexes, in either solids or solutions. It is very rare to observe the SCO phenomenon in tetrahedral complexes due to the small crystal field splitting.

In this Letter, we demonstrate the coexistence of high spin (HS) and low spin (LS) states in isolated TM (TM = Mn, Fe)-doped GaN, where the TM is located in the substitutional, tetrahedrally bonded cation site. This is the first time that a magnetic metastability has been found in DMS. The transition between the HS and LS states corresponds to an intraionic transfer of two electrons between t_2 and e orbitals, accompanied by a spin-flip process. Our results suggest that III-nitride-based DMS may present a new type of SCO materials.

We perform extensive all-electron scalar relativistic density-functional theory (DFT) calculations using the generalized gradient approximation (GGA) [11] with the DMol^3 code [12]. The wave functions are expanded in terms of accurate numerical basis sets where we use the double-numeric quality basis set with polarization functions. The local basis cutoff is taken to be 11.0 a.u. The calculated optimized wurtzite lattice constants are $a = 3.184$ Å and $c = 5.184$ Å with the internal parameter $u = 0.3765$ (experimental values: $a = 3.189$ Å, $c = 5.186$ Å, and $u = 0.377$). We use a 32-atom ($2a \times 2a \times 2c$) supercell for modeling an isolated TM dopant and a reciprocal space Monkhorst-Pack $8 \times 8 \times 4$ *k*-point mesh. Convergence tests using a larger 72-atom cell yield an identical picture. Fixed spin moment (FSM) calculations are performed, including full atomic relaxation, to trace magnetic phases and to determine their stability and existence limits [13]. In this approach, a self-consistent calculation is carried out for an assumed particular total magnetic moment—achieved by separately varying the Fermi energy of spin-up and spin-down electrons. Consequently, FSM calculations are characterized by two Fermi energies E_F(up) and E_F(down).

Our earlier studies for Cr and Mn in GaN showed that the TM strongly prefers to occupy the cation site [14]. We therefore here consider TM ions incorporated substitutionally on this site, where they are bonded tetrahedrally to the four neighboring nitrogen atoms—one apical and three planar. The dependence of the total energy as a function of the total magnetic moment per supercell for TM-doped

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TABLE I. Electronic configuration, magnetic moment (MM, in μ_B) per cell, on the transition metal ion and on the neighboring N atoms for the expected high spin and low spin states. The ground state values are shown in bold.

Ions	Elec. Config.	MM per cell	MM on TM	MM on N
$V^{3+}(3d^2)$	$e^2t_2^0$	**2**	**2.039**	**−0.046**
$Cr^{3+}(3d^3)$	$e^2t_2^1$	**3**	**2.973**	**−0.070**
	$e^3t_2^{0a}$	1	1.106	−0.007
$Mn^{3+}(3d^4)$	$e^2t_2^2$	**4**	**3.834**	**−0.055**
	$e^4t_2^0$	0	0	0
$Fe^{3+}(3d^5)$	$e^2t_2^3$	**5**	**3.965**	**0.192**
	$e^4t_2^1$	1	0.982	−0.034
$Co^{3+}(3d^6)$	$e^4t_2^{2a}$	2	1.751	0.013
	$e^3t_2^{3a}$	4	2.790	0.244
	$e^{3.2}t_2^{2.8}$	**3.6**	**2.640**	**0.186**
$Ni^{3+}(3d^7)$	$e^4t_2^3$	**3**	**1.718**	**0.280**

[a] Corresponding to a turning point in the energy curve.

GaN (TM = V, Cr, Mn, Fe, Co, and Ni) is shown in Fig. 1. For V- and Ni-doped GaN, there is only one minimum, located at $2\mu_B$/V and $3\mu_B$/Ni, respectively. For Cr:GaN, there is also one minimum at $3\mu_B$/Cr; however, there is a turning point at $1\mu_B$/Cr. Most significantly, for Mn- and Fe-doped GaN, there are two well-defined minima, with an obtained energy barrier of 75 and 55 meV, respectively. For each species, the one with the lowest energy corresponds to the expected ground HS state ($4\mu_B$/Mn and $5\mu_B$/Fe) [15] and the other one refers to a metastable LS state ($0\mu_B$/Mn and $1\mu_B$/Fe). Interestingly, for Co:GaN, the total energy is rather flat from $2\mu_B$/Co to $4\mu_B$/Co, with a slight minimum at $3.6\mu_B$/Co. It is important to note that for all systems the minima and turning-point values are all integer, except for the weak minimum of Co:GaN [16].

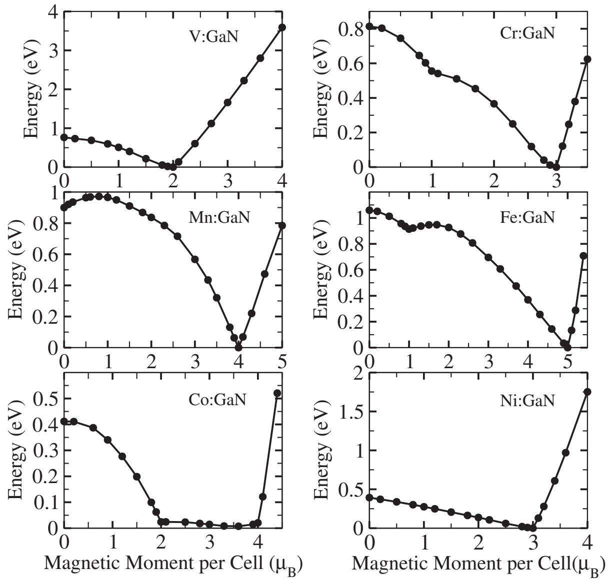

FIG. 1. Relative total energy versus the total magnetic moment per cell for transition metal-doped GaN.

The underlying mechanism of these phenomena can be understood first on the basis of "ionic" crystal field theory and its descendant "covalent" ligand field theory (LFT). In the Ga-substitutional site, the TM atom donates three electrons to the anion dangling bonds. This results in the doped ions having a $3d^2$, $3d^3$, $3d^4$, $3d^5$, $3d^6$, and $3d^7$ configuration for V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, and Ni^{3+}, respectively. The tetrahedral crystal field of the surrounding N ligands splits the fivefold degenerate d states of the free TM ion into two low-lying e (d_{z^2} and $d_{x^2-y^2}$) and three high-lying t_2 (d_{xy}, d_{xz}, and d_{yz}) subsets. Further splitting within these e and t_2 orbitals is due to the Jahn-Teller effect. The TM ions with the configuration d^n ($n = 3$ to 6) could, in principle, have a LS or HS state, depending, to a first approximation, on the competition between the crystal field splitting energy Δ_t (defined as the energy difference between the t_2 and e levels) and the mean spin-pairing energy P (defined as the energy required to pair up electrons in the same orbitals), where a large value of Δ_t favors LS states and a large value of P favors HS states. Taking Fe^{3+} with $3d^5$ as an example, there are two possible arrangements: (i) Two of the electrons occupy the e state, and three in the high energy t_2 orbital, leading to a HS state with an $e^2t_2^3$ configuration and a moment of $5\mu_B$/Fe, or (ii) four electrons occupy the e state, and one occupies the t_2 state, leading to a LS state with an electron configuration $e^4t_2^1$ and a moment $1\mu_B$/Fe. This is depicted schematically in Fig. 2. From this simple model, one can readily understand that there is only one minimum for V- and Ni-doped GaN. The expected electronic configurations, the magnetic moment per cell from LFT, and the DFT calculated moments on the TM ion and on the neighboring N atoms are tabulated in Table I.

To elucidate the origin of the magnetic metastable states, we calculate the density of states (DOS). Since the TM-3d and N-2p bands are primarily responsible for the magnetism, and only the DOS around the Fermi level is sensitive

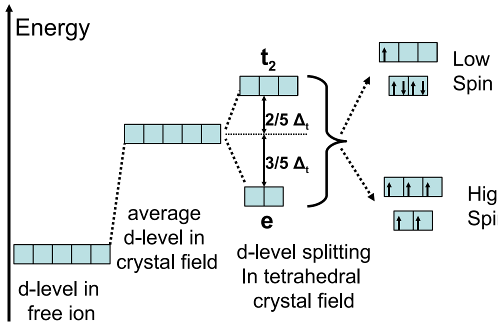

FIG. 2 (color online). Schematic description from ligand field theory of the LS and HS states for an Fe^{3+} ion in tetrahedral symmetry.

to the change of the spin moment, we display the projected DOS in the region around the E_F, as shown in Fig. 3. Increasing the total spin moment results in the spin-up DOS shifting to the left and the spin-down DOS to the right, with respect to the Fermi levels. Remarkably, for all the LS and HS states, and the turning points in the energy curves, our DFT results produce the electronic configuration as predicted in Table I from simple LFT. Taking Fe:GaN as an example, for the HS state with magnetic moment $5\mu_B$/Fe, the spin-up DOS shows that there are two electrons in the e state and three in the t_2 state; for the spin-down DOS, both the e and t_2 states are unoccupied. For the LS state with $1\mu_B$/Fe, the spin-up DOS shows that two electrons occupy the e state and one occupies the t_2 state, while the spin-down DOS have two electrons occupying the e state.

The interaction between the TM atom and the host lattice can be seen from the hybridization mainly between TM-3d and N-2p orbitals. The DOS shows that the TM-3d band is located close to the hybridization region in Co:GaN, Ni:GaN, and the HS state of Fe:GaN. One can thus expect, and understand, the large local moments found on the neighboring N atoms in these systems, as shown in Table I. The integer magnetic moment values per cell can be well interpreted by the fact that the hybridization regions in all LS, HS, and the turning-point states are well below the Fermi level, and, thus, they do not contribute to the total magnetic moment per cell. The hybridization does, however, affect the atomic moments. For the global minimum of Co:GaN at $3.6\mu_B$/Co, the DFT predicted configuration is $e^{3.2}t_2^{2.8}$; in this state, $E_F(\text{up}) = E_F(\text{down})$. It is also interesting to note that this state is metallic while all the HS, LS, and turning-point solutions are half-metallic (Cr:GaN, HS of Mn:GaN, and LS of Fe:GaN) or semiconducting (V:GaN, Ni:GaN, LS of Mn:GaN, and HS of Fe:GaN) in character.

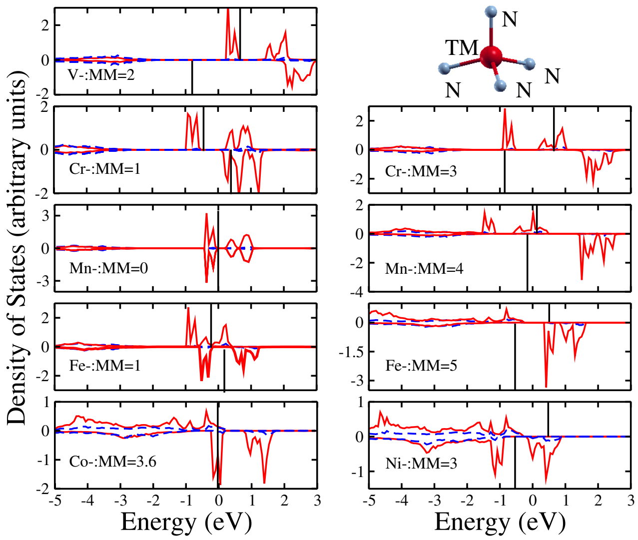

FIG. 3 (color online). Local projected density of states of transition metal 3d (red, solid line) and N-2p (blue, dashed line) for the low spin, high spin, and the ground magnetic states.

The occupancy of the high-lying t_2 orbitals is obviously higher in the HS state than in the LS state; these t_2 orbitals are more antibonding in character than the e orbitals and, thus, result in the average TM-ligand bond being longer in the HS state than in the LS state. The difference is 0.063 Å for Mn:GaN and 0.057 Å for Fe:GaN. These values are smaller than those of the octahedral complexes found in usual SCO materials, which are typically in the range of 0.14–0.24 Å for Fe^{2+}-based structures and 0.11–0.15 Å for Fe^{3+} compounds [8].

In trying to understand why some systems show the coexistence of HS and LS and not others, we estimate the difference between Δ_t and P by evaluating the overall stabilization energy (SE) for the HS and LS states, which is equal to the ligand field stabilization energies (LFSE) plus the pairing energy. For tetrahedral complexes with a $e^x t_2^y$ configuration, $\text{LFSE} = (-0.6x + 0.4y)\Delta_t$ [17]. For example, for the LS state of Fe:GaN with configuration $e^4 t_2^1$, the $\text{LFSE} = -2.0\Delta_t$, and since four electrons are paired up in the two e orbitals, we have the term $+2P$. With this simple description, taking the difference between the SE for the HS and LS states and equating it to the values calculated from DFT yields an estimate of the difference between Δ_t and P, summarized in Table II: For Mn- and Fe-doped GaN, $P - \Delta_t = 0.45$ eV, while for Cr:GaN, $P - \Delta_t = 0.55$ eV. We attribute the smaller pairing energy relative to the splitting energy as the reason for the existence of the metastable LS states in Mn- and Fe-doped GaN. For Co:GaN, $\Delta_t \approx P$, consistent with the DFT result that it can be easily stabilized at a state with a moment ranging from 2 to $4\mu_B$/Co.

Conversion between the HS and LS states in Fe:GaN and Mn:GaN involves the creation or loss of degeneracy in the antibonding states. Remarkably, this transition corresponds to an intraionic transfer of two electrons between the t_2 and e orbitals, accompanied by a spin-flip process. This is exactly the same mechanism as the SCO phenomenon, found mostly in molecular complexes. Furthermore, we find that the magnetic metastability is very sensitive to internal geometry relaxation. For both Mn- and Fe-doped GaN, we performed FSM calculations at three fixed geometries: (i) the unrelaxed ideal host structure, (ii) the relaxed HS structure, and (iii) the relaxed LS structure. We found that the metastability disappears in all cases, which shows that the mechanism is tied to the metal-ligand bond length changes, as found in traditional octahedral SCO materials [8]. Interestingly, investigations of the dependence of the metastability on the host lattice volume show that the metastability is retained with respect to volume changes ranging over −9% to +5% for Fe:GaN and −12% to +5% for Mn:GaN. Away from equilibrium, the energy barrier significantly decreases for both systems. In addition, the magnetic metastability is most likely to be a single-ion phenomenon rather than due to cooperative

TABLE II. Overall stabilization energies (SE) obtained as the LFSE plus pairing energy (see text) for the HS (SE_{HS}) and LS (SE_{LS}) states of the TM:GaN systems. The difference between them is also given as obtained from DFT-FSM calculations.

	SE_{HS}	SE_{LS}	$SE_{LS} - SE_{HS}$ (eV)
$Cr^{3+}(3d^3)$	$-0.8\Delta_t$	$-1.8\Delta_t + P$	$P - \Delta_t = 0.55$
$Mn^{3+}(3d^4)$	$-0.4\Delta_t$	$-2.4\Delta_t + 2P$	$2(P - \Delta_t) = 0.9$
$Fe^{3+}(3d^5)$	0	$-2\Delta_t + 2P$	$2(P - \Delta_t) = 0.9$
$Co^{3+}(3d^6)$	$-0.6\Delta_t + P$	$-1.6\Delta_t + 2P$	$P - \Delta_t = 0$

effects observed in conventional solid state systems [10]. Indeed, when using a 16-atom cell ($1a \times 2a \times 2c$), where the interaction between the TM ions in neighboring cells is considerably stronger, the metastability disappears.

It is well known that the crystal field splitting is much larger among $4d$ and $5d$ metals than those with $3d$ valence electrons—and is expected to force spin pairing. As a test, we performed FSM calculations for Mo:GaN, Tc:GaN, and Ru:GaN. For each, the LS state is indeed the only minimum in the energy curve, corresponding to $1\mu_B$/Mo, $0\mu_B$/Tc (nonmagnetic), and $1\mu_B$/Ru, respectively. The HS solutions ($3\mu_B$/Mo, $4\mu_B$/Tc, and $5\mu_B$/Ru, with higher energies of 0.19, 0.80, and 1.2 eV, respectively) correspond to energy turning points—in striking contrast to the $3d$-TM-doped GaN, where the HS are the ground states. We also confirmed analogous behavior in TM-doped AlN, which suggests that the TM-doped wideband gap semiconductors GaN and AlN may present a new type of metamagnetic material.

The ability to control the magnetic states is clearly highly desirable from fundamental and technological viewpoints. Now, since the HS is the ground state in both Mn:GaN and Fe:GaN, and the LS state is significantly higher in energy, thermally driven conversion from HS to LS would be unlikely. Perhaps the most promising mechanism to possibly reversibly switch between HS and LS states is light irradiation, according to the well-known LIESST effect (light-induced excited spin state trapping) [18] and the reverse-LIESST effect [19]. To facilitate potential applications of the magnetic metastability in future photomagnetic devices, the compound should be available in the form of thin films. For TM-doped III-nitride DMS, the ions prefer to form embedded clusters, except possibly at very low concentrations [14]. Recent progress in single-ion implantation techniques may hold promise to prepare the required "isolated" ions [20].

In summary, the ability to manipulate electron spins in DMS and SCO materials represents two distinctive and tantalizing routes towards new device functionality. Our studies of isolated TM-doped III-nitrides represent a link between these two fields, where the splitting of the d-orbital energies and its consequences play a major role. Magnetic metastability has been found in Mn- and Fe-doped GaN, which is the first time in DMS and, moreover, occurs in the more "unusual" tetrahedral environment. In addition to the expected HS states ($4\mu_B$/Mn and $5\mu_B$/Fe), we identified LS states ($0\mu_B$/Mn and $1\mu_B$/Fe). The transition between HS and LS always involves an intraionic two-electron transfer between t_2 and e orbitals, accompanied by a spin-flip process. Since analogous behavior was also found in AlN-based DMS, TM-doped wide-gap semiconductors appear to represent a new type of material which displays metamagnetism and possible SCO phenomena.

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[16] Using the full-potential linearized-augmented plane-wave (FLAPW) method, with fully relaxed 32-atom cells, we confirmed these consistent results: (i) The energy difference between HS and LS states, (ii) the density of states, and (iii) the energy curves for Cr-, Mn-, Fe- and Co-doped GaN, particularly around the metastable states, are reproduced. FLAPW predicts energy barriers of 65 and 40 meV for Mn:GaN and Fe:GaN, respectively. Using the $DMol^3$ code, we also confirmed the magnetic metastability in both Mn:GaN and Fe:GaN systems using local density approximation [J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992)]; and the hybrid GGA [A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. T. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988)].

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