Role of Embedded Clustering in Dilute Magnetic Semiconductors: Cr Doped GaN

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Results of extensive density-functional studies provide direct evidence that Cr atoms in Cr:GaN have a strong tendency to form embedded clusters, occupying Ga sites. Significantly, for larger than 2-Cr-atom clusters, states containing antiferromagnetic coupling with net spin in the range 0.06–1.47 μ_B/Cr are favored. We propose a picture where various configurations coexist and the statistical distribution and associated magnetism will depend sensitively on the growth details. Such a view may elucidate many puzzling observations related to the structural and magnetic properties of III-N and other dilute semiconductors.

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Dilute magnetic semiconductor (DMS) materials are increasingly attracting intense interest as promising candidates for a new generation of multifunctional spintronics devices [1]. Despite considerable efforts, the mechanism and its universality are still under active debate [2]. One striking and puzzling feature is that while the magnetization indicates ferromagneticlike ordering, the observed saturation moments are often much lower than theoretical predictions, typically 5 (20–30) times smaller for Cr-based (Mn-based) III-V DMS than the value expected, 3 μ_B/Cr(4 μ_B/Mn). Furthermore, it is intriguing that these values seem to depend sensitively on the growth conditions, such as concentration, temperature, and annealing treatment.

Given the level of dilution of the magnetic ions, it is difficult to categorically determine the nature of the ferromagnetism experimentally. Theoretically, to date, the majority of first-principles investigations into DMS—and Cr:GaN, Mn:GaN, and Mn:GaAs systems, in particular—has focused on "single" [3] and "pair"[4] doping on the cation sites; these have found that the ground states are ferromagnetic (FM), with magnetic moments that much higher than experimental observations. These studies are based mostly on the assumption of a homogeneous distribution of TM atoms; i.e., the effect of disorder and other ordering configurations are neglected.

There have been some studies on the effect of structural disorder in DMS: for Mn:GaAs, using mean-field theory, it was predicted that disorder enhances the FM Curie temperature (T_c) [5]. Subsequently, Xu *et al.* [6] for Cr and Mn in GaAs and GaN, taking into account the magnetic atom pair interaction, concluded that disorder (and clustering) reduces the T_c. Other recent studies have reported the relevance of a random distribution of magnetic impurities for the T_c, in particular, for GaN:Mn in which the magnetic interactions are short ranged [7–9]. Studies have also indicated that As antisites may play an important role for the Mn:GaAs system [10,11]. van Schilfgaarde and Mryasov [12] suggested earlier that, on the basis of density-functional theory (DFT), magnetic impurities may form clusters of a few atoms. However, no systematic search for the atomic and magnetic ground state was carried out at that time. Mahadevan and Zunger [13] found that in Mn:GaAs the ferromagnetism arises from isolated Mn as well as from substitutional-interstitial complexes; Wang *et al.* [14] demonstrated that Mn-atom pairs, which couple ferromagnetically in bulk GaN, couple antiferromagnetically on the surface. All these results clearly signal the complex nature of the magnetism in these materials, but a general picture regarding the distribution and magnetic coupling is still unclear.

In this Letter, we report extensive first-principles investigations of the spatial distribution and magnetism in Cr:GaN. The Cr atoms are found to form "embedded clusters," maintaining the wurtzite structure, and as the cluster size grows, states containing antiferromagnetic (AFM) couplings with net spin moment close to the experimental value are favored. These findings elucidate various hitherto puzzling experimental results—such as the observed strong dependence of the magnetization on the Cr concentration, growth temperature, and annealing—and represents significant progress towards understanding the intrinsic complex nature of the distribution and magnetism in TM doped DMS.

We perform DFT calculations, using the generalized gradient approximation [15] with the DMol^3 code [16]. A double set of numerical valence functions with a local basis cutoff of 11.0 a.u. and semilocal pseudopotentials [17] are used. The optimized wurtzite lattice constants are $a = 3.184$ Å and $c = 5.184$ Å (exp values: $a = 3.189$ Å and $c = 5.186$ Å) and the internal parameter is fully relaxed. To investigate the Cr distribution, supercells of 32 ($2a \times 2a \times 2c$), 72 ($3a \times 3a \times 2c$), 96 (cubic) ($2\sqrt{3}a \times 3a \times 2c$), 108 ($3a \times 3a \times 3c$) and 128 atoms ($4a \times 4a \times 2c$) are used, as well as very large 256-atom ($4a \times 4a \times 4c$) and 300-atom ($5a \times 5a \times 3c$) cells. **k**-point meshes of

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$8 \times 8 \times 6$ for the 32-atom, $4 \times 4 \times 3$ for the 72-atom, and $2 \times 2 \times 2$ for the 96-, 108-, and 128-atom supercells are employed. We allow full atomic relaxation where the forces on the atoms are less than 0.005 eV/Å.

We first calculated single Cr doping in GaN. Four high-symmetry sites are considered—two substitutional (Cr_{Ga} and Cr_N) and two interstitial Cr_i (tetrahedral and octahedral) sites. We find the formation energy [18] of Cr_{Ga} with 3 μ_B/Cr is significantly lower than the other three sites by 4–6 eV/Cr. Calculations using the 32- and 72-atom cells produce consistent results.

For "polydoping" (i.e., more than one Cr atom in the supercell), we investigate the doping of up to 5 Cr atoms for both purely substitutional structures and substitutional-interstitial complexes by performing an exhaustive search for the favored geometric and magnetic structures. For a given structure containing n Cr atoms, we investigate all the $(2^{n-1} + 1)$ spin configurations. For example, for $n = 3$, we consider nonmagnetic, FM (↑↑↑), and three involving partial AFM couplings (↓↑↑ , ↑↑↓ , ↓↑↓) by setting different initial spin configurations on the Cr atoms. (In this work, "partial AFM" also includes ferrimagnetism.) For the doping of 2 and 3 Cr atoms, a complete search is conducted in the 72-atom cell, resulting in 21 (7-atomic configurations ×3 spin states) and 105 (21-atomic configurations ×5 spin states), respectively. For the doping of 4 (and 5) Cr atoms, we tested various configurations by adding the extra Cr atom to the most favorable 3 (and 4) Cr clusters in the 96-atom cell. The total energies clearly show that Cr ions prefer to be close to each other. All the favorable structures and spin configurations are refined in larger supercells. The energetically most favorable and next most favorable configurations are shown in Fig. 1. The associated spin moments, formation energies, and magnetic states are listed in Table I.

For pair Cr_{Ga} doping, the most favorable configuration is where the Cr atoms substitute the nearest-neighbor (0001) in-plane Ga atoms with a distance of 3.19 Å [see Fig. 1(a)]. For this structure, while the 32-atom cell predicts that the "AFM" state is lower in energy than the FM state by 61 meV, the 72- and 96-atom cells show that the FM state is more favorable by 224 and 241 meV, respectively. The next most favorable structure (cf. Table I) consists of the two Cr atoms substituting out-of-plane nearest-neighbor Ga atoms [Fig. 1(b)]. Here, conversely, while the 32-atom cell calculations predict that the FM state is slightly more favorable than the AFM state (by only 6.8 meV), both the 72- and 96-atom cells predict that the AFM state is more stable than the FM state by 32 and 35 meV, respectively. These results clearly demonstrate that, for pair doping in the 32-atom cell, there are still notable interactions between the Cr atoms in neighboring supercells, and thus the results do not represent *isolated* pairs.

For 3-Cr_{Ga}-atom doping, the most favorable structure [Fig. 1(c)] is the one where all three Cr atoms occupy nearest-neighbor Ga sites in the (0001) plane. In the next

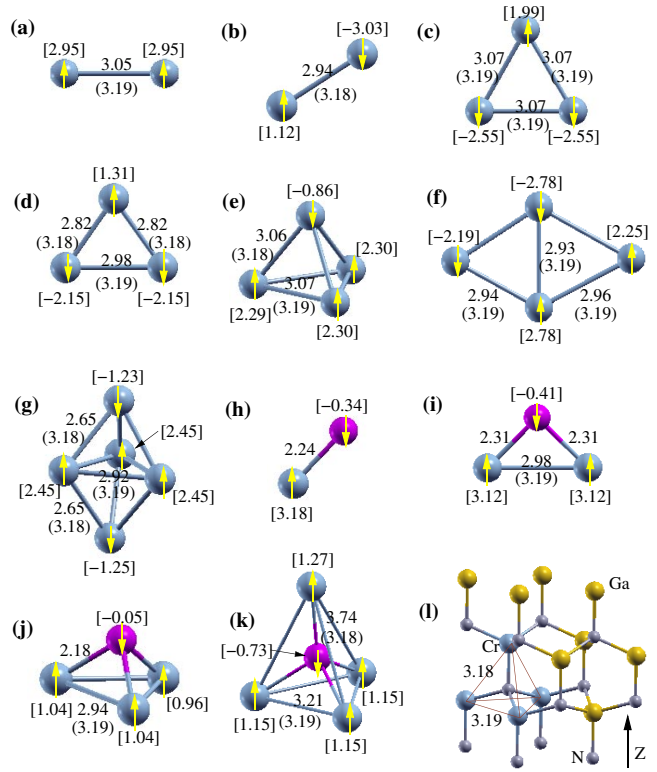

FIG. 1 (color online). Atomic geometry and magnetic structures of the most (and next most) favorable cluster configurations. The light gray circles represent substitutional Cr_{Ga}, and the dark gray octahedral-interstitial Cr. The Cr-Cr distances before (in parenthesis) and after relaxation are in Å, and the arrows indicate the directions of the atomic spin, with the spin moment values given in square brackets. The links between Cr_{Ga} atoms are a guide to the eye; the N and Ga atoms are omitted for clarity except for (l), which shows the actual structure of, e.g., (e).

most favorable structure [Fig. 1(d)], one Cr atom occupies an out-of-plane Ga site. Significantly, both configurations are AFM with net spins of 1.04 μ_B/Cr and 1.03 μ_B/Cr, respectively, as calculated in the 72- and 96-atom cells. The corresponding FM states are less favorable by 72 meV (72-atom cell) and 113 meV (96-atom cell) for the structure shown in Fig. 1(c), and by 132 meV (72-atom cell) and 243 meV (96-atom cell) for Fig. 1(d).

For higher concentrations of Cr_{Ga}, clustering is still predicted with AFM states favored. For 4-Cr_{Ga}-atom doping, the two lowest energy structures are shown in Figs. 1(e) (with net spin = 1.47 μ_B/Cr) and 1(f) (with net spin = 0.06 μ_B/Cr), where the former "pyramid structure" is lower in energy than the latter "rhombus structure." For the favored structure [Fig. 1(e)], the AFM state is lower in energy than the FM one by 525 meV. For the structure shown in Fig. 1(f), the 96-atom cell calculations show that the AFM state is lower in energy by 12 meV than the FM state, while a 128-atom cell calculation predicts that the FM state is not stable. For 5-Cr_{Ga}-atom doping, the "bipyramid structure" [Fig. 1(g)] with a net spin of 0.97 μ_B/Cr is energetically favorable. Both the 96- and a

TABLE I. Formation energies, net spin values, and magnetic states for the favorable configurations shown in Fig. 1. Note that for the net spin, contributions from N and Ga atoms are included.

Structure	No. of Cr atoms	Formation energy (eV/Cr)	Net spin (μ_B/Cr)	Ground state
Cr_{Ga}	1[a]	2.13[a]	3[a]	···
substitutional configurations				
a[a]	2[a]	1.78[a]	2.98[a]	FM[a]
b	2	1.95	0.94	AFM
c[a]	3[a]	1.59[a]	1.04[a]	AFM[a]
d	3	1.68	1.03	AFM
e[a]	4[a]	1.38[a]	1.47[a]	AFM[a]
f	4	1.53	0.06	AFM
g[a]	5[a]	1.32[a]	0.97[a]	AFM[a]
substitutional-interstitial complexes				
h	2	3.88	1.31	AFM
i	3	2.72	1.72	AFM
j	4	2.44	0.78	AFM
k	5	1.94	0.76	AFM

[a]For the substitutional doping, these quantities are for the lowest energy structure.

larger 108-atom cell calculation predict that the FM state is unstable. To check these results we use very large 300- and 256-atom cells for the structures in Figs. 1(f) and 1(g), respectively, and find identical results as for the 128- and 108-atom cells. These results clearly demonstrate that as the size of the Cr clusters increase, the AFM coupling becomes more and more favorable. This is depicted in Fig. 2. We also considered configurations involving direct Cr-Cr bonding, both with Cr on nearest-neighbor Ga and N sites, and with Cr on neighboring Ga sites with a N vacancy in between. All such geometries are highly energetically unfavorable [19].

For complexes containing one Cr_i atom, our systematic study shows that substitutional and interstitial ions also prefer to occupy adjacent sites. The most favorable complexes are shown in Figs. 1(h)–1(k). The formation energies for these complexes are much higher than for the

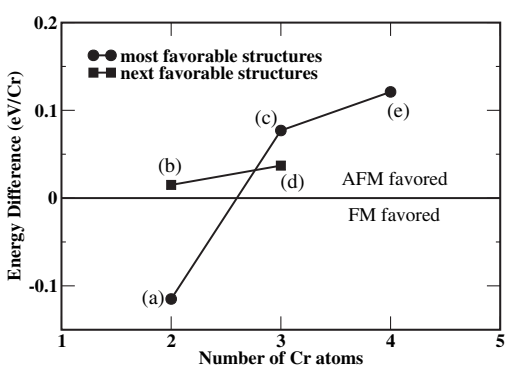

FIG. 2. Energy difference per Cr atom between the FM and AFM states for the two lowest energy structures shown in Fig. 1 as a function of Cr doping. For the structures shown in Figs. 1(f)–1(k), the FM states are not stable.

purely substitutional configurations (Table I). This is in agreement with the experimental observation that Cr occupies up to 90% substitutional sites [20]. Strikingly, for Mn:GaAs, the complexes Mn_{Ga}-Mn_i-Mn_{Ga} are found to be more stable than pure Mn_{Ga} clusters [13]. This difference may be attributed to the fact that GaAs is a *soft* semiconductor with a longer bond length and an interstitial free space of 3.7 Å in diameter (excluding the ionic radii of neighboring ions) while GaN is a *hard* one and has an interstitial octahedral (tetrahedral) free space of 2.2 Å (1.3 Å), making interstitial site doping unfavorable.

The tendency for Cr_{Ga} clustering is clearly seen from the calculated formation energies (Table I) where the values decrease with increasing size of the Cr_{Ga} clusters. The formation of such embedded Cr_{Ga} clusters leads to a strong local distortion, with the Cr-Cr distances contracted by up to 17% [cf. Fig. 1(g)] as compared to the Ga-Ga distance in the host lattice—showing a strong attractive interaction between the Cr atoms. This can be contrasted to the case of a single Cr_{Ga}, where the Cr-N bond is *longer* than the ideal Ga-N bond by 1.5%. Interestingly, the lattice constant of the Cr:GaN system is found to systematically *decrease* with growth temperature up to the optimal temperature T_o of 775 °C [20]. This trend may be explained by the fact that higher dopant mobility at elevated temperatures enhances the formation of Cr clusters. Above T_o, the fraction of substitutional Cr decreases sharply [20], suggesting that this temperature is sufficient to form substitutional-interstitial complexes which result in an *increase* of the lattice parameter c—as we found for the most favorable structure with Cr_i, Fig. 1(k), showing that the out-of-plane Cr-Cr distance is increased by 18% as compared to the Ga-Ga distance in the host lattice.

Another important feature associated with the clustering is the strong magnetic polarization on the neighboring N atoms: $0.15\mu_B$ and $0.23\mu_B$ are found for the structures shown in Figs. 1(c) and 1(e), respectively, compared to only $0.05\mu_B$ on N for the single Cr_{Ga} system. The electronic properties of Cr:GaN depend sensitively on the Cr concentration and configuration. The density of states show that the single Cr_{Ga} system is half-metallic in both the 32- and 72-atom cells, consistent with our earlier investigations [21]. But in the 96-atom cell a small gap opens at the Fermi level and the structure is a semiconductor. Similarly, the most favorable 2-, 3-, 4-, and 5-Cr-atom doped structures [Figs. 1(a), 1(c), 1(e), and 1(g), respectively] are all semiconductors in the 72- and 96-atom cells, while calculations for the 32-atom cells show that the systems are half-metallic or even metallic for the 4-Cr-atom structure [Fig. 1(e)]. Our findings are consistent with experimental work which shows that there is a significant N $2p$–Cr $3d$ hybridization and that the material is semiconducting [22].

Thus, based on the present extensive total energy calculations of Cr:GaN, it appears that the spatial distribution of the doped magnetic ions is neither random nor homogeneous: the Cr atoms prefer to form embedded clusters.

Presumably, various cluster sizes and configurations with diverse magnetic structures will coexist, particularly considering that the DMS systems are always grown under nonequilibrium conditions. Indeed, structural characterization of (Ga,Mn)N layers grown by molecular-beam epitaxy for Mn concentrations of 13.7% shows nanometer-sized Mn-rich clusters having the wurtzite structure which is coherent with the surrounding matrix [23]. Therefore, the statistical distribution, and consequently the electronic and magnetic properties of Cr:GaN, will depend sensitively on details of the growth conditions and factors such as the mobility of the dopants. While not much is known quantitatively for this system, experiments [24] for Mn:GaAs show that the substitutional ions can move several lattice constants during growth at 230 °C, and interstitial defects are believed to be more mobile than the substitutional ones [2].

With this picture, one can understand some puzzling experimental findings: (i) The observed [20,25,26] low mean magnetic moment (0.2–1.8 μ_B/Cr) may be attributed to the predicted partial AFM clusters with calculated net spin moments ranging from 0.06 to 1.47 μ_B/Cr. (ii) The net magnetic moment was found to depend strongly on both Cr concentration and growth temperature [27,28]. Indeed, higher mobility of the magnetic ions at elevated growth temperatures favors cluster formation leading to a suppressed magnetization, while an increased Cr concentration enhances the interaction *between* clusters, which, in turn, may affect the magnetic coupling *within* a cluster—as we found by comparing the magnetic states of Cr pairs in 32-, 72-, and 96-atom cells. (iii) Our picture also helps one to understand the role of annealing in relation to the magnetic properties of DMS: a gradual decay in the spin moment of Cr doped GaN has been observed upon annealing [20]. Microscopically, the annealing can be regarded as a redistribution process for the ions which enhances the formation of clusters, resulting in a change in the observed magnetization. Finally, although more evidence is required, we propose that this picture may apply in general for TM doped DMS. Indeed, our preliminary calculations on Cr(Mn):AlN and Mn:GaN, [19] show very similar "embedded clustering" behavior.

In summary, our systematic study clearly shows that in Cr doped GaN the magnetic ions prefer to occupy Ga sites and have a strong tendency to form embedded clusters while maintaining the wurtzite structure. For Cr clusters larger than 2 atoms, AFM states with net spin moment close to the experimental value are energetically preferred over FM and nonmagnetic states. We propose a picture that various configurations coexist and the statistical distribution and consequently the magnetism depend sensitively on the growth conditions. We argue that this scenario may also hold for other DMS systems and that this model may help one to understand puzzling experimental observations [2,20,25–28] in them.

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