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Ferrimagnetic Fe-doped GaN: An unusual magnetic phase in dilute magnetic semiconductors

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Most dilute magnetic semiconductors exist either in ferromagnetic (e.g., GaAs:Mn) or antiferromagnetic (ZnSe:Mn) phases at low temperature. This alignment persists even after carriers are introduced, although the preference may change as a function of doping. Using first-principles calculations, we found that the stable magnetic phase of GaN:Fe is ferrimagnetic under hole doping, in which the nearest Fe atoms have antiparallel spins with different magnetic moments. This unusual behavior is explained by the Stoner model combined with a band coupling model. Furthermore, the consequences of the formation of the ferrimagnetic phase in diluted magnetic systems are discussed.

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The discovery of ferromagnetism in dilute magnetic semiconductors (DMSs) has attracted great interest in understanding the microscopic origin of the magnetic interactions in these systems[1] because such a fundamental understanding in DMS is a prerequisite for the further development of spintronic technologies.[2–4] It is usually assumed that for DMS, the most stable magnetic structure at low temperature should be either ferromagnetic (FM) or antiferromagnetic (AFM). In a FM phase [Fig. 1(a)], the magnetic moments of the magnetic ions are aligned in the same direction and this leads to the maximum total magnetization. In an AFM phase [Fig. 1(b)], magnetic moments of neighboring ions have the same magnitude but align in the opposite direction from each other; thus, the total magnetic moment is zero. The ferrimagnetic (FIM) phase [Fig. 1(c)] has a substantial net magnetization resulting from the antiparallel alignment of the nonequivalent spins of the neighboring magnetic ions.[5,6] Macroscopically, the behavior of FIM phase is similar to the FM phase. However, FIM phase is not expected in conventional DMS systems because the FIM phase usually occurs only in systems such as Fe_3O_4 or $CuFeO_2$, in which the magnetic ions either occupy atomic sites with different environments or contain two different magnetic ions,[7] whereas in conventional DMS such as GaAs:Mn, all the substitutional sites have the same coordination environment, e.g., fourfold coordinated in GaAs:Mn.

GaN:Fe as a potential spintronic material has been widely studied in the past[8–10] because it exhibits many interesting properties, including high-temperature ferromagnetism[11–13] for *n*-type doped system and positive valence-band exchange splitting $N_0\beta$,[14] which is the opposite to most conventional diluted magnetic semiconductors.[15] In this Rapid Communication, using first-principles density-functional calculations, we show that the magnetic interaction in GaN:Fe is AFM when the system is neutral [Fig. 1(b)]. However, when holes are introduced into the system, the magnetic interaction becomes FIM [Fig. 1(c)]. In this case, nearest Fe atoms tend to have spin aligned in the opposite direction but with different magnetic moments, although the original Fe-substituted cation sites have similar coordination and chemical environment. The systems show net magnetization, but the total magnetic moment per Fe is much smaller than what is expected for a ferromagnetic GaN:Fe system. Moreover, we found that for GaN:Fe, the total magnetization increases when more hole carrier is introduced, which is the opposite to the observed trends in conventional ferromagnetic DMS systems such as GaAs:Mn.

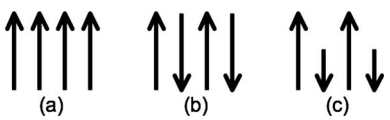

FIG. 1. Schematic magnetic phases: (a) ferromagnetic, (b) antiferromagnetic, and (c) ferrimagnetic.

Our calculations are performed using the all-electron-projected augmented-wave (PAW) method and density-functional theory (DFT) within the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE),[16] as implemented in the Vienna *ab initio* simulation (VASP) package.[17] The GaN:Fe system was simulated using zinc-blende 64-atom supercells within optimized equilibrium lattice constants. All atoms were allowed to relax until all forces were smaller than 0.02 eV/Å. A cutoff energy of 400 eV was employed for all calculations. For the Brillouin-zone integration, we employed a Monkhorst-Pack **k**-point grid of $(2\times2\times2)$. In order to check our results with cell size, calculations were also performed for 216-atom supercells and no difference in the identified trends was found. In our calculations, we considered only substitutional Fe, which is supported by experimental observations.[8]

Fe is *isovalent* with respect to Ga, except for the extra five *d* electrons; thus, no carriers are introduced in GaN by Fe_{Ga} substitution if the neutral Fe is in the Fe^{3+} ionization state. Figure 2(a) shows the calculated density of states (DOS) for GaN:Fe. We see that the majority-spin Fe *d* states are completely filled and the minority-spin Fe *d* states are completely empty, so it gives rise to a magnetic moment of $5.0\mu_B$/Fe. Due to the crystal field, the *d* states split into *e* and t_2 states. The majority *pd*-hybridized t_2 states and the minority *d* states are located inside the band gap. To study the magnetic interaction, we put two Fe atoms in the GaN supercell at the Ga-lattice nearest-neighbor sites. As expected from the band coupling model,[18] we find that the magnetic interactions between the two magnetic Fe in GaN are AFM and these are mediated by the superexchange interaction. The AFM con-

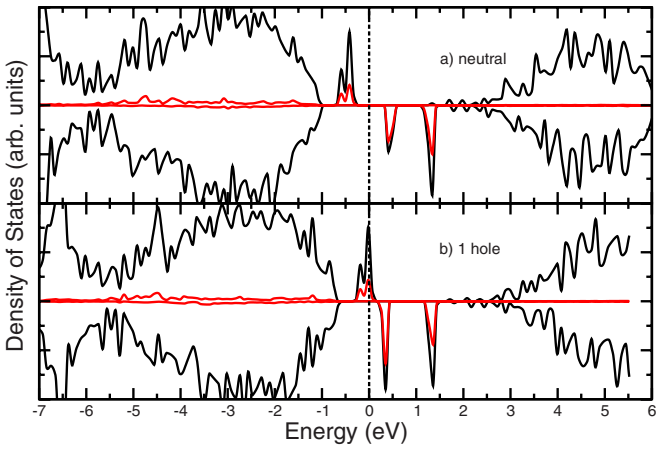

FIG. 2. (Color online) Total (black) and projected (red) densities of states for GaN:Fe by changing the number of holes in the system. (a) is for the neutral case (Fe^{3+}) and (b) is for the case when one hole is inserted (Fe^{4+}). The dashed line indicates the Fermi level of the system.

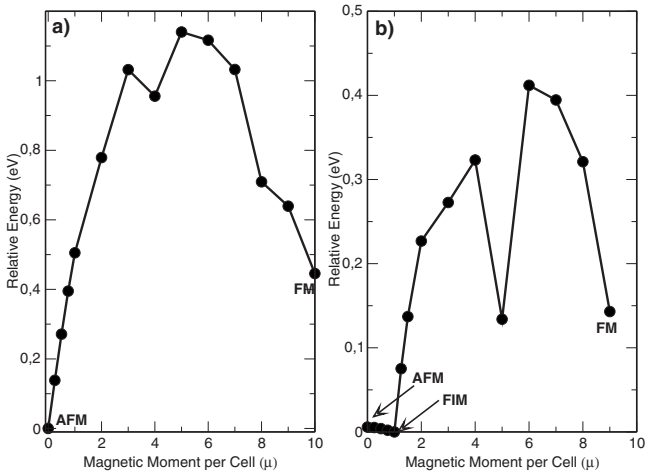

FIG. 3. Variation in the total energy as a function of the supercell total magnetic moment. (a) is for the neutral case and (b) is when one electron is removed from the system.

figuration is 440 meV/pair lower in energy than the FM configuration. Besides the FM and AFM configurations, we find that the system can also have metastable low-spin FM configurations, with a smaller local magnetic moment at each Fe site. Its energy is 60 meV/pair higher than the high-spin FM phase. This is in agreement with previous calculations.[19]

The above results indicate that the experimentally observed ferromagnetic behavior in the GaN:Fe system cannot be explained by doping GaN with Fe alone. According to the band coupling model,[18] a DMS such as GaN:Fe can become ferromagnetic only if the system have partially filled *pd* levels. For GaN:Fe, this can be done through the introduction of holes, which can lead to the reduced occupation of Fe *d* states in the majority-spin channel. Figure 2(b) shows the DOS of GaN:Fe with one hole per Fe. In this case, we observe a large shift of the minority-spin *d* levels to lower energies due to the decrease in the exchange splitting and Coulomb *U* for these levels. For the majority-spin states, the shifts due to the exchange splitting and Coulomb *U* are in the opposite direction so the net shift is small.

After holes were inserted into GaN:Fe, the stability of the AFM phase decreases. However, instead of finding the FM ground state, we find that the system assumed a FIM configuration, where the local magnetic moments of each Fe are antiparallel but have different magnitudes. This unexpected result indicates that the holes inserted into the system are not shared by both Fe, but they prefer to localize around a single Fe site. Our calculations show that the magnitude of the local moment is smaller for the Fe atom that has shorter Fe-N bonds. This can be understood by noticing that shorter bonds lead to a larger *p-d* repulsion between the host *p* levels and the impurity *d* levels, pushing the t_2 levels associated with the Fe atom to higher energy. Due to the reduced electron occupation at this high-energy site, the local magnetic moment around this atom will be smaller than the others. Consequently, the different charge ordering at the Fe sites also breaks the symmetry of the system, allowing FIM configurations to be the ground state.

Figure 3 depicts the variation in the total energy of the system for different magnetic configurations and for different number of holes, in which Fig. 3(a) is for the neutral charge case, where no holes were inserted. In each case, we forced the supercell total magnetic moment to a specific value and let the magnetic moment on each Fe site relax to the lowest-energy configuration. When the total moment is zero, the interaction between the Fe atoms is AFM. When the total moment is 10, the configuration is FM. We find that for the neutral-charged system, the AFM state has the lowest energy. Figure 3(b) shows the results for a similar case, except that one hole is inserted into the system. As we can see, the most stable magnetic configuration has a FIM phase with total magnetic moment equal to $1\mu_B$/cell. In the ground state, one Fe atom has a local magnetic moment equal to $3.5\mu_B$ and the other equal to $-3.0\mu_B$ (see Table I). In this case, both the AFM (m_T=0) and the FM (m_T=9) phases have higher energies.

We have also calculated the magnetic stability as a function of hole concentrations. At each hole concentration, we search for the ground state by calculating the total energies of the FM, AFM, and FIM phases as a function of the total magnetic moment. The calculated results are shown in Table I, where the energy difference between different phases and the local moments is presented. For all the configurations, we find that the global minimum has always a FIM configuration with the total magnetic moment equal to the number of holes added, i.e., when one hole is inserted, the total magnetic moment is $1\mu_B$. When two holes are inserted, the total magnetic moment is $2\mu_B$. As more holes are inserted into the system, the total magnetic moment and, consequently, the magnetization, increases. This is exactly opposite to what happens in other conventional FM DMS systems such as GaAs:Mn and ZnTe:Cr,[20] where adding holes reduces the electron occupation in the majority-spin channel, thus, reducing the total magnetic moment. This difference between the FM and FIM systems provides an opportunity to distinguish the FIM from FM systems in experimental measurements.

The unexpected appearance of FIM in GaN:Fe can be

TABLE I. Relative energies and magnetic moments (in units of μ_B) for GaN:Fe in different magnetic phases. The magnitude of n_e indicates the number of electrons removed from GaN:Fe per cell. m_T is the total magnetic moment in the supercell, while m_1 and m_2 indicate the local moments on the two Fe atoms. The relative energies are given with respect to the most stable configuration with the same n_e.

n_e	State	m_T	m_1	m_2	Relative energy (eV)
0	AFM	0	3.6	−3.6	0.0
0	FM	10	3.7	3.7	0.445
−1	AFM	0	3.3	−3.3	0.006
−1	FIM	1	3.5	−3.0	0.0
−1	FM	9	3.4	3.4	0.141
−2	AFM	0	2.9	−2.9	0.063
−2	FIM	2	3.3	−1.8	0.0
−2	FM	8	3.2	3.2	0.113
−3	AFM	0	2.3	−2.3	0.093
−3	FIM	3	3.2	−0.8	0.0
−3	FM	7	2.8	2.8	0.228

understood through the phenomenological Stoner model.[21,22] In this model, a material is expected to show a net magnetization when the Stoner criteria are satisfied; that is, $D(\epsilon_f)J \geq 1$, where $D(\epsilon_f)$ is the density of states at the Fermi energy and J is the Stoner parameter, which is large for the pd-hybridized nitrides.[23] When the system has no holes, the $D(\epsilon_f)$ is zero and, hence, the system should not have a net magnetic moment, i.e., the AFM phase is stable. When one or two holes are present in the GaN supercell with two substitutional Fe atoms, the calculated total and partial densities of states [Fig. 4(a)] have a large density of states at the Fermi level for the AFM phase and, hence, the system should not be stable at the AFM phase, which is verified by our calculations. Then, for one or two holes, the system should be FM or FIM. For GaN:Fe, as mentioned above, the superexchange is larger than the double exchange, which favors an antiparallel spin configuration; however, it should lead to a net magnetization according to the Stoner criteria and, hence, the FIM phase should be the most stable.

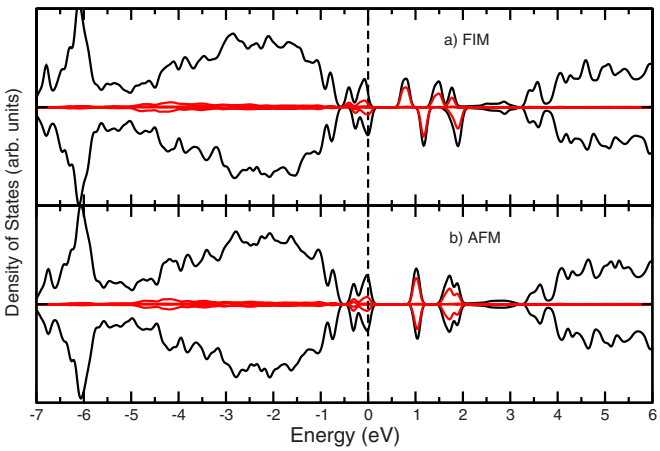

FIG. 4. (Color online) Total (black) and projected (red) densities of states for GaN doped with two Fe atoms and one hole for different magnetic configurations. (a) is ferrimagnetic and (b) is antiferromagnetic.

It is interesting to notice that in this GaN:Fe system, the AFM phase is always more stable than the FM phase, even with the inclusion of holes. This can be understood by using the band coupling model.[18] When the magnetic ion d levels are located within the band gap of the semiconductor, the stable magnetic configuration depends on the competition between the direct exchange and superexchange terms. The former stabilizes FM configurations, and the latter stabilizes the AFM configurations. For fully occupied or fully empty bands, the direct exchange term is zero. When holes are inserted, the local magnetic moment decreases. The reduced exchange splitting causes the empty d levels to move down in energy [see Fig. 2(b)]. This increases the superexchange interaction between the Fe d orbitals, thus, stabilizing the AFM configuration. Our numerical calculations show that for GaN:Fe with hole doping, the superexchange interaction is always stronger than the direct exchange; thus, the AFM configuration is always lower in energy than the FM one.

Some nominally ferromagnetic DMS systems often show magnetic moments that are much smaller than what is expected by Hund's rules. For example, Mn has a half-filled $3d$ shell and, according to the Hund's rule, free Mn atom has a magnetic moment of $5\mu_B$. When Mn substitutes on the cation site in a ferromagnetic III-V semiconductor, each Mn is expected to contribute with $4.0\mu_B$ to the total magnetization ($5.0\mu_B$/Mn for the substitution in a ferromagnetic II-VI semiconductor). However, experimental studies have reported magnetization as low as $2\mu_B$/Mn for GaAs:Mn with Mn concentration of about 8.5%.[24] To explain the low magnetization in the DMS systems, several models have been proposed. For example, it has been suggested that interstitial Mn atoms can easily form in p-type GaAs:Mn.[25] These interstitial Mn_i atoms behave as donors and couple with the substitutional Mn_{Ga} by antiferromagnetic interactions. Consequently, the formation of those Mn_{Ga}-Mn_i-Mn_{Ga} complexes leads to the reduction in the total magnetic moment per magnetic ion. It has also been shown that low magnetic moments can occur in systems, such as heavily doped GaN:Mn, in which the exchange splitting of the transition-metal impurity

levels is smaller than the crystal-field splitting; thus, a charge transfer from the majority spin to the minority-spin channels can occur, resulting in a low-spin configuration.[19,26]

In this Rapid Communication, we present a type of phenomena that could be responsible for the reduced magnetization in a nominally ferromagnetic DMS. To show that our findings are present in other semiconductor systems, we performed also calculations for AlN:Fe. We found the same trends also for AlN:Fe, i.e., the FIM phase has the lowest energy under hole doping. Consequently, the FIM configurations can easily be used to explain the low magnetic moments observed in some diluted magnetic semiconductors.[27]

In conclusion, we have observed and explained the existence of an unusual type of magnetic phase in DMS, i.e., the ferrimagnetic phase. This configuration occurs due to the increased superexchange interaction between the magnetic ions, the strong localization of the partially occupied Fe *pd* hybridized orbitals, and the associated large exchange interaction parameter for these states. We propose that this unusual behavior could be responsible for the observation of low magnetic moments in several DMS samples.

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