

Giant Magnetic Moments of Nitrogen-Doped Mn Clusters and their Relevance to Ferromagnetism in Mn-Doped GaN

B. K. Rao and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

(Received 24 April 2002; published 14 October 2002)

Calculations based on density-functional theory show that the stability and magnetic properties of small Mn clusters can be fundamentally altered by the presence of nitrogen. Not only are their binding energies substantially enhanced, but also the coupling between the magnetic moments at Mn sites remains ferromagnetic irrespective of their size or shape. In addition, these nitrogen-doped Mn clusters carry giant magnetic moments ranging from $4\mu_B$ in MnN to $22\mu_B$ in Mn_5N . It is suggested that the giant magnetic moments of Mn_nN clusters may play a key role in the ferromagnetism of Mn-doped GaN which exhibit a wide range (10–940 K) of Curie temperatures.

DOI: 10.1103/PhysRevLett.89.185504

PACS numbers: 61.46.+w, 36.40.Cg, 75.50.Pp

Among all the elements in the $3d$ transition metal series, manganese is unique as an atom, cluster, crystal, or impurity. In this Letter, we show that the properties of small Mn clusters can be dramatically altered by introducing nitrogen. For example, otherwise weakly bound Mn clusters can bind strongly, their ferrimagnetic coupling could transform into ferromagnetic coupling resulting in giant magnetic moments, and the sensitivity of magnetic moments to cluster geometry can disappear. In addition, the N doped Mn clusters with their giant moments could play a major role in the observed ferromagnetism of Mn-doped GaN.

The atomic configuration of Mn is characterized by a half-filled $3d$ and filled $4s$ shell, namely, $3d^54s^2$. The large energy gap (~ 8 eV) between $3d^5$ and $4s^2$ prevents significant s - d hybridization in clusters and crystals. Consequently, the chemistry of Mn is influenced by the filled $4s$ shell and Mn atoms do not bind strongly with each other. As a matter of fact, Mn_2 is a weakly bonded dimer with a binding energy [1] of 0.1 ± 0.1 to 0.56 ± 0.26 eV. Similarly, the cohesive energy of bulk Mn is the least among the $3d$ -transition metal elements. However, as an electron is removed from Mn_2 , the resulting cation, namely Mn_2^+ , binds strongly [2] and its interatomic distance of 3.06 \AA is shorter than that of its neutral dimer, namely 3.4 \AA . In contrast, the interatomic distances in bulk Mn vary between 2.25 and 2.94 \AA . As Mn atoms begin to form clusters, their interatomic distances are around 2.9 \AA and their binding energy per atom remains small, namely ~ 1.0 eV/atom.

The magnetic properties of Mn as clusters or crystals are also unique and are governed by their $3d$ electrons. The half-filled $3d$ shell, according to Hund's rule, yields an atomic magnetic moment of $5\mu_B$. The magnetic moments of Mn_2 isolated in rare gas matrix are coupled antiferromagnetically [3] while Mn_2^+ is ferromagnetic with a total magnetic moment of $11\mu_B$. Small clusters of Mn containing up to five atoms and isolated in matri-

ces exhibit ferromagnetic coupling with a magnetic moment of $5\mu_B$ /atom [3]. As clusters become large, the coupling between Mn atoms becomes ferrimagnetic [4], and the net magnetic moments/atom are significantly smaller than that in the free atom. This has been confirmed in recent experiments [5], where Mn clusters containing 11 to 100 atoms carry magnetic moments which are less than $1.5\mu_B$ /atom.

As an impurity in semiconductors, Mn also exhibits unique properties. For example, recent discovery of ferromagnetism [6] in Mn-doped InAs and GaAs and subsequent theoretical prediction [7] that the Curie temperature, T_C , of Mn-doped GaN could be as high as the room temperature have created a lot of interest in the study of dilute magnetic semiconductors. In addition to the scientific interest in a fundamental understanding of the origin of ferromagnetism in these systems, the studies are driven by the potential technological merit of spin injection into wideband gap materials [8]. Different experimental techniques have been tried and T_C ranging from 10 to 940 K have been reported. For example, Overberg *et al.* [9] reported a T_C between 10 and 25 K in GaN samples containing 7% Mn. Reed *et al.* [10] have been able to achieve a T_C of 288–370 K by varying the growth and annealing conditions of Mn-doped GaN. Recently, Sonoda *et al.* [11] succeeded in incorporating up to 9% Mn in GaN and suggested a T_C of 940 K. The reasons behind such a wide variation in the T_C are not known. Clearly, the growth conditions are important as is the proper characterization of the sample. In this connection, it is interesting to note that Overberg *et al.* [9], by using only the Mn cell and the N plasma under similar conditions, were able to grow samples that showed x-ray diffraction peaks corresponding to the Mn_4N stable phase. This phase is known to be ferromagnetic [12] with a T_C as high as 745 K. Overberg *et al.* [9], however, ruled out the possibility of the existence of Mn_4N in the GaMnN film. We wonder if it is possible, under suitable

growth conditions, to induce clustering of Mn atoms, stabilize their ferromagnetic phase, and retain a large value for their individual magnetic moments—all at the same time.

In this Letter, we show that this may indeed be possible. We find that the binding energy of Mn clusters can be substantially enhanced by N atoms by having their hybridized s - d electrons bond with the p electrons of N. This stabilization is accompanied by ferromagnetic coupling between the Mn atoms which, in turn, are antiferromagnetically coupled to N atoms. This N mediated ferromagnetic coupling also gives rise to giant magnetic moments of Mn_xN clusters with total magnetic moments of $4\mu_B$, $9\mu_B$, $12\mu_B$, $17\mu_B$, and $22\mu_B$ for $x = 1-5$, respectively. We also suggest that these giant “cluster magnets” may play a significant role in the observed ferromagnetism in Mn-doped GaN semiconductors. In the following, we give a brief outline of our theoretical procedure, a discussion of the results based on the bonding characteristics, and its relevance to our understanding of the origin of ferromagnetism in dilute magnetic semiconductors.

The calculations are done using the molecular orbital theory where we represent the atomic orbitals of Mn and N atoms with the LANL2DZ Gaussian basis available in the GAUSSIAN98 code [13]. The accuracy of this basis set has been tested [2] in small Mn clusters earlier against a more elaborate basis involving all electrons augmented with diffuse functions. While the equilibrium geometry and the interatomic distances do not differ, the binding energy/atom obtained using the LANL2DZ basis is somewhat overestimated compared to that using the all-electron basis. However, the systematics, i.e., the energy gain [2] in adding an atom to an existing cluster, remains relatively unaffected. In this work, the total energies for a given cluster geometry are computed using the density-functional theory. The exchange-correlation contribution to the potential is treated using the generalized gradient approximation (GGA). We have used the Becke-Perdew-Wang form (BPW91) [13] for the GGA. The energetics of Mn_x clusters have been previously studied using different forms of GGA. With the exception of Mn_2 , the results are not sensitive to these choices. The geometries of the clusters are optimized without symmetry constraint by calculating the forces at every atom site and relaxing the geometry until the forces vanish. The threshold of these forces was set at 1.02×10^{-4} a.u./Bohr. Several initial structures were tried to ensure that the globally optimized geometry does not correspond to a local minimum. For each cluster, we have also examined various spin multiplicities, $M = 2S + 1$ to determine the magnetic moment of the ground state configuration.

In Fig. 1, we give the ground state geometries of Mn_xN ($x \leq 5$) clusters. No isomers lying close in energy to the ground state of Mn_xN ($x \leq 3$) were found. For Mn_4N , we found two isomers (Mn₄ tetrahedron encapsulating N

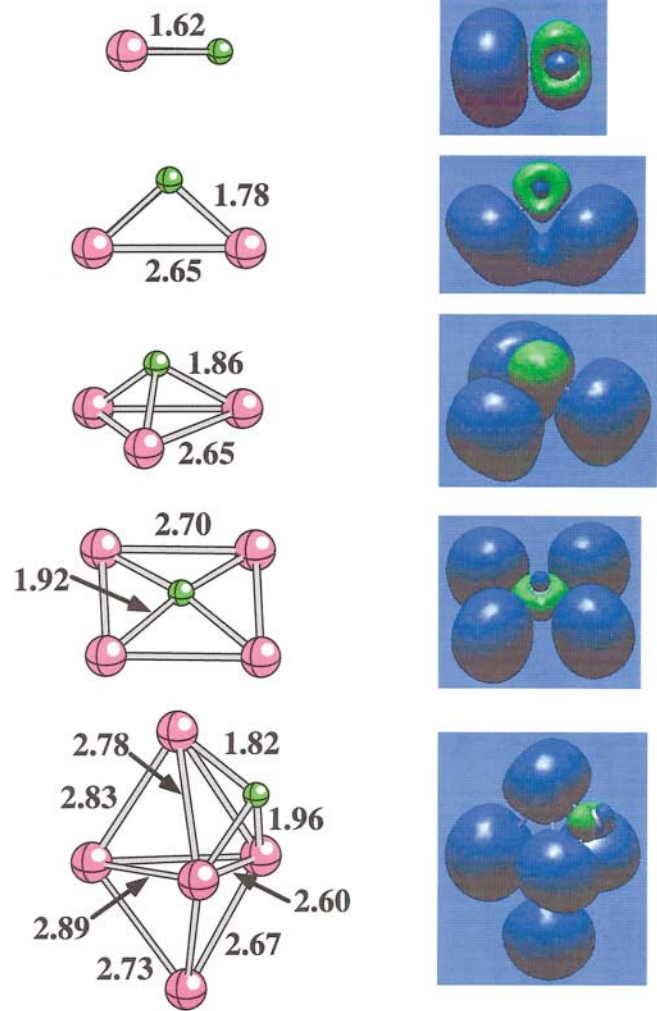


FIG. 1 (color). Geometries of Mn_xN (left column) clusters in their ground states. The bond lengths are given in Å. The spin density surfaces corresponding to 0.005 a.u. for these clusters are plotted in the right column. The green surfaces represent negative spin densities around the N site while the blue represents positive spin density around Mn sites.

atom and Mn_4 tetrahedron with N at a face cap) whose energies lay 0.10 and 0.30 eV, respectively, above its ground state structure. For Mn_5N , we identified three isomers (square pyramid Mn_5 with N at a triangular face cap, square pyramid Mn_5 with N at the square face cap, and triangular bipyramid Mn_5 encapsulating the N atom) whose energies lay 0.54, 0.72, and 0.94 eV above the ground state. The geometries of these isomers along with their magnetic properties will be presented elsewhere. It is sufficient to mention here that the preferred spin multiplicities of the isomers were the same as their ground state structures. We note that the bond length of the MnN dimer is rather small, namely 1.62 Å. We have repeated the calculations of the MnN dimer using an all-electron (6-311G**) basis and have obtained the optimized bond length of 1.59 Å. As more Mn atoms are added, the

structures assume two- and three-dimensional shapes but the Mn-N distances change little from that in the dimer. The Mn-N-Mn bond angle in Mn_2N is 96.1° and results from the interaction of the p orbitals of N with s - d hybridized orbitals of Mn. This nearly 90° bond angle between Mn-N-Mn remains a guiding rule for ground state geometries as we proceed to larger Mn_xN clusters. For example, the angles between Mn-N-Mn in the Mn_3N cluster are all 90.7° and the structure is three-dimensional. The three Mn atoms form an equilateral triangle with the N atom 1.06 \AA above the plane. In Mn_4N , these angles are 89.1° as the N atom lies only 0.24 \AA above the Mn_4 square plane. The ground state structure of Mn_5N is that of a triangular bipyramid of Mn atoms with one of the triangular faces capped by the N atom. The Mn-Mn distances in all these clusters are about $2.8 \pm 0.1 \text{ \AA}$ which are significantly shorter than the 3.4 \AA bond length of a Mn_2 dimer. We recall that, in bulk Mn, the interatomic distances vary between 2.25 and 2.95 \AA . The Mn-N distances in Fig. 1 vary between 1.62 and 1.96 \AA . We should point out that, in the epitaxial film [14] of Mn_3N_2 , the Mn-N distance is 2.1 \AA and the Mn-N-Mn angle is 90° .

The energetics of the clusters can be analyzed from the total energies of Mn_xN and Mn_x clusters corresponding to their respective ground state geometries. We have computed the atomization energies/atom, E_b^0 , of Mn_x clusters necessary to dissociate the cluster into individual atoms. We have also calculated the energy gain, Δ in adding a Mn atom to an existing Mn_{x-1}N cluster. Similarly, Δ^0 corresponds to the energy gain in adding a N atom to a Mn_x cluster. These are defined as follows: $E_b^0 = -[E(\text{Mn}_x) - xE(\text{Mn})]/x$, $\Delta^0 = -[E(\text{Mn}_x\text{N}) - E(\text{Mn}_x) - E(\text{N})]$, and $\Delta = -[E(\text{Mn}_x\text{N}) - E(\text{Mn}_{x-1}\text{N}) - E(\text{Mn})]$.

We first discuss the energetics of the pure Mn_x clusters, which also have been studied by previous authors [2,15]. These calculations, using different levels of exchange-correlation functionals and basis sets, have reported binding energies of Mn_2 ranging from 0.06 to 1.5 eV . Mn_2 is a weakly bound dimer because of the filled $4s$ shell of Mn, as is evident from the low experimental binding energy [1]. Therefore, we cannot believe that density-functional theory can quantitatively account for the finding in Mn_2 . The situation improves significantly in Mn_2^+ and larger clusters. As the s and d electrons begin to hybridize, the sensitivity of binding energies to the choice of GGA forms and basis sets begins to disappear. Nevertheless, the binding is still weak as atomization energies, E_b^0 of Mn_3 , Mn_4 , and Mn_5 , are only 0.87 , 1.16 , and 1.22 eV/atom , respectively.

As the N atom is added, the binding energies of Mn_xN clusters improve significantly. To demonstrate this we examine the energy gained, Δ^0 , in adding a N atom to a Mn_x cluster. We find Δ^0 for Mn_x to be 3.08 , 4.79 , 5.31 , 5.15 , and 5.61 eV , respectively, for $x = 1-5$. This enhancement in bonding due to N can be understood clearly by

examining the bonding in Mn_2N versus that in Mn_2 . As noted earlier, the lack of hybridization between the s and the d electrons due to the filled $4s$ shell of Mn prevents Mn_2 from forming a strong bond. However, as a N atom is attached, the $4s^2$ electrons of Mn interact with the $2p^3$ electrons of N resulting in a strong bond. The charge transfer from Mn to N leaves the two Mn atoms in the charged state and it is well known [2] that Mn_2^+ is a strongly bound dimer cation.

The next question is how many Mn atoms can be bound to a single N atom. For this, it is instructive to analyze the value of Δ , the energy gained in adding a Mn atom to a Mn_{x-1}N cluster which are 3.08 , 2.91 , 1.94 , 1.87 , and 1.67 eV , respectively, for $x = 1-5$. Note that the energy gain, Δ , decreases as the number of Mn atoms in the cluster increases. However, even for Mn_5N , it is still significant, namely 1.67 eV . Thus, it is energetically favorable to certainly add at least five Mn atoms to a single N and this number could easily go further up. Other factors such as available space may also play an important role in determining the number of Mn atoms that could cluster around a single N site in GaN.

Now we address the next important issue: Are these N doped Mn clusters magnetic and, if so, what are their magnetic moments? As mentioned earlier, this was obtained by minimizing the total energy of each cluster with respect to all spin multiplicities ($M = 2S + 1$). The total magnetic moments of Mn_xN clusters corresponding to the ground state geometries are 4 , 9 , 12 , 17 , and $22\mu_B$, respectively, for $x = 1-5$. The magnetic moments of MnN and Mn_2N can be represented by the formula, $(5x - 1)\mu_B$, while those of Mn_3N , Mn_4N , and Mn_5N can be expressed by the formula $(5x - 3)\mu_B$. Here, x denotes the number of Mn atoms. Note that in the latter structures N is bonded to three or four Mn atoms. These large magnetic moments arise from ferromagnetic coupling between the moments at Mn sites. We note that the Mn moments are coupled antiferromagnetically with the magnetic moment at N site. The nature of this coupling is determined from the Mulliken population analysis of spins as well as by mapping the spin density distribution. The Mulliken analysis yields a spin magnetic moment of $4.30\mu_B$ at the Mn site and $-0.30\mu_B$ at the N site in MnN dimer. In Mn_2N , the magnetic moments at Mn and N sites are $4.54\mu_B$ and $-0.08\mu_B$, respectively. In the Mn_3N cluster, the Mulliken analysis yields a moment of $4.12\mu_B$ at each Mn site and $-0.36\mu_B$ at the N site. Similarly, the $17\mu_B$ moment of Mn_4N results from $4.28\mu_B$ at each of the Mn sites and $0.10\mu_B$ at the N site. The magnetic moments in Mn_5N are $4.41\mu_B$ in the average at the Mn and $-0.07\mu_B$ at the N sites. These couplings can be better seen in a plot of the spin density surfaces. In Fig. 1, we show these surfaces corresponding to a value of 0.005 a.u. Here the blue color represents positive and green represents negative spin densities. Note that these results are consistent with the above Mulliken population analysis.

From these cluster studies, one can, therefore, conclude that N not only induces the clustering of Mn atoms but also causes their magnetic moments to align ferromagnetically. The total magnetic moments of these clusters can be very large due to these interactions. What relevance can this have to the ferromagnetism of Mn-doped GaN and the variety of Curie temperatures that have been reported? We have carried out separate studies [16] of magnetic coupling between Mn atoms in GaN by studying clusters of $(\text{GaN})_x\text{Mn}_2$ as well as crystals of Mn-doped GaN. In the latter case, two Mn atoms were substituted at different Ga sites using a 32 atom supercell. We have found the coupling to be ferromagnetic both in clusters and crystals with magnetic moments of $\sim 3.5\mu_B$ at the Mn sites. Thus, Mn in GaN, whether forming clusters or substituted at Ga sites, tend to couple ferromagnetically.

We believe that the clustering of Mn around N could be responsible for the ferromagnetism of Mn-doped GaN as well as the large variation in the Curie temperatures of different samples. This could arise from having N induced Mn clusters of different sizes in samples grown under different conditions. Note that the Curie temperature of Mn_4N is 745 K. Thus, if Mn-doped GaN, under suitable growth conditions, could contain Mn_4N clusters, then their large magnetic moment, namely $17\mu_B$, could give rise to a large Curie temperature. On the other hand, if these clusters are small or Mn replaces isolated Ga atoms, the small magnetic moment would then yield low Curie temperatures. This analysis suggests the importance of the growth mechanism. It is important to understand if clusters of Mn around N are, indeed, present in samples exhibiting large Curie temperature. EXAFS experiments could prove to be very useful in this regard. It may also be interesting to dope Mn into porous GaN which contains many defect sites and, thus, may precipitate Mn clustering.

This study also suggests that further investigations of clustering of Mn around As and oxygen may be useful. The former could illustrate if such clustering could lead to ferromagnetism of Mn-doped GaAs while the latter could suggest if Mn-doped ZnO may be a candidate, like Mn-doped GaN, for dilute magnetic semiconductors. Independent gas phase experiments involving Mn clustering in a N-seeded chamber can yield direct information on the magnetic character of Mn_xN clusters. The ability to change magnetic coupling of Mn that carries a large atomic magnetic moment by chemical means would, in-

deed, be exciting. We hope that our study will stimulate such experiments.

We thank Dr. G. P. Das for bringing to our attention the work of Overberg *et al.* [9] which prompted this investigation. We are grateful to Dr. A. K. Rajagopal for many stimulating discussions and a critical reading of the manuscript. This work was supported in part by a DURINT grant from the Office of Naval Research. B. K. R. and P. J. also received support from a grant (DEFG02-96ER45579) by the Department of Energy.

-
- [1] M. D. Morse, Chem. Rev. **86**, 1049 (1986).
 - [2] S. K. Nayak, B. K. Rao, and P. Jena, J. Phys. Condens. Matter **10**, 10863 (1998); S. K. Nayak and P. Jena, Chem. Phys. Lett. **289**, 473 (1998).
 - [3] R. J. Van Zee and W. Weltner, Jr., J. Chem. Phys. **89**, 4444 (1988); C. A. Bauman, R. J. Van Zee, S. Bhat, and W. Weltner, Jr., J. Chem. Phys. **78**, 190 (1983).
 - [4] S. K. Nayak, M. Nooijen, and P. Jena, J. Phys. Chem. A **103**, 9853 (1999).
 - [5] M. Knickelbein, Phys. Rev. Lett. **86**, 5255 (2001).
 - [6] H. Ohno, H. Munekata, T. Penney, S. Von Molnar, and L. L. Chang, Phys. Rev. Lett. **68**, 2664 (1992); H. Ohno *et al.*, Appl. Phys. Lett. **69**, 363 (1996).
 - [7] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
 - [8] Y. Ohno, Science **281**, 951 (1998); Y. Ohno, D. K. Yound, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature (London) **402**, 790 (1999).
 - [9] M. E. Overberg, C. R. Abernathy, and S. J. Pearton, Appl. Phys. Lett. **79**, 1312 (2001).
 - [10] M. L. Reed, N. A. El-Masry, H. H. Stadelmaier, M. K. Ritums, M. J. Reed, C. A. Parker, J. C. Roberts, and S. M. Bedair, Appl. Phys. Lett. **79**, 3473 (2001).
 - [11] S. Sonoda, S. Shimizu, T. Sasaki, Y. Yamamoto, and H. Hori, cond-mat/0108159, 2001.
 - [12] A. F. Guillermet and G. Grimvall, Phys. Rev. B **40**, 10582 (1989).
 - [13] GAUSSIAN98, Revision A.7, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA, 1998. Also see references therein.
 - [14] H. Yang, H. Al-Brithen, A. R. Smith, J. A. Borchers, R. L. Cappelletti, and M. D. Vaudin, Appl. Phys. Lett. **78**, 3860 (2001).
 - [15] M. R. Pederson, F. Reuse, and S. N. Khanna, Phys. Rev. B **58**, 5632 (1998); N. Desmarais, F. A. Reuse, and S. N. Khanna, J. Chem. Phys. **112**, 5576 (2000); A. Terasaki, A. Matsushita, K. Tono, R. T. Yadav, T. M. Briere, and T. Kondow, J. Chem. Phys. **114**, 9367 (2001).
 - [16] G. P. Das, B. K. Rao, and P. Jena Phys. Rev. B (to be published).