

## Emergence of antiferromagnetic ordering in Mn clusters

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(Received 6 September 2002; published 20 June 2003)

First-principles density-functional-theory investigations of small  $Mn_n$  ( $n=2-7,13$ ) clusters reveal a competition between ferromagnetic and antiferromagnetic ordering of atomic magnetic moments. For smaller sizes ( $n \leq 6$ ), this competition results in a near degeneracy between the two types of orderings, whereas AF arrangements are clearly favored for larger clusters. The calculations thus predict a size-dependent transition in the magnetic ordering of Mn clusters.

DOI: 10.1103/PhysRevA.67.061202

PACS number(s): 36.40.Cg, 61.46.+w, 75.25.+z

The study of magnetism in transition-metal clusters is motivated largely by the desire to understand how magnetic properties change when the dimensions of a material are reduced to nanometer length scales, a question of potentially great technological importance. A variety of interesting magnetic behavior has been discovered, ranging from enhanced magnetic moments in clusters of ferromagnetic metals such as Fe [1], to the prediction of net magnetic moments in clusters of nonmagnetic bulk materials [2]. Generally, the magnetic properties of clusters show a dependence on cluster size [3–5] and systematic studies of these systems hold the promise of yielding new insight into magnetic ordering in materials.

Manganese clusters are particularly interesting. An early electron-spin-resonance study [6] on small Mn clusters in an inert matrix suggested ferromagnetic ordering with atomic moments of  $\sim 5\mu_B$ , the Hund's rule value for the free atom. More recently, Stern-Gerlach (SG) molecular-beam experiments [5] were carried out on larger clusters ( $Mn_{11}$ – $Mn_{99}$ ). Analysis of the data assuming superparamagnetic behavior [7] in the clusters found small, but nonzero, average atomic magnetic moments. This result can be interpreted in one of two ways. If ferromagnetic (FM) ordering is assumed, the atoms must all have small individual moments. A second possibility is that the atomic moments remain large, but their orientation flips from site to site, so that the net cluster moments are small. The latter possibility has been found to be the preferred one for small  $Fe_n$  ( $n=2-4$ ) clusters of low spin [8]. This antiferromagnetic (AF) interpretation is compelling, since  $\alpha$ -Mn, the most stable form of bulk manganese, is AF. It is also supported by new density-functional theory (DFT) calculations that found AF solutions to be more stable than FM solutions in intermediate size  $Mn_n$  clusters ( $n=13, 15, 19, \text{ and } 23$ ) [9].

Given these results, it appears that Mn clusters undergo a change in magnetic behavior from FM ordering for the smallest sizes to AF ordering for intermediate sizes and beyond. We address the nature of this transition in this paper. Our DFT calculations on  $Mn_n$  clusters ( $n=2-7,13$ ) show that the smaller clusters are characterized by a close competition between FM and AF solutions. FM ordering is clearly favored for  $n=2$  and 4, but AF and FM states are nearly degenerate for  $n=3, 5, \text{ and } 6$ . A radical change occurs at  $n=7$  where the AF solution is much more stable than the FM. A similar behavior is found for  $n=13$ , suggesting that AF

ordering is a general feature of the larger clusters. Interestingly, we find that like atomic spins tend to congregate in the AF clusters, reflecting a competition between FM ordering and AF ordering even in these clusters. In the following paragraphs, we discuss our calculations and present a simple picture of the bonding in  $Mn_n$  clusters that rationalizes their magnetic behavior.

The DFT calculations were performed using the generalized gradient approximation (GGA) [10]. The all-electron formalism features large Gaussian basis sets for the Mn atoms and a robust numerical integration scheme [11,12]. Gradient-based geometry optimizations were terminated when the largest atomic force fell below 0.001 hartree/bohr. Combining this relaxation scheme with carefully adjusted integration mesh parameters, we can reliably distinguish energy differences as small as 0.03 eV (0.001 hartree) between different structures.

In previous theoretical investigations of small  $Mn_n$  clusters [13,14], the geometrical parameters and the net spin of the clusters were optimized in the search for the optimal states without explicit consideration of the relative orientation of atomic moments. The lowest-energy clusters found in this way were FM, leading to the conclusion that  $Mn_n$  with  $n \leq 8$  are FM. However, given the possibility of AF ordering in these clusters, the relative orientations of the individual atomic spins in a cluster must also be considered in the optimization process. We find that for a given structure, several different, magnetically stable [15] arrangements of the atomic spins can exist for the same total spin, each corresponding to a different total energy. We, therefore, explicitly consider *all possible* relative orientations of atomic spins in our search procedure.

To determine the optimal structures, we considered the lowest-lying isomers found previously in unbiased searches of the energy surfaces for Fe clusters [16] for further optimization. For each arrangement, we considered several different total spins, around  $5(N_\uparrow - N_\downarrow)$ , where  $N_\uparrow(N_\downarrow)$  is the number of atoms with spin-up (down) atomic moments and all inequivalent relative orientations of atomic moments associated with each total spin. Local magnetic ordering within the cluster is obtained by integrating the spin density within atom centered spheres of radius 1.18 Å—the covalent radius of Mn.

The case of  $Mn_6$  illustrates the complexity of the full optimization process. Two structural isomers were studied,

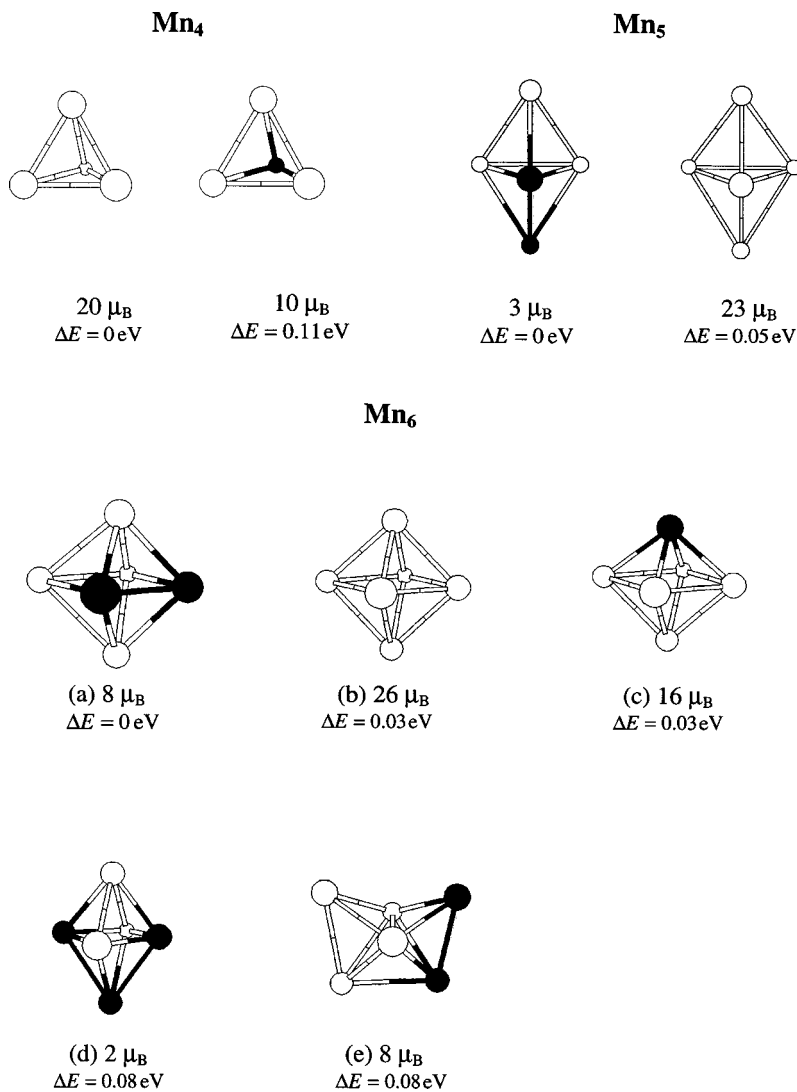


FIG. 1. Atomic spin ordering, optimal total spin, and relative energies for FM and AF isomers of Mn<sub>4</sub>, Mn<sub>5</sub>, and Mn<sub>6</sub>. White atoms have positive (up) and black atoms have negative (down) magnetic moments.

the octahedron and a bicapped tetrahedron. The former has only six independent arrangements of the atomic moments because of its high symmetry, while the latter has 19. In Fig. 1, we show the structures, net moments, and spin arrangements of the solutions that lie within 0.08 eV of the ground state. The three lowest-energy structures are almost degenerate, possess the same basic geometry, with small differences in the bond lengths, but have different total spins and relative orientations of atomic spins ranging from a FM ordering (structure *b*) to an AF ordering in structures *a* and *c*. Generally, we find the bonds between atoms of opposite spin to be somewhat shorter (2.5–2.7 Å) than the bonds between atoms with the same spin (2.6–2.8 Å). Two higher-energy structures *d* and *e* represent additional higher-energy AF solutions.

To investigate the transition in the magnetic behavior of Mn clusters, we first reexamined the smaller clusters that were studied previously within the DFT [13,14]. For both Mn<sub>2</sub> and Mn<sub>3</sub>, there are only two possible orientations of the atomic spins. For Mn<sub>2</sub> the optimal state is FM, with total spin  $10\mu_B$ . The AF arrangement has no net spin and lies 0.44 eV above the FM state. Mn<sub>3</sub> is triangular and the lowest-spin arrangement is FM, with a net moment of  $15\mu_B$ ;

however, the AF state with net moment  $5\mu_B$  lies only 0.05 eV higher. These results agree with those of the previous calculations [13,14].

Figure 1 shows our lowest-energy solutions for Mn<sub>4</sub> and Mn<sub>5</sub>. The tetrahedron is the optimal geometry for Mn<sub>4</sub> and it has three possible inequivalent spin arrangements. We find that the FM structure with net spin of  $20\mu_B$  is the ground state, in agreement with the earlier calculations [13,14]; however, the AF structure with one minority spin moment and a net spin of  $10\mu_B$  lies only 0.11 eV higher in energy. The third possible magnetic ordering (not shown in Fig. 1) has zero net spin and lies 0.24 eV above the FM ground state.

In the case of Mn<sub>5</sub>, we examined a triangular bipyramid and a square pyramid. Both geometries have six inequivalent atomic spin arrangements. We find that the triangular bipyramid is generally more stable, independent of the specific spin arrangement. The lowest-energy solution is AF with  $N_{\uparrow}=3$  and a net spin of  $3\mu_B$ . The FM solution with net spin  $23\mu_B$  lies 0.05 eV above the ground state. Other spin arrangements including two low-lying AF solutions—one with a net spin of  $13\mu_B$ , 0.03 eV higher in energy, and a second with a spin of  $3\mu_B$ , 0.05 eV higher in energy—are not shown.

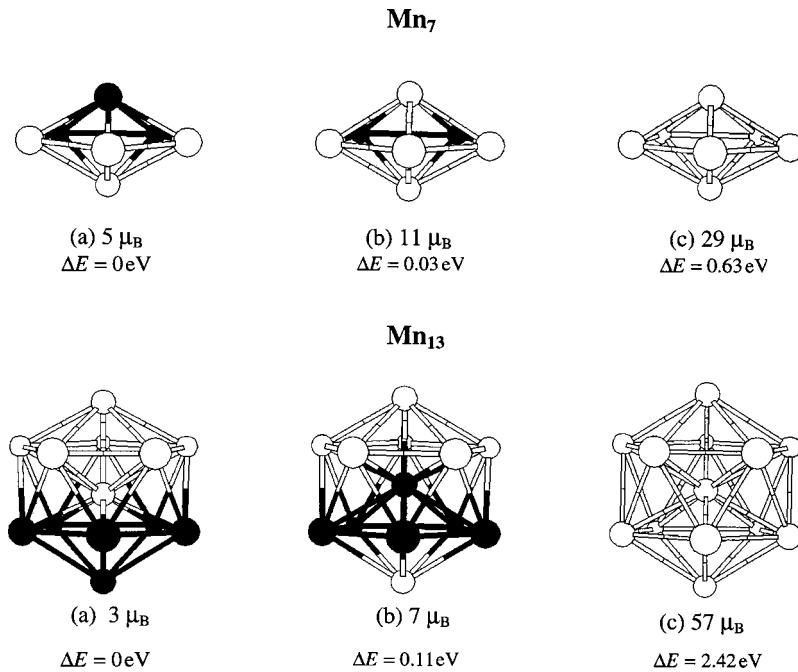


FIG. 2. Atomic spin ordering, optimal total spin, and relative energies of low-lying isomers of Mn<sub>7</sub> and Mn<sub>13</sub>. White atoms have positive and black atoms have negative magnetic moments.

We investigated the pentagonal bipyramid and the capped octahedron for Mn<sub>7</sub>. The former structure has 12 inequivalent atomic spin arrangements, while the latter has 20. The two lowest-energy solutions (see Fig. 2) have the pentagonal bipyramid structure and are AF. The ground state has  $N_{\uparrow} = 4$  and a net spin of  $5 \mu_B$ . The next lowest cluster has  $N_{\uparrow} = 5$  and a net spin of  $11 \mu_B$  and lies 0.03 eV higher. The lowest capped-octahedron solution for Mn<sub>7</sub> (not shown in Fig. 2) has  $N_{\uparrow} = 4$  and a net spin of  $3 \mu_B$  and lies 0.35 eV above the ground state.

Unlike the smaller clusters, for which FM and AF solutions are nearly degenerate, in Mn<sub>7</sub> the FM solution, with a net spin of  $29 \mu_B$ , lies high above the ground state. As shown in Fig. 2, it has a relative energy of 0.63 eV. In fact, this structure has the highest energy of all the 12 possible spin arrangements for the pentagonal bipyramid.

The high symmetry of the icosahedral structure for Mn<sub>13</sub> and the presence of a central atom reduces the number of inequivalent combinations of the atomic moments to 50. Figure 3 shows the two lowest-energy AF solutions along with the lowest-energy FM arrangement. Our ground-state structure is identical to that found recently by Briere *et al.* [9]. It has  $N_{\uparrow} = 7$  and a net spin of  $3 \mu_B$ . The next lowest-energy

combination also has  $N_{\uparrow} = 7$ , but the spins of the central atom and the bottom cap atom are switched. This arrangement has an optimal total spin of  $7 \mu_B$ . The energy difference between these AF combinations is only 0.11 eV. The next four solutions are all AF and are essentially degenerate, lying 0.14 eV above the ground state. One of these AF solutions has a total spin of  $1 \mu_B$ , and three have total spin of  $5 \mu_B$ . The relative energy of the FM Mn<sub>13</sub> structure is very high, 2.42 eV (Fig. 2), clearly showing that the FM ordering is not energetically favorable for Mn<sub>13</sub>.

Including the error bars, the net magnetic moment found in the recent SG experiment for Mn<sub>13</sub> corresponds to  $(5-9) \mu_B$ . The low-energy DFT solutions shown in Fig. 2 are in good agreement with this range, although the best structure has a somewhat smaller moment of  $3 \mu_B$ . The difference between theory and experiment may be due to the presence of more than one low-lying magnetic isomer in the experiment.

The pronounced relative stability of AF vs FM solutions for both Mn<sub>7</sub> and Mn<sub>13</sub>, combined with the experimental data showing small net moments for clusters with  $n \geq 11$ , strongly suggests that AF ordering is a general feature in Mn<sub>n</sub> clusters with  $n \geq 7$ , that is, a transition to AF behavior

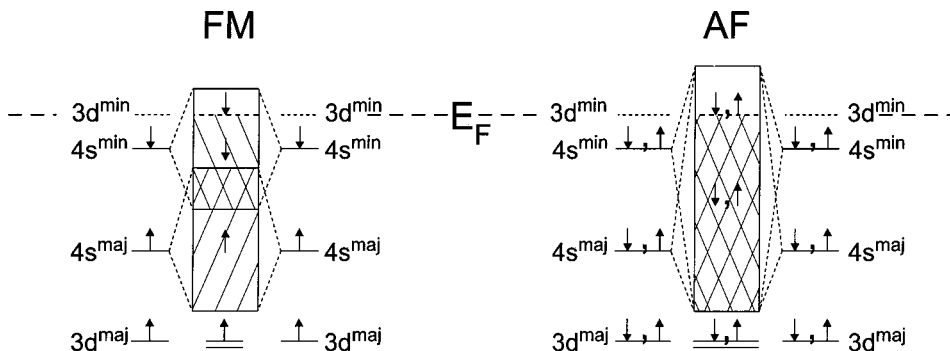


FIG. 3. Schematic bonding diagram for Mn<sub>n</sub>. The solid lines mark the relative positions of majority and minority 4s energy levels in the Mn atom. The shaded areas represent the spread of the 4s energy levels in a cluster due to bonding effects. The dashed line represents the position of the minority 3d level in the atom.

occurs at  $Mn_7$ . This conclusion is supported by new unpublished SG data indicating that small average magnetic moments for  $Mn_n$  extend down to  $n=7-10$  [17]. A striking feature of the AF solutions shown in Figs. 1 and 2 is the strong tendency for like spins to congregate in a cluster. This is particularly clear in  $Mn_{13}$ , where the minority spins are grouped together in one-half of the cluster. A similar grouping is also clearly seen in  $Mn_7$ , where the three minority spin atoms are bonded together on a triangle at the rear of the cluster.

A simple rationale for the magnetic behavior of Mn clusters emerges from the schematic bonding diagrams given in Fig. 3. The positions of the majority and minority  $3d$  and  $4s$  energy levels in free Mn atoms (i.e., neglecting bonding effects) are indicated. The majority spin  $4s$  levels lie somewhat deeper than the minority spin  $4s$  levels due to a deeper exchange potential. The shaded regions represent the energy range spanned by the energy levels of the  $4s$ -derived molecular orbitals. The most bonding states lie near the bottom of these regions, while the most antibonding states lie near the top. The dashed line represents the position of the minority spin  $3d$  levels that are unoccupied in the atoms. In this simple picture, it is assumed that the  $3d$  orbitals have little overlap with other orbitals.

Since the  $4s$  levels are fully occupied in the Mn atom, all the bonding and antibonding levels in  $Mn_n$  would be fully occupied if the minority  $3d$  levels were to lie above the shaded regions in Fig. 3. However, since the minority  $3d$  levels lie within the shaded region, electron transfer from the most antibonding  $4s$  derived states to the minority  $3d$  states lowers the energy. The basic bonding mechanism in both FM and AF clusters therefore involves transferring electrons from the antibonding levels to the minority spin  $3d$  level. The binding energy is equal to the energy difference between these levels in this simplified picture. The situation in the actual DFT calculations is somewhat more complex. For example, the minority  $3d$  levels move up sharply as they are occupied due to the Coulomb repulsion among the highly localized  $d$  electrons, so that, in practice, the highest occupied molecular orbitals (HOMO) have a mixture of  $3d$  and  $4s$  characters, representing a partial transfer of charge.

There is an essential difference between the FM and AF cases in the formation of the  $4s$  manifold of states. In the FM case, the majority electrons on each atom have the same spin orientation. Therefore, the majority and minority  $4s$  orbitals form separate manifolds, with the minority spin states lying, on an average, higher than the majority spin states. In the AF case, the minority spin electrons on a down atom have the same spin as the majority spin electrons on an up atom. Thus, the minority and majority levels can couple in AF clusters. This extra coupling pushes the highest antibonding states up in energy, as shown in Fig. 3, compared to the minority spin manifold in the FM case. This implies greater binding energy for the AF case. Because the highest antibonding states involve mainly the minority  $4s$  orbitals, the  $4s \rightarrow 3d$  electron transfer tends to preserve large moments on individual atoms. This also explains why grouping the atoms of like spin together in the AF solutions is favorable. To get the highest antibonding  $4s$  levels possible, a strong coupling between the minority spin  $4s$  levels lying in the upper part of the manifold is required and occurs when like spin atoms occupy neighboring sites in the clusters.

In this paper, we have described a transition in the magnetic behavior of  $Mn_n$  clusters. By optimizing structural parameters, net spins, and all possible arrangements of atomic magnetic moments, we find that in clusters with  $n < 7$  FM and AF solutions are found to be nearly degenerate, while for larger clusters AF solutions are clearly much lower in energy than the best FM state. Our calculations thus provide an unambiguous AF interpretation of the small net cluster moments observed experimentally for manganese clusters [5,17]. In all the cases, the AF solutions are characterized by a large number of nearly degenerate magnetic isomers. Thus, a painstaking search of various isomers is required to determine the lowest-energy structure. Finally, we present a simple picture of the bonding mechanism of these clusters that explains the relative stability of AF spin arrangements and the clustering of like spins in these clusters.

This work was supported by a State of Michigan REF Grant and by NSF Grant Nos. DMR 9977582 and DMR-RUI 9972333. The authors thank Dr. M. R. Pederson for discussions of our work prior to publication.

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- [1] D.M. Cox, D.J. Trevor, R.L. Whetten, E.A. Rohlfing, and A. Kaldor, *Phys. Rev. B* **32**, 7290 (1985).  
 [2] M. Moseler, H. Häkkinen, R.N. Barnett, and U. Landman, *Phys. Rev. Lett.* **86**, 2545 (2001).  
 [3] I.M.L. Billas, A. Chatelain, and W.A. de Heer, *Science* **265**, 1682 (1994).  
 [4] A.J. Cox, J.G. Louderback, and L.A. Bloomfield, *Phys. Rev. Lett.* **71**, 923 (1993).  
 [5] M.B. Knickelbein, *Phys. Rev. Lett.* **86**, 5255 (2001).  
 [6] C.A. Baumann, R.J. Van Zee, S.V. Bhat, and W. Weltner, Jr., *J. Chem. Phys.* **78**, 190 (1983).  
 [7] S.N. Khanna and S. Linderth, *Phys. Rev. Lett.* **67**, 742 (1991).  
 [8] G.L. Gutsev, *Phys. Rev. B* **65**, 132417 (2002).  
 [9] T.M. Briere, M.H.F. Sluiter, V. Kumar, and Y. Kawazoe, *Phys. Rev. B* **66**, 064412 (2002).  
 [10] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).  
 [11] M.R. Pederson and K.A. Jackson, *Phys. Rev. B* **41**, 7453 (1990).  
 [12] M.R. Pederson, D.V. Porezag, J. Kortus, and D.C. Patton, *Phys. Status Solidi B* **217**, 197 (2000).  
 [13] M.R. Pederson, F. Reuse, and S.N. Khanna, *Phys. Rev. B* **58**, 5632 (1998).  
 [14] S.K. Nayak and P. Jena, *Chem. Phys. Lett.* **289**, 473 (1998).  
 [15] We characterize an arrangement as magnetically stable if the lowest unoccupied molecular orbital of the minority spin lies above the HOMO of the majority spin and vice versa.  
 [16] P. Bobadova-Parvanova, K.A. Jackson, S. Srinivas, M. Horoi, C. Köhler, and G. Seifert, *J. Chem. Phys.* **116**, 3576 (2002).  
 [17] M.B. Knickelbein (unpublished).