Magnetic transition in Mn_n $(n = 2-8)$ clusters

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Theoretical electronic structure studies on Mn_n $(n = 2-8)$ clusters have been carried out using a linear-combination-of-atomic-orbitals–molecular-orbital approach within the density-functional formalism. It is shown that Mn_2 and Mn_3 have energetically close ferromagnetic and antiferromagnetic or frustrated antiferromagnetic solutions. Mn_4, Mn_5, Mn_6, Mn_7, and Mn_8 are all ferromagnetic with moments of 20, 23, 26, 29, and $32\mu_B$. The appearance of ferromagnetic character is shown to be accompanied by bonding between minority d states. The relation between geometry and multiplicity and the possibility of closely spaced multiplet states are discussed. [S0163-1829(98)03333-5]

I. INTRODUCTION

Manganese is a unique $3d$ transition element. It has the lowest bulk modulus and binding energy per atom. It does not crystallize into fcc, bcc, or the hcp lattices but has an α Mn structure containing fifty eight atoms per unit cell which transforms to other structures at different temperatures.[1] The magnetic properties of Mn are equally fascinating. α Mn is antiferromagnetic (AF) while dilute solutions of Mn in Cu lead to spin glass behavior of the Mn moments.[2] On a nanoscale $Mn_{12}O_{12}$ acetate[3] has been found to exhibit quantum tunneling of the spins and is drawing considerable attention. These unusual and interesting magnetic behaviors continue even to the smallest size, namely, pure Mn_n clusters. Electron spin resonance (ESR) (Ref. 4) and absorption spectrum studies[5] show that Mn_2 exists in a Van der Waal (VdW) AF state. However, ESR studies on Mn_n (Ref. 6) clusters in a matrix observe a ferromagnetically coupled cluster with a moment (number of unpaired spins) of $S = 25\mu_B$. The authors of this work stated that this cluster contained more than four atoms but it was unclear whether this cluster was Mn_5 or a larger cluster. Studies on Mn_3 and Mn_4 are not conclusive and it is not clear how the AF to ferromagnetic (FM) coupling evolves as the size is changed. In the remainder of the text we refer to moments (S) in terms of the total number of unpaired electrons.

There have been only limited theoretical studies on Mn_n clusters. In particular the case of Mn_2 has been a source of controversy. The earlier calculations by Nesbet[7] using Hartree-Fock and Heisenberg exchange interaction predicted Mn_2 to have an AF ground state. Subsequent local density calculations[8,9] have, however, found conflicting results ranging from a complete FM ground state with a total moment of $10\mu_B$ to a triplet ground state. For other Mn clusters most calculations[11,12] have assumed fixed geometries and investigated only specific spins. Recently Nayak *et al.* have performed some calculations on small Mn clusters.[10]

In this paper we report what we believe is the first in-depth study of the electronic structure and the magnetism of Mn_n clusters containing 2–8 atoms. The clusters are fully relaxed with respect to all electronic, magnetic, and geometrical configurations. The key issues we want to focus on are the evolution of the ferromagnetism starting from an AF dimer, the possibility of multiple closely spaced magnetic states, and the progression of the structure and bonding. We show that Mn_2 and Mn_3 each have AF and FM solutions which are energetically nearly degenerate but that FM character starts at Mn_4 which has a magnetic moment of $5.0\mu_B$ per atom. As the size of the cluster increases the moment per atom decreases but the clusters definitely retain a FM character. Mn_5, Mn_6, Mn_7, and Mn_8 are all FM with moments of 4.6, 4.33, 4.14, and 4.00 μ_B per atom, respectively. The progression of magnetic behavior is shown to be closely associated with the change in binding energy and the interparticle separation. Further the antiferromagnetic instabilities are intimately tied to the minority-spin $4s$-$3d$ energy spacing.

In Sec. II we discuss the computational methodology and give details about the basis sets and energy functionals used in these studies. In Sec. III we discuss the results on Mn_n for $n = 2-8$. The dimer is discussed in great detail to make contact with earlier work. While none of the neutral Mn_n appear to have a moment of $25\mu_B$ we show that the negatively charged Mn_6, with two inequivalent atoms, does indeed exhibit this moment. In Sec. IV we summarize our findings.

II. COMPUTATIONAL DETAILS

The general method used here is the linear-combination-of-atomic-orbitals (LCAO) molecular-orbital approach.[13,14] All of the all-electron calculations have been performed using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) which is described in Ref. 15. This methodology uses large basis sets, an analytic methodology for evaluating the potentials on a mesh of points, and a numeri-

cally precise variational mesh to solve the Schrödinger equation self-consistently. The molecular orbitals are expanded as a combination of Gaussian functions centered at the atomic sites and the exchange correlation effects were treated within the density functional scheme.[16] We have used both the local density approximation (LDA) (Refs. 17,18) and the generalized gradient approximations (GGA's).[18,19] We have verified that there are no quantitative differences between the two GGA's (Refs. 18,19) and only one small difference between the LDA and GGA results for Mn$_3$. The calculations were carried out at the all-electron level. The basis sets used here were optimized fully for density-functional based calculations using the procedure described in Ref. 20. As discussed in Ref. 20 it is necessary to determine the total number of Gaussian exponents, the values of the Gaussian exponents, and the contraction coefficients that are required to obtain accurate total energies in atoms and molecules and clusters. For Mn, the 20 optimized Gaussian decay parameters are given by: 0.35848985×10^7, 0.52158600×10^6, 0.11723769×10^6, 0.32994698×10^5, 0.10724510×10^5, 0.38631793×10^4, 0.15049752×10^4, 0.62371803×10^3, 0.27180369×10^3, 0.12328609×10^3, 0.57764299×10^2, 0.27551906×10^2, 0.13384117×10^2, 0.65772154×10^1, 0.31824545×10^1, 0.14884972×10^1, 0.67404844, 0.28489897, 0.11006157, and 0.04161537. In addition to the four s-type, two p-type, and one d-type contracted atomic orbitals we use the three longest-range s Gaussians, the three longest-range p Gaussians, and the fourth, third, and second longest-range d Gaussians. The contraction coefficients for the $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, and $3d$ atomic orbitals may be obtained by performing an SCF calculation on the spherical unpolarized Mn atom using the PW91 energy functional.[21] All geometries are optimized fully with Hellmann-Feynman forces smaller that 0.001 hartree/bohr.

Further details about the calculations are given in earlier papers.[15] With respect to the determination of magnetic moments we have taken special care to ensure that the nonvariational magnetic moments are well converged. First, we have converged the total energies to a tolerance of 10^{-6} hartree which corresponds to ten-decimal-place accuracy of the total energy. The eigenvalue sum and total kinetic energy, neither of which are variational quantities, are found to be converged to approximately 0.0001–0.0005 hartree which corresponds to seven-decimal-place accuracy. We expect that the nonvariational magnetic moments are converged to similar accuracy. A second way of determining whether the magnetic moments lead to a *metastable* state is to examine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of each spin. The spin gaps which we define as $\Delta_1 = -(\epsilon_{HOMO}^{majority} - \epsilon_{LUMO}^{minority})$ and $\Delta_2 = -(\epsilon_{HOMO}^{minority} - \epsilon_{LUMO}^{majority})$ correspond to the energy required to move an infinitismal amount of charge from the HOMO of one spin to the LUMO of the other. If both spin gaps are positive the system is magnetically stable.

We have also carried out limited studies (on Mn$_2$, Mn$_3$, and Mn$_4$) using an alternate approach where the atomic cores were replaced by norm conserving non-local pseudopotentials proposed by Bachelet, Hamann, and Schlüter.[23] These pseudopotentials are based on the relativistic atoms calculated using local spin density and therefore include, in some way, the relativistic effects. The pseudopotential calcu-

lations were carried out using local spin density approximation with no gradient corrections. We have used two independent Gaussian-based implementations of pseudopotentials.[22,24] One implementation[24] used the representations of Perdew and Zunger and Ceperly and Alder[17] and a least-square Gaussian representation of the numerical pseudoatomic orbitals. The other[22] used the PW91 functional and energy-optimized Gaussian orbitals. The pseudopotential results discussed here are not dependent on either the implementation or the energy functional. We find that the unpolarized pseudopotential calculations are in very good agreement with the unpolarized all-electron calculations.

III. RESULTS

In the following subsections we discuss the results obtained in our applications to Mn$_n$ with ($n=2-8$). Unless explicitly noted the binding energies correspond to the GGA energy functional.[18,19] We start by discussing the dimers and trimer which exhibit low lying antiferromagnetic and ferromagnetic states and then turn to the larger systems which exhibit ferromagnetic coupling.

A. Bistability in Mn$_2$ and Mn$_3$

While the Mn$_2$ dimer is the smallest cluster we have studied it is the most complex in terms of the number of stable and metastable magnetic and geometrical states that it possesses. Experiments based on ESR (Ref. 4) and resonance Raman spectroscopy[5] observe an AF state with a bond length of 6.0 a.u. The binding energy is estimated to be 0.44 ± 0.30 eV.[25] The LDA BHS pseudopotential results predict a symmetry-broken AF state with an equilibrium bond length of 6.02 bohr and an atomization energy of 0.37 eV. Slightly above this AF state is an $S=10\mu_B$ FM dimer with an atomization energy of 0.30 eV. Analysis of the bonding in both of these states shows that their electronic structure is equivalent to that of the separated atoms. Each atom has a majority spin with the $4s$ and $3d$ shells fully occupied and a minority spin with an empty d shell and an occupied $4s$ state. These states are mildly reminiscent of a van der Waals molecule since the electronic configuration on each atom consists of either fully populated or completely empty shells of electrons. Further the AF state appears to correspond with the experimentally observed Mn$_2$ dimer in the matrices.

Interestingly, as summarized in Table I, this is not the density-functional ground state of the gas-phase Mn$_2$ dimer. Our all-electron calculations show that at even shorter bond lengths a FM $S=10\mu_B$ state with a *different* electronic configuration is most stable. We find the ground state of the Mn$_2$ to have an equilibrium separation of 4.927 bohr and an atomization energy of 0.99 eV. We have performed detailed investigations of the bonding of this molecule and find that it is mediated by the minority spin valence electrons. Instead of a minority spin electron configuration of $[\sigma_g(4s),\sigma_u(4s)]$ the $\sigma_u(4s)$ state is depopulated and one of two degenerate bonding $\pi_g(3d)$ is occupied instead. We find that the pseudopotential results reproduce the all-electron calculations for spin unpolarized calculations. However, for the fully polarized calculations, we find that the pseudopotential leads to minority spin d states that are pushed up by approxi-

TABLE I. We present the GGA binding energy (B), equilibrium bondlength (R), and spin gaps (Δ_1 and Δ_2) for several different magnetic states of the Mn_2 dimer. As discussed in the text, positive spin gaps imply that the structure is locally stable. Energies are in eV and bondlengths are in bohr. Energies are calculated with respect to the $S=5$ μ_B Mn atom. A negative binding energy indicates that the molecule is unbound with respect to the separated atoms.

State	B	R	Δ_1	Δ_2
FM $S=0$ μ_B	-0.59	3.19	0.58	0.58
FM $S=2$ μ_B	-0.41	3.19	0.84	0.90
FM $S=4$ μ_B	-0.62	3.47	0.51	0.05
FM $S=6$ μ_B	-0.06	3.76	1.18	0.65
FM $S=8$ μ_B	0.53	4.29	1.79	-0.22
FM $S=10$ μ_B	0.99	4.93	0.65	1.30
AF	0.54	5.13	0.44	0.44

mately 5.0 eV relative to their all-electron counterparts. While we suggest that the pseudopotential results reproduce the experimental antiferromagnetic state for the incorrect reason, an enhancement of the $4s$-$3d$ splitting due to a physical effect that is not present in GGA or LDA could lead to an antiferromagnetic ground state dimer. For example, it is possible that self-interaction corrections (SIC) could change the ground state configuration. While the SIC shift associated with a $3d$ state is significantly larger than that of the $4s$ state, SIC also tends to favor systems with fully closed shells. We expect that the former effect is more important than the latter and that the correct gas-phase state is the $S=10\mu_B$ FM dimer with the 4.927 bohr bond length within SIC also. An inert substrate would have a negligible effect on the electronic structure of the Mn_2 dimer. However, since the binding between the two atoms is reasonably weak VdW interactions between the Mn atoms and neighboring surface atoms might be able to stretch the Mn_2 bonds. Such an interaction could reduce the overlap between the minority spin electrons which would reduce the energy spacing between the FM and AF states.

In addition to the two different states discussed here we have found several different metastable states with different magnetic moments and cohesive energies. The results for each spin are presented in Table II. We find that the bond length of Mn_2 decreased monotonically as the net moment

TABLE II. Average bond distance R, number of bonds per atom (B), moment per atom (μ_B) and atomization energy (D_2) as a function of the number of atoms. For the FM clusters we also include the spin gaps (G1 and G2). As discussed in the text $\Delta_1 = \epsilon_{HOMO}^{majority} - \epsilon_{LUMO}^{minority}$ and $\Delta_2 = \epsilon_{HOMO}^{minority} - \epsilon_{LUMO}^{majority}$. A state can be magnetically stable only if both spin gaps are positive.

Size	R (au)	B	μ_B	D_e (eV/atom)	Δ_1(eV)	Δ_2(eV)
2	4.927	0.50	5.00	0.50	0.65	1.30
3	5.093	1.00	5.00	0.81	0.46	1.38
4	5.162	1.50	5.00	1.19	0.62	2.31
5	5.053	1.78	4.60	1.39	0.50	0.79
6	5.002	2.00	4.33	1.56	0.90	1.13
7	4.970	2.14	4.17	1.57	0.70	0.47
8	4.957	2.25	4.00	1.67	0.93	0.37

decreases. This is in accord with the fact that as the moment decreases the number of $3d$-bonding minority spin wave functions increases and the number of antibonding majority spin d wave functions decreases. Since the Mn_2 dimer exhibits multiple magnetic and structural minima it is not surprising that earlier calculations have predicted other ground states. The earlier work is reviewed here for completeness. Nesbet,[7] using Hartree-Fock theory and a Heisenberg treatment, found it to be AF with a bond length of 5.44 a.u. and a binding energy of 0.79 eV. All electron density functional calculations by Harris and Jones[8] found a FM ground state with a total spin (S) of 10 in accord with the work here. Salahub and Baykara[9] found a triplet ground state.

The case of Mn_3 is extremely interesting. The compact ground state is a triangle. Each atom has five majority spin d electrons with a total moment of $5.0\mu_B$. An equilateral triangle is incompatible with perfect AF coupling of atomic spins. On the other hand one could envision a ferromagnetic coupling of d spins. We examined triangular and linear structures with all the spin multiplicities. The all-electron GGA studies predict a triangular FM ground state with a moment of $15.0\mu_B$, an atomization energy of 0.81 eV/atom, and one short and two long bond lengths of 4.800 and 5.240 bohr. A frustrated AF solution where the atomic d spins on the shorter side are ferromagnetically coupled while the spins on the third atom are antiferromagnetically coupled to the other atoms was only 0.014 eV less stable than the FM solution within the GGA. This structure has a net spin of $5\mu_b$ and has one long and two short bond lengths of 4.786 and 4.759 bohr, respectively. Within LDA the frustrated AF configuration was 0.26 eV more stable than the FM solution. The pseudopotential calculations also predicted the frustrated AF ground state corresponding to an isoceles triangle with a moment of $5.0\mu_B$. All these results indicate that Mn_3 has very close magnetic solutions and had two distinct spin states with similar stability. To our knowledge the only experimental data on Mn_3 are the resonance Raman spectra studies by Bier et al.[5] These studies suggest a ground state to be a slight Jahn-Teller distorted D_{3h} structure and low, odd-integer magnetic moment.

B. The larger ferromagnetic clusters: Mn_4-Mn_8

For Mn_4 we investigated a planar (rhombus) and three dimensional D_{2d} and T_d structures. The AF and the FM solutions with different multiplicities were tried. The all-electron calculation predict a T_d ground state with bond lengths of 5.13 a.u. as shown in Fig. 1. The binding energy was 1.19 eV per atom and the total moment was $20\mu_B$ which corresponds to $5.0\mu_B$ per atom. The pseudopotential calculations yielded a similar ground state geometry with a bond length of 5.58 a.u. and a binding energy of 0.68 eV/atom. The ground state multiplicity was identical. Ludwig, Woodbury, and Carlson[26] have observed Mn_4 in solid silicon and suggest that the four atoms are in interstitial sites and are in the form of a tetrahedron. The ground state multiplicity, however, is not experimentally known.

The case of Mn_5 has received attention ever since the ESR experiments by Baumann et al.[6] discovered a cluster with a spin of $25\mu_B$. Baumann et al. determined that this cluster was not Mn_3 or Mn_4 and that it contained more than
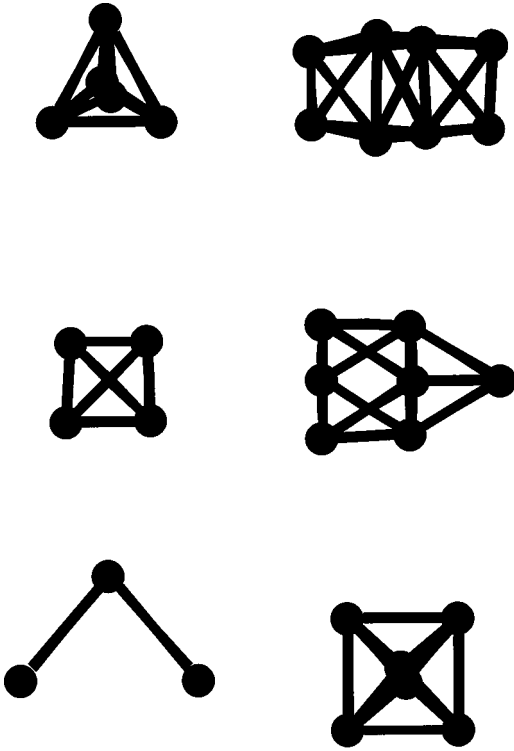
FIG. 1. Geometries for Mn$_n$ with $n = 3-8$. The cohesive energies, average bond lengths, bond order, and moments are given in Table I.

one inequivalent atom. The possibility that this cluster would be Mn$_5$ was suggested but Baumann *et al.* also suggested that it may be due to a larger Mn cluster. A five-atom cluster with such a moment would occur if all the atomic d spins on all the atoms were ferromagnetically aligned. The most likely structures are a triangular bipyramid, a square pyramid, or a pentagon with possible Jahn-Teller distortions. The previous calculations by Anderson[11] using a simple Huckel theory found a pentagonal low spin structure as the ground state. We investigated all three geometries. The planar pentagonal structure was much higher in energy than the other geometries. The ground state corresponds to a triangular bipyramid (see Fig. 1) with a total spin of $23\mu_B$ an atomization energy of 1.39 eV/atom and bond lengths of 4.962 (3) and 5.08 (2), respectively. The state with a moment of $25\mu_B$ was 0.62 eV less stable. The square pyramid with a total moment of $23\mu_B$ was 0.18 eV less stable than the triangular bipyramid. A square pyramid with a moment of $25\mu_B$ was less stable than the $23\mu_B$ state by 1.02 eV. As mentioned before the matrix isolation experiments find a cluster with a moment of $25\mu_B$. The present studies indicate that either the matrix has an effect on the ground state multiplicity or the cluster seen in experiments is other than Mn$_5$.

For Mn$_6$ we investigated a square bipyramid and a pentagonal pyramid structure with possible Jahn-Teller distortions. The ground state corresponds to a square bipyramid structure shown in Fig. 1. The four atoms forming the squre are generated by placing an atom at $\mathbf{R} = (2.498.2.498,0.000)$ bohr and the two capping atoms are generated by placing an atom at $\mathbf{R} = (0.000,0.000,3.543)$ bohr. The square bipyramid had a binding energy of 1.56 eV per atom and a total moment of $26\mu_B$. Note that the moment per atom ($4.3\mu_B$) is

less than in Mn$_5$ ($4.60\mu_B$). The pentagonal pyramid was less stable by 1.6 eV and had a moment of $28\mu_B$.

Another possible candidate for the $25\mu_B$ cluster observed in the ESR experiments of Baumann *et al.*[6] may be the negatively charged Mn$_6$ cluster. We find that the square bipyramid has an electron affinity of 1.36 eV and that the $S = 25\mu_B$ state, with spin gaps of 1.51 and 0.60 eV, respectively, is indeed a magnetically stable cluster.

For Mn$_7$ we have studied several different structures which include the pentagonal bipyramid, a planar square capped from above by a dimer and below by an atom, and a bicapped square with an extra atom at the middle. These structures have moments of 35, 29, and 25, respectively, but have per-atom cohesive energies that are *smaller* than the Mn$_6$ cluster. The lowest energy structure that we have found for Mn$_7$, pictured in Fig. 1, consists of two eclipsed triangles with a single atom cap. This structure has three inequivalent atoms and C$_{3v}$ symmetry. It is generated by placing atoms at all sites that are equivalent to $\mathbf{R}_1 = (1.402,1.402,-2.084)$, $\mathbf{R}_2 = (-3.270,-3.270, 0.376)$, and $\mathbf{R}_3 = (2.541, 2.541, 2.541)$, respectively. This structure has a spin of 29 and an atomization energy of 1.57 eV/atom which is only slightly larger than the atomization energy of Mn$_6$. Recently Koretsky and Knickelbein[27] have measured ionization energies of gas-phase Mn clusters. For Mn$_7$ they find an ionization energy of 5.44 eV which is in good agreement with our calculated vertical ionization energy of 5.51 eV. We find that Mn$_7 I + 1$ is closed structure with positive spin gaps.

For the case of Mn$_8$ we explored capped pentagonal bipyramid, bicapped trigonal prism, cube, D_{2d} star, and D_{2d} bisdisphenoid structures. The ground state has inequivalent atoms at $\mathbf{R} = (4.024,1.744,1.698)$ and $\mathbf{R} = (1.088,2.178, -2.199)$ and is invariant under 180° rotations about any of the three Cartesian axes. The resulting geometry is shown in Fig. 1. It has a moment of $32\mu_B$ and a binding energy of 1.67 eV per atom. The bond distances are in the range of 4.8–5.2 a.u. For Mn$_8$ the experimental ionization energy is observed to be 4.91 eV.[27] We performed an SCF calculation on the positively charged Mn$_8$ cluster and find it to lie 5.49 eV above the neutral Mn$_8$ cluster. In contrast to the ionized Mn$_7$ cluster, the ionized Mn$_8$ cluster has an open minority spin shell with two electrons occupying three degenerate states. This state would have multiplet structure so our 5.49 eV ionization energy should be viewed as a bound to the actual ionization energy.

IV. DISCUSSION

The above results show that the Mn$_n$ clusters undergo an interesting progression of electronic and magnetic behaviors with size. Mn$_2$ and Mn$_3$ have very close FM and AF or frustrated AF solutions. However, starting from Mn$_4$, the FM character sets in. The moment per atom retains its atomic value up until Mn$_4$ and then decreases. An analysis of the resulting electronic orbitals indicates that all the atomic unpaired d spins remain ferromagnetically aligned in Mn$_4$. Starting from Mn$_5$, the minority spin d bonding states are populated rather than the majority spin d antibonding states. While this enhances the bonding, it leads to a decrease of the

average interparticle spacing and a reduction of the moment. The decrease in the interparticle spacing with size is quite anomalous since the interparticle spacing in metals generally increases with size. Note that the interparticle spacing in Mn_8 is 4.96 a.u. compared to the nearest-neighbor distance of 4.23 a.u. in α Mn. This compression in interparticle distance is probably responsible for the decrease in the magnetic moment which assumes a value of $1.1\mu_B$ in α Mn. What is surprising is that α Mn is antiferromagnetic. The decrease in moment must therefore be accompanied by a change in the magnetic ordering. Thus it will be very interesting to see how the FM character in Mn_n clusters changes to AF as the size is increased.

In the above we have mainly focussed on the ground state geometries and spin. In many clusters the ground state had several other close lying spin states. This indicates that it may be possible to change the magnetic state easily. What is interesting is that the geometry and spin are intimately linked in the sense that the ground state geometries for different spins are different. Consider the case of Mn_2. As mentioned before the all-electron results find a FM bond length of 4.93 a.u. while the AF state has a bond length of 5.13 a.u. As the

moment decreases from $S=10$ to $S=0\mu_B$ the equilibrium separation decreases monotonically to 3.184 a.u. However the $S=0-6\mu_B$ moment states are locally stable but unbound with respect to the separated atoms. These changes can be related to the exchange striction, namely, the distortion of the lattice upon application of the magnetic field in solid Mn. We are in the process of investigating these aspects and bigger Mn_n clusters and these results will be reported in a later publication. In the meantime we hope that the current results will stimulate experiments on Mn_n clusters in beams to establish the bistability in dimer and trimer and the FM character in bigger clusters.

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