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First-principles study of the onset of noncollinearity in Mnn clusters: Magnetic arrangements in Mn5 and Mn6

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First-principles study of the onset of noncollinearity in Mn_n clusters: Magnetic arrangements in Mn_5 and Mn_6

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First-principles theoretical investigations of the noncollinearity of atomic spin moments in manganese clusters have been carried out within a gradient-corrected density-functional approach. Our studies on Mn_5 and Mn_6 include investigation of both collinear and noncollinear arrangements. It is shown that while the atomic structure of the ground state of Mn_5 is a triangular bipyramid, the collinear and noncollinear arrangements have comparable energies and hence are degenerate. For Mn_6, while the ground state has a square bipyramid arrangement, the noncollinear configuration is most stable making it the smallest cluster to feature a noncollinear ground state. The results are discussed in view of the recent experimental Stern-Gerlach profiles.

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I. INTRODUCTION

Atomic clusters containing two to a few thousand atoms provide a bridge between the free atoms and the bulk. Extensive research over the past 20 years has shown that properties of small clusters can be significantly different from the bulk.[1] One of the key questions, then, has been to determine the size at which the bulk features first appear in clusters. The answer, of course, depends on the property and one of the properties that has attracted considerable interest is the magnetic behavior.[2] It is now known that small clusters of itinerant bulk ferromagnets like Fe, Co, and Ni are superparamagnetic,[3–5] while atoms in small clusters of otherwise nonmagnetic solids like Rh have finite spin moments coupled ferromagnetically.[6,7] From the magnetic standpoint, an interesting metal that has attracted attention is manganese. Mn atom has an electronic configuration of $3d^5 4s^2$ and a high spin moment of $5\mu_B$ due to filled d subshell.[8–10] The unfilled d states are about 2.14 eV above the filled states and hence the atomic moment is fairly resilient to minor changes. This is partly why Mn maintains its moment in doped semiconductors and they exhibit ferromagnetism.[11] Apart from atom, the magnetic properties of bulk Mn are equally fascinating. For example, α-Mn exhibits a complex antiferromagnetic (AF) order below the Néel temperature of 95 K and is nonmagnetic (NM) at room temperature.[12] The unit cell in the crystal has a large size of 58 atoms. Recent theoretical studies by Hobbs *et al.*[13] indicate that the magnetic state of α-Mn has a noncollinear (NCL) ground state. In a follow-up paper, Hafner *et al.*[14] showed that β-Mn also has a stable NCL magnetic configuration even though the ground state is weakly ferrimagnetic. Both of these results are in good agreement with available experiments. In contrast to the bulk, Mn_3 and Mn_4 clusters are proposed to be ferromagnetic with total moments of 15 and $20\mu_B$, respectively.[8,9] This raises the question that if the atomic moments are ferromagnetically coupled in clusters of three and four atoms, and if the bulk is characterized by NCL arrangement, then what is the smallest cluster that features a NCL ground state?

In this paper we present the investigations of NCL arrangement in Mn_5 and Mn_6 clusters within the density-functional formalism. Our interest in these clusters is partly motivated by the recent Stern-Gerlach experiments.[15] In these experiments, the clusters in a beam are passed through a gradient magnetic field that tries to orient the moments as well as deflect them. For the case of Fe_n, Co_n, or Ni_n clusters, the beam undergoes a net deflection upon application of the gradient fields. For Mn_5 and Mn_6, however, the observed deflection profiles do not exhibit any net deflection but simply broaden with increasing gradient field. The absence of a net deflection could be accounted by a weak ferromagnetic or antiferromagnetic coupling between the atomic spins. Our studies, here, focus on two issues. First, starting from a collinear ferromagnetic coupling in Mn_3 and Mn_4, does the magnetic coupling remain collinear as we go to higher sizes? If not, what is the smallest size at which the NCL state becomes the ground state? It is interesting to note that the NCL arrangements can also be looked at from the perspective of frustration. It is known that in systems marked by antiferromagnetic coupling between the near neighbors and having geometries with odd member rings, a collinear arrangement can lead to frustration.[16] The lowest-energy configurations exhibit degeneracy and the system lacks a well-defined ground state. The inclusion of NCL arrangements can remove this degeneracy and lead to a well-defined ground state. The purpose of this paper is to explore these issues. Indeed, we show that while the ground state of Mn_5 has a collinear arrangement of spins, Mn_6 is the smallest cluster to exhibit a NCL ground state.

II. CALCULATION METHODOLOGY

The theoretical studies were carried out within a generalized gradient approximation (GGA) for the exchange and correlation[17,18] within a density-functional theory.[19,20] The NCL spin calculation was performed within a projected aug-

mented wave-function (PAW) formalism[21] as implemented[22] with the Vienna *ab initio* simulation package (VASP).[23]

In brief, in this approach for NCL spin calculation, Kohn-Sham orbitals is expressed by spinors

$$\Psi_i(\mathbf{r},s) = \begin{pmatrix} \Psi_i^{\alpha}(\mathbf{r}) \\ \Psi_i^{\beta}(\mathbf{r}) \end{pmatrix}, \tag{1}$$

where i is the index of occupied orbital and α,β are the spin indices. The density matrix $\mathbf{n}$ is made from Eq. (1), i.e.,

$$\mathbf{n} = \begin{pmatrix} n_{\alpha\alpha} & n_{\alpha\beta} \\ n_{\beta\alpha} & n_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \sum_i \Psi_i^{\alpha^*}(\mathbf{r})\Psi_i^{\alpha}(\mathbf{r}) & \sum_i \Psi_i^{\alpha^*}(\mathbf{r})\Psi_i^{\beta}(\mathbf{r}) \\ \sum_i \Psi_i^{\beta^*}(\mathbf{r})\Psi_i^{\alpha}(\mathbf{r}) & \sum_i \Psi_i^{\beta^*}(\mathbf{r})\Psi_i^{\beta}(\mathbf{r}) \end{pmatrix}. \tag{2}$$

Using this $\mathbf{n}$, we can obtain the equivalent magnetization density,

$$\vec{m}(\mathbf{r}) = \mathbf{Tr}(\mathbf{n}\vec{\sigma}) = (\mathbf{Tr}(\mathbf{n}\sigma_x),\mathbf{Tr}(\mathbf{n}\sigma_y),\mathbf{Tr}(\mathbf{n}\sigma_z)), \tag{3}$$

where σ_x,σ_y, and σ_z are the Pauli spin matrices. The exchange-correlation energy is defined with this magnetization density and the total charge density, $\mathbf{n}_{\mathrm{Tr}}=n_{\alpha\alpha}+n_{\beta\beta}$ as outlined below,

$$\begin{aligned} E_{XC}[\mathbf{n}] &= \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta \mathbf{n}_{Tr}(\mathbf{r})}\mathbf{n}_{Tr}(\mathbf{r})d\mathbf{r} + \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta \vec{m}(\mathbf{r})}\vec{m}(\mathbf{r})d\mathbf{r} \\ &= \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta \mathbf{n}_{Tr}(\mathbf{r})}\mathbf{n}_{Tr}(\mathbf{r})d\mathbf{r} + \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta |\vec{m}(\mathbf{r})|}\frac{\partial |\vec{m}(\mathbf{r})|}{\partial \vec{m}(\mathbf{r})}\cdot \vec{m}(\mathbf{r})d\mathbf{r} \\ &= \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta \mathbf{n}_{Tr}(\mathbf{r})}\mathbf{n}_{Tr}(\mathbf{r})d\mathbf{r} + \int \frac{\delta E_{XC}[\mathbf{n}]}{\delta |\vec{m}(\mathbf{r})|}|\vec{m}(\mathbf{r})|d\mathbf{r}. \end{aligned} \tag{4}$$

In Eq. (4), $\delta E_{XC}[\mathbf{n}]/\delta \mathbf{n}_{tr}(\mathbf{r})$ and $\delta E_{XC}[\mathbf{n}]/\delta|\vec{m}(\mathbf{r})|$ can be transformed and calculated from the equations used in the conventional collinear spin calculation. As seen in Eq. (3), the $|\vec{m}(\mathbf{r})|$ has not only $n_{\alpha\alpha}$ and $n_{\beta\beta}$, but also $n_{\alpha\beta}$ and $n_{\beta\alpha}$. Therefore the exchange-correlation potential made from E_{XC} can be divided into diagonal and off-diagonal parts. Using the notation $V_{XC}^{\alpha\alpha}$ and $V_{XC}^{\beta\beta}$ for the diagonal part, and $V_{XC}^{\alpha\beta}$ and $V_{XC}^{\beta\alpha}$ for the off-diagonal part, the Kohn-Sham equation is finally written as

$$\begin{pmatrix} -\frac{1}{2}\nabla^2 + V_{ee} + V_{ext} + V_{XC}^{\alpha\alpha} & V_{XC}^{\alpha\beta} \\ V_{XC}^{\beta\alpha} & -\frac{1}{2}\nabla^2 + V_{ee} + V_{ext} + V_{XC}^{\beta\beta} \end{pmatrix} \times \begin{pmatrix} \Psi_i^{\alpha}(\mathbf{r}) \\ \Psi_i^{\beta}(\mathbf{r}) \end{pmatrix} = \varepsilon_i \begin{pmatrix} \Psi_i^{\alpha}(\mathbf{r}) \\ \Psi_i^{\beta}(\mathbf{r}) \end{pmatrix}, \tag{5}$$

where V_{ee} is the Coulomb potential between electrons and V_{ext} is the external potential.

As mentioned above, we used the VASP4.6.12 (Ref. 23) package to carry out the actual calculations. The exchange-correlation effects were included via the GGA. To study finite system such as Mn_5 and Mn_6, we used the supercell approximation where the cluster occupies the central position within the cell. To avoid interactions between clusters in neighboring cells, we chose a large supercell of size 15 Å. Further, the cutoff energy of the plane wave was set at 337.4 eV (24.8 Ry). The geometry and the spin orientations were optimized.

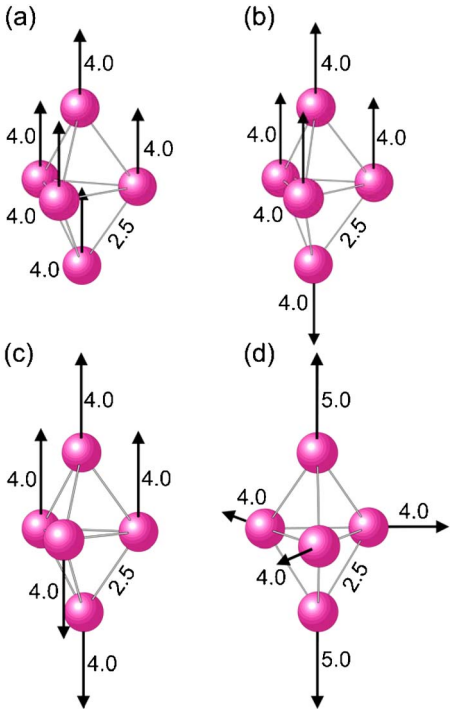

FIG. 1. (Color online) Various starting configurations of the atomic spins for determining the ground state of Mn_5. The bond lengths are in Å and the local atomic moments are in μ_B.

III. RESULTS AND DISCUSSION

Before we present our calculations, let us briefly review the recent studies on Mn_5. Jones *et al.*[10] have investigated the magnetic arrangement in Mn_5 looking into collinear arrangements. They find that the ground state has a distorted triangular bipyramid arrangement. The local atomic moments are antiferromagnetically aligned and the cluster has a net magnetic moment of $3\mu_B$. They also found that magnetic arrangements of the atomic spin moments that lead to total moments of 13 and $20\mu_B$ are only 0.02 and 0.09 eV above the ground state and have only minor changes in the bond lengths. Bobadova-Parvanora *et al.*[9] have studied the antiferromagnetic ordering in Mn_n clusters and find a similar ground state as Jones *et al.*[10] Fujima[24] has investigated the effect of noncollinearity in Mn_5 using a local-density functional. He, however, did not optimize the geometry but simply studies NCL for various bond lengths in a triangular bipyramid arrangement.

In this work, we started our investigations of NCL arrangement by assuming triangular bipyramid geometry with different spin arrangements as the initial guess (the square pyramid was found to be higher in energy). Further, we started with three types of collinear spin configurations as shown in Fig. 1, i.e., ferromagnetic (FM) [Fig. 1(a)] and two ferrimagnetic [Figs. 1(b) and 1(c)] as initial guesses. These were motivated by the ground states obtained by Jones *et al.* We also included a spiral configuration (SP) [Fig. 1(d)] to the

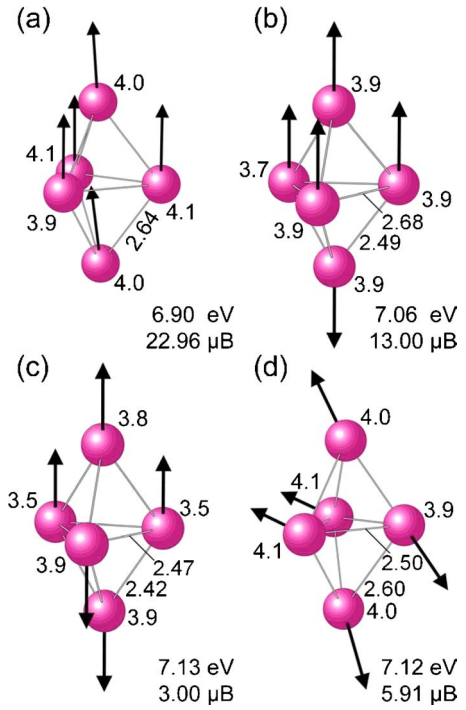

FIG. 2. (Color online) Various minimum-energy configurations obtained by starting from different initial configurations in Fig. 1. The bond lengths are in Å and the atomization energies (eV) are listed below each structure. Also given are the local atomic moments (μ_B) and the total spin moment.

initial guess. Hobbs *et al.*[22] had previously shown that such an arrangement is metastable for Cr_5 and has an energy close to the ground state. In all cases, the geometry and the spin arrangements were optimized. For FM and two ferrimagnetic configurations, the collinear spin calculation was also carried out for a comparison with NCL. The results of these investigations are shown in Fig. 2. In these results, FM, and ferrimagnetic arrangements [Figs. 1(a)–1(c)] do not show drastic changes in their structures comparing with the results of the collinear spin calculation. In fact, they have almost the same configurations, atomization energies, and net magnetic moments as those obtained in a corresponding collinear calculation in spite of the inclusion of the NCL effects. The initial SP configuration [Fig. 1(d)], however, changed to the configuration shown in Fig. 2(d). In this configuration, all atomic moments can be moved to lie in the same plane. Hereafter, this configuration will be called coplanar (CP). Figure 2 also shows the atomization energy of various arrangements and the local magnetic moments at the various sites. The atomization energy (A.E.) is defined as

$$\mathrm{A.E.} = [nE(\mathrm{Mn}) - E(\mathrm{Mn}_n)], \tag{6}$$

where E is the total energy of the respective atoms/clusters. Note that the ground state is a ferrimagnetic collinear configuration suggested by Jones *et al.* However, almost degenerate with this is a noncollinear state. Within the accuracy of the calculation, both states can be considered as ground-state isomers. As mentioned before, Fujima also carried out the NCL spin calculations on Mn_5, although he did not optimize

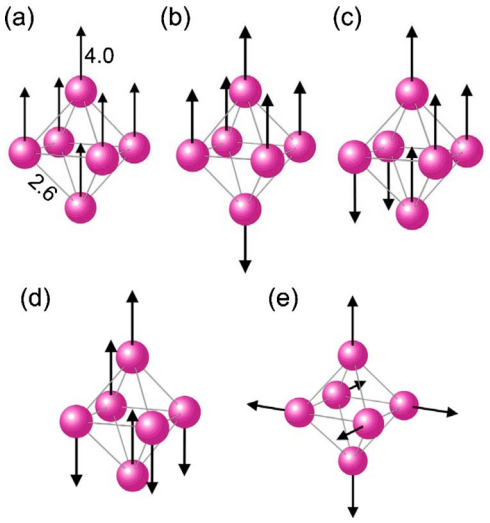

FIG. 3. (Color online) Various starting configurations of the atomic spins for determining the ground state of Mn_6. All structures are the same, and the unit of the bond length written in (a) is Å. The magnitudes of the local atomic moments are all $4.0\mu_B$ as written in (a).

the structure. He calculated the magnetic configurations for various Mn–Mn bond lengths and showed that the direction of each atomic moment in Mn_5 changes with size within the same plane. He also showed that when the Mn–Mn bond length is changed to 80% of its bulk values, the CP magnetic configuration changes to ferrimagnetic configuration in Fig. 2(c). Combined with the present results, these studies indicate that the atomic moment in Mn_5 can change their directions easily in the same plane. This conclusion supports the earlier view of Jones *et al.*[10]

For Mn_6, the recent studies predict a square bipyramid ground state. Investigations by Jones *et al.* using a collinear

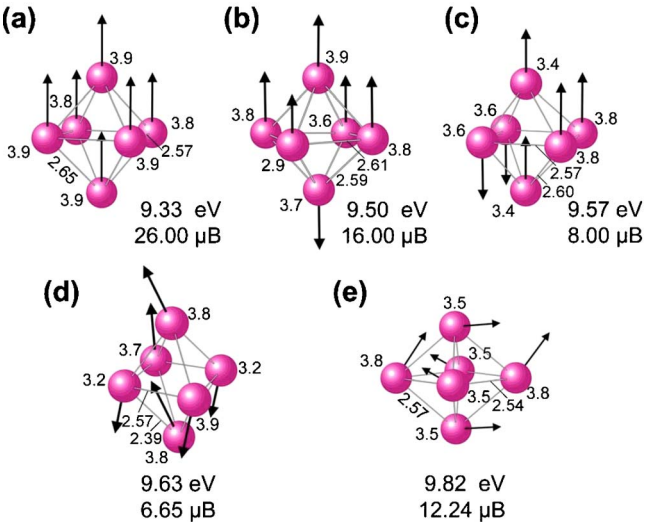

FIG. 4. (Color online) Various minimum-energy configurations obtained by starting from different initial configurations in Fig. 3. The bond lengths are in Å and the atomization energies (eV) are listed below each structure. Also given are the local atomic moments (μ_B) and the total spin moment.

formalism indicate that the ground state has a spin magnetic moment of $8.0\mu_B$. States with moments of 16, 26, and $2\mu_B$ are only 0.03, 0.03, and 0.06 eV above the ground state and can be regarded as isomers. As before, the isomers obtained by Jones *et al.* were adopted as the starting points. These initial configurations were ferromagnetic [Fig. 3(a)] and three ferrimagnetic [Figs. 3(b)–3(d)]. To these, we added a spiral (SP) configuration shown in Fig. 3(e) as initial guesses. We carried out collinear spin calculation for the first four systems to compare the results of NCL spin calculations as we did for Mn_5. The results are shown in Fig. 4. For (a)–(c), NCL spin calculation gave us almost the same atomization energy, net magnetic moment, and local atomic moments as those from collinear spin calculation. However, for Fig. 4(d), the initial collinear arrangement changes to a NCL configuration. The transition lowers the atomization energy and enhances the net magnetic moment by 0.02 eV and $4.65\mu_B$, respectively. We would like to add that even though the moments are no longer collinear and have different magnitudes, the change is only minimal. More interesting is the result of SP initial configuration. As shown in Fig. 4(e), this configuration is more stable than any other configuration by almost 0.2 eV. Note that although we started with a SP state, the relaxed configuration is no longer spiral. However, this configuration does have some order, i.e., atoms in each pair located at opposite sites have almost the same atomic moments. Note also that while the initial configuration had zero net moment, the optimized configuration acquired a net moment of $12.24\mu_B$.

IV. SUMMARY

The present studies present a systematic investigation of the magnetic transition and the appearance of NCL magnetism in small Mn_n clusters. The earlier studies[8–10] have shown that Mn_3 and Mn_4 have ferromagnetically coupled atomic spins. The present studies indicate that Mn_5 has a degenerate ground state with collinear and NCL arrangements. Mn_6 is then the smallest manganese cluster to posses a NCL ground state. This transition is a signature that the ferromagnetic coupling is weakened and an antiferromagnetic component emerges with increasing size. It is consistent with our earlier view[10] that the weakening in the ferromagnetic coupling leads to an absence of net deflection in the Stern-Gerlach profiles. A study of the electronic structure of the clusters shows[9] that the mixing between the valence *d* and *s* states increases with increasing size. It is then reasonable to assume that the increased mixing leads to the change in the magnetic coupling. While Mn_6 is the smallest manganese cluster to exhibit a NCL state, it is important to note that the magnetic properties are dependent on the symmetry of the cluster. It is then possible that both collinear and NCL states may appear at higher sizes depending on the number of atoms and the symmetry of the cluster.

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[1] *Quantum Phenomena in Clusters and Nanostructures*, edited by S. N. Khanna and A. W. Castleman, Jr. (Springer, New York, 2003).
[2] D. D. Awschalom and D. P. Di Vicenzo, Phys. Today **48**, 43 (1995).
[3] W. A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).
[4] J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).
[5] S. N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).
[6] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).
[7] A. J. Cox, J. G. Louderback, and L. A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993).
[8] M. R. Pederson, F. Reuse, and S. N. Khanna, Phys. Rev. B **58**, 5632 (1998); S. K. Nayak and P. Jena, Chem. Phys. Lett. **289**, 473 (1998).
[9] P. Bobadova-Parvanova, K. A. Jackson, S. Srinivas, and M. Horoi, Phys. Rev. A **67**, 061202(R) (2003).
[10] N. O. Jones, S. N. Khanna, T. Baruah, and M. R. Pederson, Phys. Rev. B **70**, 045416 (2004).
[11] Y. Ohno *et al.*, Nature (London) **402**, 790 (1999).
[12] R. S. Tebble and D. J. Craik, *Magnetic Materials* (Wiley, New York, 1969), p. 48.
[13] D. Hobbs, J. Hafner, and D. Spišák, Phys. Rev. B **68**, 014407 (2003).
[14] J. Hafner and D. Hobbs, Phys. Rev. B **68**, 014408 (2003).
[15] M. B. Knickelbein, Phys. Rev. Lett. **86**, 5255 (2001); J. Chem. Phys. **116**, 9703 (2002).
[16] *Magnetism in Condensed Matter*, edited by S. Blundell (Oxford University Press, New York, 2001), p. 167; S. N. Khanna and D. Sherrington, Solid State Commun. **36**, 653 (1980).
[17] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[18] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996).
[19] P. Hohenberg and W. Kohn, Phys. Rev. **A136**, 864 (1964).
[20] W. Kohn and L. J. Sham, Phys. Rev. **B140**, 1133 (1965).
[21] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994); L. Nordstrom and D. J. Singh, Phys. Rev. Lett. **76**, 4420 (1996).
[22] D. Hobbs, G. Kresse, and J. Hafner, Phys. Rev. B **62**, 11556 (2000).
[23] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[24] J. Fujima, J. Phys. Soc. Jpn. **71**, 1529 (2002).