Anomalous Magnetic Moments of Mn_{13} and Mn_{19} Clusters *

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Recently, sharply reduced magnetic moments were measured in Mn_{13} and Mn_{19} clusters with values of about $0.5 \mu_B$ /atom, while other clusters had moments of 1 to $1.4 \mu_B$ /atom. It was postulated that this sharply reduced magnetic moment results from the icosahedral growth sequence. We confirm the stability of the icosahedral structures. The icosahedral Mn_{13} and Mn_{19} clusters have several nearly degenerate low energy states, each with a low magnetic moment. It is shown that the mixture of ferromagnetic and antiferromagnetic coupling is responsible for the low net magnetic moments.

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1. Introduction

Studies of manganese clusters are fascinating because bulk manganese is antiferromagnetic with a complex structure while small clusters with 3–8 atoms are ferromagnetic.^{1,2)} The $3d^5 4s^2$ atomic electronic configuration makes Mn_2 very weakly bonded with van der Waals interaction and the nature of the magnetic coupling in the dimer is still disputed. In bulk, manganese has the lowest cohesive energy (2.92 eV/atom) and large compressibility among the 3d metals. This again reflects relatively weak bonding in Mn. A transition to the bulk metallic behavior as well as a change from a ferromagnetic to an antiferromagnetic ground state should occur with an increase in the cluster size.

Studies on 2–8 atom clusters show large magnetic moments of 4 to $5 \mu_B$ /atom.^{1,2)} Recent experiments on Mn clusters with 11–99 atoms show magnetically ordered clusters with significantly reduced moments and a maximum value of about $1.4 \mu_B$ /atom.³⁾ This is close to the magnetic moments of about $1 \mu_B$ in bulk Mn. Most interestingly, a sharply reduced magnetic moment of about $0.5 \mu_B$ has been observed in Mn_{13} and Mn_{19} clusters³⁾ while clusters with one more or one less Mn atom have moments of about $1 \mu_B$ per atom. It was postulated that the sharply reduced magnetic moment results from the icosahedral growth sequence. It is surprising that the magnetic moment per atom would change drastically from about $5 \mu_B$ for Mn_5 to $0.5 \mu_B$ for Mn_{13} . This suggests that these clusters may have complex magnetic ordering. In this paper we present results of our studies on the anomalous behavior of Mn_{13} and Mn_{19} .

Mn_{13} and Mn_{19} isomers were studied with a planewave method employing ultrasoft pseudopotentials.⁴⁾ The local density approximation of the density functional theory was used, with the gradient corrected exchange-correlation potential of Perdew and Wang.⁵⁾ The cutoff energy for the plane waves was set to 283.9 eV for Mn_{13} and to 227.2 eV for Mn_{19} . Reciprocal space integrations were carried out using the Gamma point only. Clusters were positioned in a cubic box with an edge of 1.5 nm. Structural optimizations

were performed using quasi Newton-Raphson and conjugate gradient methods. Typically, structural optimizations were deemed sufficiently converged when the forces were less than 100 meV/nm. We defined local moments by integrating the spin density over Voronoi atomic volumes, and refer to these as ‘integrated spin densities’ to avoid confusion with LCAO-type local moments.

Electronic structure calculations of small Mn clusters are much complicated by the multiple local moments that Mn atoms can assume, so that there are many nearly degenerate magnetic states, each of which converges to a slightly different geometry. Therefore, great care was taken to consider various magnetic starting configurations. The total magnetic moment during some optimizations was initially constrained to a particular value, with the constraint being lifted after initial convergence in the forces was reached. In other cases, the total magnetic moment was kept free during the entire optimization process. Additionally, various ferromagnetic and ferrimagnetic spin configurations were used as initial guesses in the search for the lowest energy magnetic state.

Three different initial structures were considered in the optimization of Mn_{13} : icosahedral, decahedral, and cuboctahedral (Fig. 1). The resulting structures have icosahedral-like symmetry and moments of 1, 3, 5, 11, and $29 \mu_B$, with the $3 \mu_B$ cluster having the lowest energy. Interestingly, distortion during the optimization of both the decahedral and cuboctahedral structures led to icosahedral geometries. Based on the experimental results,³⁾ the optimal moment should be expected to be 5 – $9 \mu_B$. There is surprisingly little difference in the total energies among the structures (Fig. 2), with three local minima occurring within 0.2 eV of each other, and all five local minima occurring within a range of 0.5 eV. Such small energy differences suggest that several magnetic states will exist even at the low temperature of 68 K used in experiments. The current result, in which all but one of the most favorable structures have small effective moments, supports the experimental findings of a very small *net* moment per atom.

Calculation of the band gaps, defined as $\Delta = \min(LUMO_{up}, LUMO_{down}) - \max(HOMO_{up}, HOMO_{down})$, for the structures discussed above shows that these are positive and therefore, the structures are magnetically stable (Fig. 3). There is, how-

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Fig. 1 Structures considered in this study: Mn₁₃ (a) icosahedron, (b) decahedron, (c) cuboctahedron; Mn₁₉ (d) double icosahedron, (e) double decahedron, (f) cuboctahedron. In icosahedral clusters atoms with positive and negative integrated spin densities have been indicated, respectively, with black and white spheres for the lowest energy state.

Fig. 2 Total energy (E) of icosahedral Mn₁₃ cluster as a function of the total moment (μ).

ever, no clear correlation between energy and band gap. In fact the $3\mu_B$ state, which is most energetically favorable, has the smallest gap.

The average nearest neighbor distances for Mn₁₃ are shown in Fig. 4, and we see that this average depends only weakly on spin. The bond lengths themselves vary between 0.228 and 0.287 nm, with the shortest distances generally involving the central atom of the icosahedron. The range of values is in accord with those for bulk α -Mn, whose nearest-neighbor distances vary from 0.235 to 0.287 nm. The minimum bond lengths are somewhat smaller than those seen in small Mn clusters, where theoretical results for Mn₃–Mn₈ calculated at the GGA level¹⁾ give bond lengths from 0.254 to 0.277 nm. Indeed this behavior is expected as in small clusters the interaction is weak with longer bonds than in the bulk. As the cluster size increases, the metallic character of bonding is expected to increase resulting in reduced bond lengths.

In small clusters ferromagnetically aligned effective moments of $4\text{--}5\mu_B/\text{atom}$ were found, whereas in the bulk antiferromagnetic coupling and effective moments of $1\mu_B/\text{atom}$ occur. In Ref. 1) it was suggested that this change is caused by compression of the interatomic distance. Examination of the integrated spin densities of Mn₁₃ for differing spin configurations reveals that the spins are not purely ferromagnetically aligned—both ferromagnetic and antiferromagnetic couplings exist in the clusters (Fig. 1). Thus, a transition from pure ferromagnetic to ferrimagnetic ordering must take place

Fig. 3 Gap (Δ) in icosahedral Mn₁₃ clusters as a function of the total moment (μ).

Fig. 4 Average nearest neighbor distance ($\bar{d}$) in icosahedral Mn₁₃ clusters as a function of the total moment (μ).

Fig. 5 Minimum and maximum nearest neighbor distances ($d_{\min}$, $d_{\max}$) in cuboctahedral (+) and icosahedral (x) Mn₁₉ clusters as a function of the total moment (μ).

somewhere between Mn₈ and Mn₁₃. Akin to the bulk, the lower effective moments may be partially explained by compression of the bonds relative to the smaller clusters.

For Mn₁₉ clusters, cuboctahedral, double icosahedral, and double decahedral symmetry have been considered (Fig. 1). A constrained moment structural optimization of the cuboctahedral isomer gave almost perfectly 'fcc' like clusters for $1\text{--}7$, 13 , and $15\mu_B$ states as is readily apparent in Fig. 5 from the nearly identical minimal and maximal nearest neighbor distances. The integrated spin density was typically about -1 or $-2\mu_B$ on the central site, while on the surrounding 18 atoms the integrated spin density took values of about $0.5\mu_B$. For other fixed total moments similar solutions could be obtained when starting from a well-chosen magnetic configuration. However, for the constrained total moments of 9 , 11 , and $17\text{--}31\mu_B$, another type of solution occurred spontaneously during structural optimizations. The 6 sites most distant from the central site assumed much larger integrated spin densities of about $4.5\mu_B$, while the 12 nearest neigh-

Fig. 6 Total energy (E) of cuboctahedral (+) and icosahedral (x) Mn_{19} clusters as a function of the total moment (μ).

Fig. 7 Average nearest neighbor distance ($\bar{d}$) in cuboctahedral (+) and icosahedral (x) Mn_{19} clusters as a function of the total moment (μ).

bors of the central site took small positive or negative values depending on the total magnetic moment. As might be expected, the strong polarization on the outermost sites caused these sites to be repelled outward and Fig. 5 shows that the minimal and maximal nearest neighbor distances in these clusters differ considerably. The strong polarization of the outermost sites is energetically favorable and this magnetic configuration is clearly separated from the weak surface-polarized configuration (Fig. 6). The average nearest neighbor distance too, clearly distinguishes the strong and the weak surface-polarized configurations (Fig. 7). The strong surface-polarized configuration is not magnetically stable for small total magnetic moments as is apparent from Fig. 8 where the gap is shown as a function of the constrained total moment. A negative gap indicates that the magnetic configuration cannot be stable without an applied field. The gap reaches the most negative value of -0.615 eV for the strong surface-polarized case at a constrained total moment of $11 \mu_B$. For large total moments ($31 \mu_B$ and up) the strong surface-polarized configuration appears stable.

The cuboctahedral magnetic configurations are not nearly as stable as the double icosahedral isomers (Fig. 6). Initially, the double icosahedral isomer was structurally optimized while fixing the total moments at values from 1 to $19 \mu_B$. This gave clusters with mostly positive gaps (Fig. 8) and with widely varying nearest neighbor distances and a much larger average nearest neighbor distance than occurred in the cuboctahedral clusters. The integrated spin density indicated that the two sites sandwiched between the 5 membered rings have very small moments and correspondingly short nearest neighbor distances, while surface sites have moments from 3 to $5 \mu_B$. The 5 membered rings have mixed spin up and spin down occupancies (Fig. 1).

Fig. 8 Gap (Δ) in cuboctahedral (+) and icosahedral (x) Mn_{19} clusters as a function of the total moment (μ).

Most noticeable is the very flat minimum of the energy with the total moment. The energy difference between clusters with 9 and $11 \mu_B$ is only about 5 meV. When the constraint on the total moment was removed, the $9 \mu_B$ configuration took on a larger moment and converged to the $11 \mu_B$ configuration. Due to the small energy differences several magnetic states will be expected to co-exist even at the low temperature of 68 K used experimentally. The band gap for the $11 \mu_B$ state is 100 meV and as in the lowest energy state of the Mn_{13} cluster, it is not the largest gap.

For the double decahedral isomer an annealing calculation, where the Fermi temperature was gradually lowered from 600 meV to 10 meV, was performed. This unconstrained total moment calculation was initialized with a magnetic configuration similar to that found in the most stable double icosahedral cluster. This calculation did not fully converge, but it appears that this cluster deforms towards a double icosahedral shape. The unconverged geometries had energies of about -142 eV, which is above the double icosahedral minimum, but below the cuboctahedral isomers. The gap was negative by about 100 meV. The calculated double icosahedral ground state with a total moment of $11 \mu_B$ agrees well with the experimental measurement of about $0.5 \mu_B/\text{atom}$ for Mn_{19} .

As anticipated by experimental results, the icosahedral structures of Mn_{13} and Mn_{19} were found to be the ground states. The energy differences between different magnetic configurations are rather small. However, the low magnetic moment states have the lowest energy, as found experimentally. There is a mixture of ferromagnetic and antiferromagnetic coupling between atoms. Further detailed studies are in progress.

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Note added in proof: After acceptance of this manuscript, more accurate calculations have revealed the existence of lower energy spin configurations for Mn_{19} , details of which will be published elsewhere.

REFERENCES

- 1) M. R. Pederson, F. Reuse and S. N. Khanna: Phys. Rev. B **58** (1998) 5632–5636.
- 2) S. K. Nayak, B. K. Rao and P. Jena: J. Phys. Condens. Matter **10** (1998) 10863–10877.
- 3) M. B. Knickelbein: Phys. Rev. Lett. **86** (2001) 5255–5257.
- 4) G. Kresse and J. Furthmüller: Comp. Mater. Sci. **6** (1996) 15–50.
- 5) J. P. Perdew and Y. Wang: Phys. Rev. B **45** (1992) 13244–13249.