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Structures of Mn clusters

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Abstract. The geometries of several Mn clusters in the size range Mn_{13}–Mn_{23} are studied via the generalized gradient approximation to density functional theory. For the 13- and 19-atom clusters, the icosahedral structures are found to be most stable, while for the 15-atom cluster, the *bcc* structure is more favoured. The clusters show ferrimagnetic spin configurations.

Keywords. Clusters; magnetism.

1. Introduction

The beauty and challenge of modelling magnetic materials is exemplified in Mn. The dimer is weakly bound and most likely antiferromagnetic (though there is some disagreement about this), while Mn_3–Mn_8 are clearly ferromagnetic (Pederson *et al* 1998; Nayak *et al* 1998), and the most stable bulk structure, α Mn, is an antiferromagnet. A recent Stern–Gerlach study by Knickelbein (2001) has added fresh interest to the study of Mn. The experimental results show that clusters in the size range of 11–99 atoms have significantly smaller moments per atom than ferromagnetically coupled clusters, and anomalously small moments for Mn_{13} and Mn_{19}. An icosahedral growth sequence was suggested for Mn_{13}–Mn_{19}. In order to more clearly understand these results, we have studied four clusters in the size range of 13–23 atoms. The results confirm icosahedral structures for Mn_{13} and Mn_{19}. Ferrimagnetic spin structures for all the clusters are preferred, in agreement with the experimental finding of relatively small net magnetic moments.

Mn clusters were studied with a planewave method employing ultrasoft pseudopotentials (Kresse and Furthmüller 1996). The generalized gradient approximation to density functional theory was used, with the exchange–correlation potential of Perdew and Wang (1992). The cutoff energy for the plane waves was set to 283·9 eV, and reciprocal space integrations were carried out using the Gamma point. Clusters were positioned in a cubic box with an edge of 15 Å (Calculations performed with a 20 Å box confirmed that the energy is adequately converged at 15 Å). Structural optimizations were performed using quasi Newton–Raphson and conjugate gradient methods. The optimizations were deemed sufficiently converged when the forces were about 1 meV/Å. The net magnetic moments were determined by unrestricted optimization after either freezing the initial net moment or specifying the initial magnetic moments on each atom. Both symmetric and asymmetric spin arrangements were considered. We defined local moments by integrating the spin density over Voronoi atomic volumes, which we refer to as 'integrated spin densities' to avoid confusion with LCAO-type local moments.

Differing geometries and spin structures were considered for each cluster size. For Mn_{13} and Mn_{19}, icosahedral, decahedral, and cuboctahedral structures were examined. The hexagonal close-packed structure was also examined for Mn_{13}. For Mn_{15}, icosahedral, hexagonal, and *bcc* structures were studied. For Mn_{23}, only the icosahedron was optimized.

The most stable geometry for each cluster size is shown in figure 1. The results show that the icosahedral structure is most stable for Mn_{13} and Mn_{19}, while the *bcc* structure is preferred for Mn_{15}. As mentioned in an earlier work (Briere *et al* 2002), the decahedral structures for Mn_{13} and Mn_{19} tend to deform to icosahedral, as does the cuboctahedral structure for Mn_{13}. Mn_{13}'s hexagonal close-packed structure is about 1·40 eV higher in energy than the lowest energy icosahedron, which is in general agreement with an earlier calculation by Nayak *et al* (1999), though the binding energy per atom for the icosahedral structure is slightly higher (~ 0·07 eV) than the previous result. The most stable Mn_{15} icosahedral cluster is only 0·28 eV higher in energy than the *bcc* structure.

The binding energies for Mn clusters having 3 to 23 atoms are shown in figure 2. The energies for Mn_3–Mn_8 are taken from the work of Pederson *et al* (1998), who also used a gradient corrected exchange–correlation potential. Even for the largest cluster, the binding energy reaches only about 70% of the bulk. The minimum bond lengths decrease with increasing cluster size, and for Mn_{19} and Mn_{23}, the shortest bond lengths are very close to those found for bulk α Mn.

Determination of the spin configurations for each cluster geometry presents a significant computational

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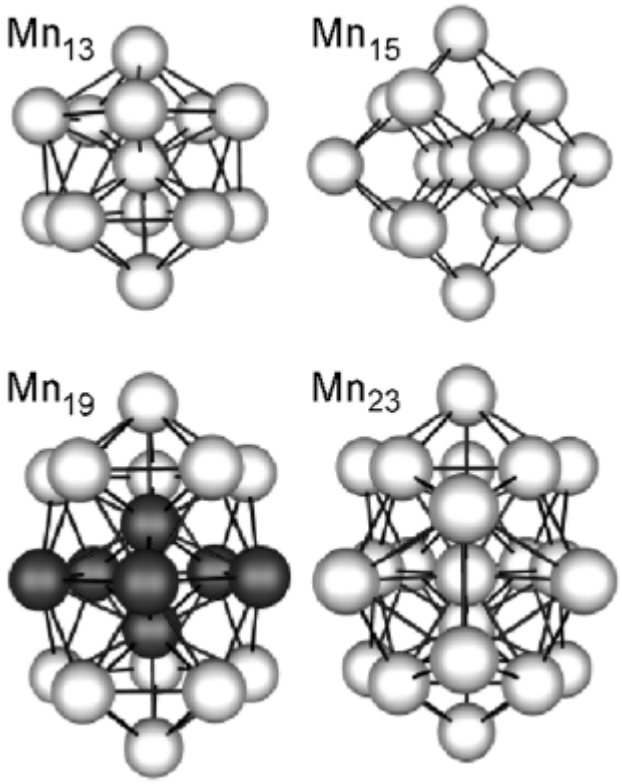

Figure 1. Geometries of the Mn clusters discussed in this work. The spin configuration of Mn_{19} is shown as an example. Light grey represents spin up and black, spin down.

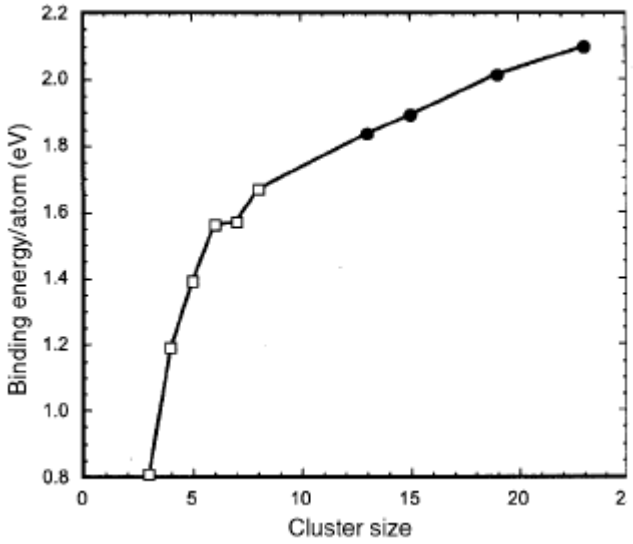

Figure 2. Binding energy per atom as a function of cluster size. The data for Mn_3–Mn_8 (empty squares) are taken from Pederson *et al* (1998). The filled circles are from the present calculation. The bulk cohesive energy is 2·92 eV/atom.

challenge. From earlier studies (Nayak *et al* 1998; Pederson *et al* 1998), we know that small clusters have ferromagnetic coupling, and we also know there is antiferromagnetic coupling in the bulk. The small moment per atom for Mn_{11}–Mn_{99} determined by experiment (Knickelbein 2001) indicates a transition from ferromagnetic to ferrimagnetic behaviour between Mn_8 and Mn_{11}. Thus we have considered many spin configurations, some with fixed total moments, and others with specified initial moments on each atom.

The resulting lowest energy spin configurations have integrated local spin densities of about $\pm 4\,\mu_B$ per atom. As might be expected, those atoms with highest coordination have smaller spin densities and the lower-coordinated surface atoms have the highest densities. The icosahedral structures of Mn_{13} and Mn_{19} show ferromagnetic coupling within the planes of the 5-membered rings and antiferromagnetic coupling between planes (figure 1). The spin configuration of Mn_{15} is one in which the corner atoms of the *bcc* structure are antiferromagnetically coupled with the central and face-centred atoms. For Mn_{23}, the four atoms capping the icosahedral faces are ferromagnetically coupled to the central pentagonal plane. The spin configuration is otherwise similar to that of Mn_{19}. While the most symmetric spin configurations seem to be favoured in general, there is often a small energy difference between this and a less symmetric structure.

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