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Electronic structure and magnetism of $Mn_{12}O_{12}$ clusters

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To address the ferrimagnetic state of the Mn_{12} acetate matrix $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ we have performed all-electron gradient-corrected density-functional calculations on $(MnO)_n$ with $n=1$, 2, 4, and 12. In contrast to bulk MnO which is antiferromagnetic, the small $(MnO)_n$ ($n=1$, 2, and 4) clusters are ferromagnetic with Mn moments of $5.0\mu_B$ but the ground state of $Mn_{12}O_{12}$ is ferrimagnetic with a total magnetic moment of $20.0\mu_B$ as observed experimentally. The inner Mn sites in $Mn_{12}O_{12}$ are found to have localized moments of $4.1\mu_B$ which are antiferromagnetically coupled to two types of outer Mn with moments of $4.2\mu_B$. The cluster is shown to be marked by ionic as well as covalent bonds between Mn d and O p electrons and a strong intracluster magnetic coupling. [S0163-1829(99)51102-8]

Observation of quantum phenomena at a macroscopic scale has always been a challenging problem. There are only a few known examples, notably the Josephson effect and the quantum Hall effect in two-dimensional electron gas. Nanoscale materials or clusters are ideal systems for observing quantum effects because of their reduced size. However, the difficulties of making size-selected clusters in bulk quantities and assembling them in a manner that the intracluster interactions and the statistical fluctuations are sufficiently small to prevent an overshadowing of the quantum effects, remain major obstacles.

Recently Friedman *et al.*[1] have reported the observation of resonant quantum tunneling[2] of spins in single-crystal $Mn_{12}O_{12}$ acetate. The magnetically interesting part of the compound, observed by Lis,[3] has D_{2d} symmetry with a composition of $Mn_{12}O_{12}$ and has an isolated configuration shown in Fig. 1. In addition the magnetically interesting part of the compound is isolated within an organic matrix which ensures that each of the Mn atoms is nominally sixfold coordinated and that the $Mn_{12}O_{12}$ units are well separated from one another. Each of the eight outer Mn atoms are passivated by two acetate radicals (CH_3COO) and the sixfold coordination of the inner Mn atoms is approximately maintained by weakly interacting H_2O molecules placed in close proximity to the Mn atoms. The composition of the unit cell is completed by adding four additional H_2O molecules and two additional acetic acid molecules (CH_3COOH) which act as hard-sphere space-filling spectators. Each $Mn_{12}O_{12}$ cluster is magnetic with a total spin of 10 (moment of $20\mu_B$).[4,5] What is interesting is that the hysteresis loops and relaxation times[6–11] obtained by applying a varying magnetic field exhibit features that appear to be associated with quantum effects. Starting from a high-saturation magnetic field, as the field is reduced below the zero into negative values, the magnetization exhibits steps as a function of the field. Similar steps are observed as one increases the field beyond zero starting from the negative saturation field. The magnetic relaxation time is significantly enhanced at the fields corresponding to the steps.

Based on assumed charge states of -2 for the oxygen atoms and -1 for the acetate radicals, it has been suggested[6] that each $Mn_{12}O_{12}$ cluster has a D_{2d} symmetry and is composed of four Mn^{4+} and eight Mn^{3+} ions which are antiferromagnetically coupled. Based on these oxidation states and the experimental moment of $20\mu_B$ it has been further suggested that the Mn atoms possess localized moments of $-3.0\mu_B$ and $4.0\mu_B$, respectively. In the solid, the $Mn_{12}O_{12}$ clusters are organized with their fourfold symmetry axis along the c axis of the lattice. Since the organic matrix isolates these clusters they are magnetically decorrelated. Each cluster is oriented along an S_4 easy axis, has a total spin of 10 and can assume 21 ($2S+1$) orientations along the z axis. The crystal has a large magnetocrystalline anisotropy and the energies of the $2S+1$ azimuthal (m) states are not degenerate. Application of the external magnetic field along a z direction enhances the binding energy of the parallel azimuthal magnetic ($+m$) states while decreasing that of the antiparallel azimuthal magnetic ($-m'$) states. It has been proposed that for field values at which the energy of an m state coincides with that of a $-m'$ state, the relaxation time increases and a resonant quantum tunneling[11] of the spins takes place, accounting for the observed steps in magnetization and the changes in relaxation times.

While the above picture explains the observed effect, a basic understanding of the electronic structure is still missing. The current picture assumes highly ionic Mn oxidation states of $+4$ and $+3$ which if taken literally would lead to extremely well-localized Mn d states and therefore decorrelated atomic spins. Further a total moment of $20\mu_B$ can be obtained by several other sets of local Mn-atom magnetic states (for example, eight parallel and four antiparallel Mn atoms with moments of $5\mu_B$). In contrast to decorrelated atomic spins, in the $Mn_{12}O_{12}$ cluster, the Mn atoms are coupled via the O atoms and the cluster behaves like a single unit with a moment of $20.0\mu_B$. This requires that there must be states which couple the localized moments on various Mn sites and span across the whole cluster. It is therefore inter-

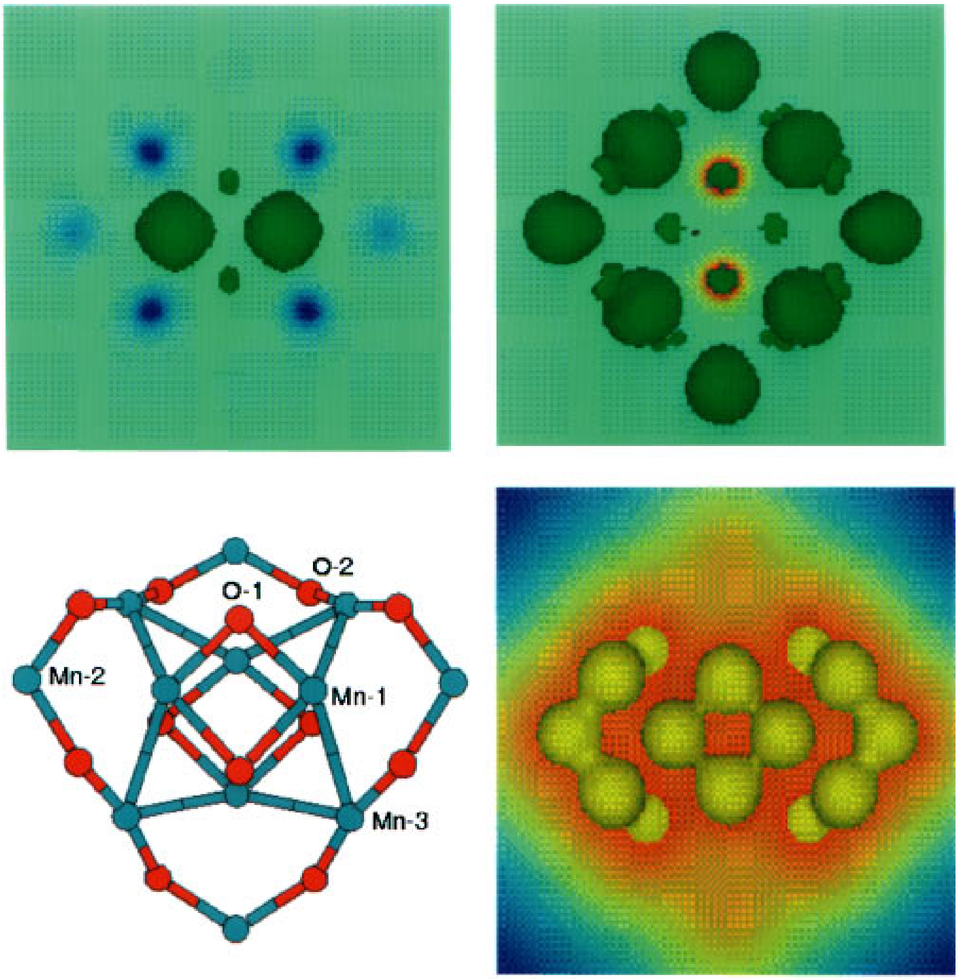

FIG. 1. (Color) Optimized structure (lower left), valence density (lower right), and the minority and majority spin densities (upper left and right, respectively) for the isolated $Mn_{12}O_{12}$ atoms. Darker (red) atoms are oxygen. Lighter (blue) atoms are Mn. Superimposed on the majority (minority) three-dimensional spin density plots are contour plots of the minority (majority) spin densities through planes which contain the minority (majority) atoms. The valence density plot shows that there is covalent bonding between the O and Mn atoms. The spin-density plots clearly show the antiferromagnetic coupling between the interior (minority spin) and the exterior (majority spin) of the cluster.

esting to determine the value and degree of localization of the individual moments, the strength of the intracluster exchange coupling, and the nature of the bonding between the Mn and O atoms.

In this paper we provide *ab initio* calculations of the electronic structure and the nature of magnetic coupling in an $Mn_{12}O_{12}$ cluster. We have also looked at the $(MnO)_n$ clusters with $n=1$, 2, and 4, since studies of these smaller fragments help to understand the electronic and magnetic features of the larger cluster. All the $(MnO)_n$ $(n=1$, 2, and 4) clusters are ferromagnetic (FM) with a net moment of $5.0\mu_B$ per Mn atom. For $Mn_{12}O_{12}$, we find a D_{2d} ground state with a total spin of $20\mu_B$ as observed experimentally. As anticipated earlier, the inner four Mn are antiferromagnetically coupled with the outer eight Mn atoms. We have ascertained that a completely FM cluster $(S=60\mu_B)$ with the same geometry is less stable by 3.46 eV. Further if we flip the moments of the four innermost atoms from minority to majority and allow for an antiferromagnetic (AF) alternation of the outer chain of Mn atoms, the net spin is still $S=20\mu_B$ but this cluster has an energy that is 2.0 eV higher than the other AF state. This confirms that the spins on different atoms are coupled.

The local magnetic moments on the Mn sites are completely different from the current simplistic ionic picture. The spin states are spread over the various Mn sites and the moments are strongly coupled leading to a cluster that behaves like a super atom with a large moment. The electronic binding is shown to have mixed ionic and covalent character.

The calculations presented here were performed with the Naval Research Laboratory Molecular Orbital Library (NRLMOL). The numerical aspects of this Gaussian-based density-functional methodology[12] has been discussed elsewhere.[13] We use the generalized-gradient approximation[14] (GGA) to approximate exchange-correlation effects. For Mn we used 20 optimized Gaussians to construct a $(7s,5p,4d)$ basis set. For O we used a total of 13 optimized Gaussians to construct a $(5s,4p,3d)$ basis set. Details about optimization of the Gaussians appear in Ref. 15 and ASCII files of these basis sets are available electronically upon request to the authors.

Building blocks of the $Mn_{12}O_{12}$ *cluster.* We start with the small $(MnO)_n$ clusters $(n=1$, 2, and 4). For MnO, with a bond length of 1.63 Å, our calculated binding energy of 5.45 eV is comparable to the experimental value of 4.18 eV.[16] The molecule has a magnetic moment of $5.0\mu_B$. In order to calculate the local magnetic moment and charge associated with the Mn and O sites, we calculated the total charge and spin polarization within spheres of various sizes drawn around Mn and O atoms. As we will discuss later, a sphere of radius $2.5a_0$ around the Mn site and $2.37a_0$ around the O atom are able to capture most of the local quantities. The results indicate that the moment is mainly localized at the Mn sites and is primarily due to $3d$ states. The Mn s and p states contribute $0.4\mu_B$ and $0.1\mu_B$, respectively, while the O $2p$ states contribute around $0.1\mu_B$. There is a charge transfer of $1e^-$ from Mn to O. An analysis of the resulting charge density shows that in addition to being ionic, the bonding has a covalent contribution. For Mn_2O_2, we find the ground state is characterized by a distorted square (Mn-O-Mn bond angles, Mn-O bond lengths, and cohesive energies of 87°, 1.86 Å, and 6.86 eV, respectively) and carries a FM moment of $10\mu_B$. Most of the spin is again due to Mn $3d$ states and there is a charge transfer of $1e^-$ from Mn to O. An analysis of the electronic states shows that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are nearly degenerate with energies at -0.141 hartree.

The case of Mn_4O_4 is important since it forms the core of the $Mn_{12}O_{12}$ cluster. The ground state is a distorted cube with a MnO distance of 2.02 Å compared to 1.86 Å in Mn_2O_2 and 1.63 Å in MnO. The binding energy per MnO pair is 7.84 eV. The interparticle distance and binding energy therefore increase with cluster size. The ground state has a total magnetic moment of $20.0\mu_B$ which, interestingly, is the same as that of a $Mn_{12}O_{12}$ cluster. The magnetic moments are primarily localized at the Mn sites. These results indicate that while bulk MnO is an antiferromagnet, the fragments Mn_2O_2 and Mn_4O_4 are all ferromagnetic with moments of $5.0\mu_B$ per Mn atom. The local moments (defined with Mn radii of 2.5 bohr) are found to be $4.0\mu_B$ and $4.2\mu_B$, respectively, which are essentially the same as those found for the $Mn_{12}O_{12}$ cluster below. It is interesting to note that the magnetic moment associated with Mn sites in bulk MnO (Ref. 17) is $4.58\mu_B$, close to the moments obtained here. Our findings are also in agreement with recent experiments by Li *et al.*[18] on nanostructured MnO particles which indicate that the small particles are ferromagnetic. We would like to add that this magnetic behavior is also shared by other oxides. For example, Kudama *et al.*[19] have recently measured the magnetic moments and coercivities of NiO nanoparticles and have found anomalously large moments. Since bulk NiO is antiferromagnetic, they propose that their results in nanoparticles could be understood within a model where the reduced coordination causes a fundamental change in the magnetic order. These results indicate that one probably needs to go to the larger shells to get the bulk antiferromagnetic character. The electronic spectrum of Mn_4O_4 shows that the HOMO level is primarily composed of O p states, is triply degenerate, and lies at -0.144 hartree. The LUMO, however, lies significantly higher at -0.128 hartree. For Mn_2O_2, on the other hand, the HOMO and LUMO both lie at -0.141 hartree. This shows that surrounding Mn_4O_4 by Mn_2O_2 units could lead to stable structures, if one could transfer charge from Mn_4O_4 to Mn_2O_2 units. These charge transfers would involve minimal energies but the resulting structure could gain energy via long-range Coulomb interactions. The open $Mn_{12}O_{12}$ structure seems to be stabilized by these interactions.

While the local D_{2d} symmetry of the experimental crystalline structure proposed by Lis[3] is formally (albeit weakly) broken by the introduction of the acetate groups, the isolated $Mn_{12}O_{12}$ cluster allows for a D_{2d} structure and the geometry in Fig. 1 is stable with this symmetry. It is marked by the inner core of Mn_4O_4 surrounded by eight Mn and eight O atoms and has three kinds of Mn_n $(n=1-3)$ and two kinds of O_m $(m=1,2)$ atoms. The inner core of Mn_1 atoms are linked to outer Mn_3-O_2-Mn_2-O_2 chains. The calculated Mn_1-Mn_1 distances in the inner Mn_4O_4 core are 2.82 and 3.14 Å compared to the corresponding experimental values of 2.82 and 2.94 Å in the bulk $Mn_{12}O_{12}$ acetate. The nearest-neighbor MnO distances in the inner core are 2.09 and 2.15 Å compared to 1.90 and 1.92 Å, respectively. The calculated Mn_1-Mn_2 and Mn_2-Mn_3 distances are 2.65 and 3.35 Å compared to the bulk values of 2.77 and 3.33 Å, respectively. The only major difference between the calculated and the proposed bulk structure is the location of Mn_3 atoms. We find that in the free cluster, the Mn_3 atoms are significantly closer to the inner Mn_1 atoms. This may be due to the incomplete coordination of the outer ring of the isolated $Mn_{12}O_{12}$ cluster. The calculated Mn_1-Mn_3 separation of 2.60 Å is smaller than the proposed value of 3.45 Å. We repeated our calculations with Mn_3 atoms far removed from Mn_1 atoms, but the atoms always converged to the close separation. As shown below, the current structure explains the available magnetic data. The cluster had a binding energy of 8.33 eV per MnO pair.

Electronic and magnetic structure of the isolated $Mn_{12}O_{12}$ *cluster.* The ground state of the isolated $Mn_{12}O_{12}$ cluster had minority-spin and majority-spin HOMO/LUMO gaps of 0.38 eV and 1.14 eV, respectively. Majority-minority and minority-majority spin gaps were both positive (0.79 and 0.73 eV, respectively), which guarantees that this is a stable magnetic and electronic state. In order to determine the magnetic moment and the charge associated with Mn and O sites, we calculated the total charge Q and the spin polarization M within spheres of various radii drawn around the Mn and O sites. The choice of the radii is a difficult problem and both Q and M will depend on the choice. The ionic radius of O^{2-} is $2.65a_0$ and the size of Mn atom in compounds is $2.59a_0$. We therefore started with these sizes and tried to change them so that the total charge and the total spin within the spheres is close to the total number of electrons and the total spin moment of the cluster. A radius of $2.50a_0$ for Mn and $2.37a_0$ for O was found to be a reasonable choice. The results show that each of the oxygen sites labeled O_1 in Fig. 1 gain $1.1e^-$ while each of the O_2 gains $1.5e^-$. Mn_1 and Mn_2 each lose $1.4e^-$ while each Mn_3 loses $1.1e^-$ leading to charge states that are quite different from the formal oxidation states assigned in previous works. In order to further examine the nature of bonding, we examined the valence charge-density distribution. Figure 1 shows a three-dimensional plot of the valence density. Note that there is significant charge in the MnO bonds. This along with an angular momentum decomposition of the valence states shows that there is mixing between Mn *d* and O *p* states. The bonding, therefore, has contributions from ionic and covalent character. An examination of the valence states showed that they have contribution from several sites. It is these delocalized states that couple different atoms and enable the cluster to behave like a giant magnet. We now turn to the magnetic character of these clusters.

As mentioned above the cluster has a total magnetic moment of $20.0\mu_B$. Integration of the spin polarization within spheres around Mn and O sites gives a magnetic moment of $-4.1\mu_B$, $4.2\mu_B$, and $4.2\mu_B$ associated with Mn_1, Mn_2, and Mn_3, respectively. The spheres around O_1 and O_2 also have a small polarization of $-0.1\mu_B$ and $0.3\mu_B$, respectively. The positive sign indicates the majority spins and the negative sign the minority spins. Moments at the Mn_1 (interior) sites are therefore antiferromagnetically coupled to the Mn_2 and Mn_3 (outer) atoms. As mentioned above, the Mn moments in a Mn_4O_4 cluster are ferromagnetically coupled even though the bulk MnO is an antiferromagnet. The above result shows that the addition of a second layer of Mn sites (as in $Mn_{12}O_{12}$) generates antiferromagnetically coupled Mn sites. In order to clearly illustrate the nature of magnetic coupling, we show in Fig. 1 a projection of the minority and majority spin polarization. In each case, the green spheres give the corresponding spin polarization. In addition, in Fig 1 we superposed a two-dimensional projection of the minority spins on the interior atoms. From these figures, it is clear that although the majority (minority) spin polarization is mainly distributed in the outer (inner) region, there is also a small component in the inner (outer) region. The small spin polarization on O sites is also apparent and is due to the *p* states.

A primary difference between the isolated structure and the experimental x-ray data is the Mn_1-Mn_3 separation which we find to be 2.60 Å in contrast to experiment which finds a 3.45 Å separation. We have ascertained that if we start our geometry at a D_{2d} geometry with similar Mn_3-Mn_1 separations the structure relaxes to the geometry shown in Fig. 1. Further, the net moment associated with larger Mn_1-Mn_3 separations is larger than $20\mu_B$ so it does not reproduce the experimental magnetic measurements. In contrast to our relaxed isolated geometry, the geometry with large Mn_1-Mn_3 separations is gapless, which suggests that this structure would readily react with passivators or reconstruct. Additional bonding of the large separation structure with radicals could decrease the net moments of the system and stabilize it. Our relaxed (short Mn_1-Mn_3) structure leads to the correct total moment and local (Mn_3 and Mn_2) moments that are slightly larger than what is expected from the experimental model. Both geometries studied suggest that the Mn atoms give up between one and two electrons.

To summarize, we have shown that while the bulk MnO is an antiferromagnet, small MnO fragments containing two and four units are ferromagnetic in agreement with recent experiments on MnO nanoparticles. Our studies on $Mn_{12}O_{12}$ show that the cluster is marked by both ionic and covalent bonds. While there is charge transfer from Mn to O, the extent of the charge transfer is far less than proposed by arguments based on formal oxidation states. This has a profound effect on the value of magnetic moments at the Mn sites which have values around $-4.1\mu_B$, $4.2\mu_B$, and $4.2\mu_B$. There is also a small spin polarization located at the O sites which arises due to mixing between Mn *d* and O *p* states. From an analysis of the spin densities, the valence molecular orbitals, and total-energy calculations with different magnetic states, we find that the local moments within a given cluster are strongly coupled. Because the spin states are spread over the entire cluster the strong intracluster magnetic coupling leads to a cluster that behaves like a single unit with a large magnetic moment.

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