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Structural growth in iron oxide clusters: Rings, towers, and hollow drums

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It is shown that the transition from an elementary FeO molecule to the bulk rock-salt FeO proceeds via hollow rings, towers, and drums. Our first-principles electronic structure calculations carried out within a gradient-corrected density functional framework show that small Fe_nO_n ($n=2, 3, 4, 5$) clusters form single, highly stable rings. Starting at Fe_6O_6, these elementary rings begin to assemble into nano columnar structures to form stable Fe_6O_6, Fe_7O_7, Fe_8O_8, Fe_9O_9, $Fe_{10}O_{10}$, and $Fe_{12}O_{12}$ towers. The rings and the empty towers can be further stabilized by capping O atoms at the ends, leading to Fe_nO_{n+1} and Fe_nO_{n+2} sequences. The theoretical results provide insight into the progression of mass intensities in the experimental mass spectra and account for the observed peaks in the negative ion photodetachment spectra of iron oxide clusters.

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An important theme of research on clusters is to probe the manner in which the properties evolve as individual atoms are brought together to form solids, and to investigate the minimum size at which the clusters begin to mimic bulk behaviors.[1,2] It is now established that in most cases, this transition is nonmonotonic. The atomic arrangements in small sizes are generally different from those in bulk, leading to an entirely novel class of properties and behaviors.[1,2] For example, the atomic clusters of nonmagnetic solids (Rh) are found to be magnetic,[3,4] the band gaps (in Si_n nanostructures) are found to evolve considerably with size,[5] and the clusters of noble solids (Au) (see Ref. 6) have been shown to be potential catalysts. Further, the properties change with size and composition. The excitement in this line of research stems from the observation that some of the elemental motifs can be quite stable, thus offering the potential of making new materials using these motifs as building blocks. Since the properties of small clusters can be tailored by changing size and composition, this offers the potential of making materials with desirable properties. Identification of stable cluster motifs and the demonstration of their stability upon assembly are the critical steps in translating this novelty into material design. The identification of fullerenes,[7] met-cars,[8] quasi-one-dimensional structures in semiconducting oxides,[9] and recently, the aluminum-based clusters[10] as stable elemental blocks, are examples of this line of research.

The purpose of this article is to provide evidence for the existence of families of very stable motifs in Fe_nO_m clusters that assemble to form an entirely new class of nanostructures. Bulk iron oxides occur in compositions FeO, Fe_3O_4, and Fe_2O_3, which are all compact solids. In particular, for equiatomic composition, bulk FeO has a compact NaCl arrangement. In this work we demonstrate that, as opposed to compact bulk, Fe_nO_n ($n=2$, 3, 4, and 5) clusters are all single hollow rings. Quite amazingly, these rings are exceptionally stable, and beyond $n=5$, assemble to form decorated and undecorated nanotowers. Our findings are supported by recent experiments by Shin *et al.*,[11,12] who generated iron oxide clusters by laser ablation of the iron metal and subsequent reaction of the gas phase metal atoms and clusters with oxygen. While their mass spectra exhibit a variety of sizes and compositions, the most intense features in the mass spectra are of the form Fe_nO_n, Fe_nO_{n+1}, and Fe_nO_{n+2} similar to the earlier observations by Riley *et al.*[13] Further, while Fe_nO_n are more prominent for $n<10$, Fe_nO_{n+1} are present throughout, but only become dominant beyond $n=10$. In this work we focus mainly on Fe_nO_n and on some Fe_nO_{n+1} clusters. Our detailed first-principles calculations carried out within a gradient-corrected functional show that the Fe_nO_n clusters corresponding to $n=2$, 3, 4, and 5 are very stable, elementary rings. The higher sizes in this sequence consist of structures built via vertically assembling stable rings to form columnar units called towers. The coupling between the rings is weaker than the intra-ring coupling and hence the towers offer unique opportunities to control properties by combining the intra- and inter-ring couplings. Further, Fe_6O_6 is the first tower formed of two Fe_3O_3 rings. Subsequently, the Fe_9O_9 cluster consists of three Fe_3O_3 rings, while $Fe_{12}O_{12}$ consists of four Fe_3O_3 or three Fe_4O_4 rings assembled vertically. The end Fe sites in the Fe_nO_n towers are susceptible to absorbing O atoms, and this leads to the Fe_nO_{n+1} and Fe_nO_{n+2} sequences, where the additional O lies outside the tower at an axis site as if to cap the open end. In the Fe_nO_{n+2} series, both the ends are capped and the structure resembles a hollow drum. What is important is that the binding energy of the additional oxygen increases with the size of the tower and becomes comparable to the binding energy of an FeO molecule around $n=10$. At this point, the Fe_nO_{n+1} sequence begins to dominate the mass spectrum. While our current discussions are confined to iron oxide clusters, we propose that the same class of behaviors may be observed in oxides of other transition elements.

The theoretical investigations were carried out using the NRLMOL set of codes developed by Pederson and co-workers.[14–16] The codes are based on a linear combination of atomic orbitals, a molecular orbital approach, and use a gradient-corrected functional[17] to include exchange and correlation effects. Essentially, for a given cluster of atoms, the

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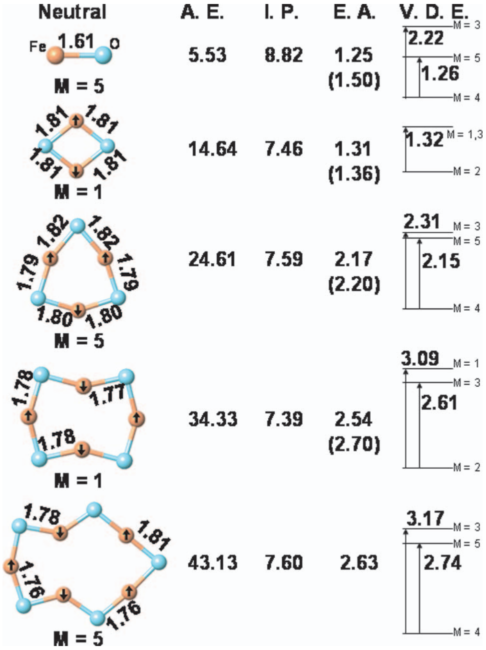

FIG. 1. (Color) Calculated ground state geometries including bond lengths (Å), A.E. (eV), I.P. (eV), E.A. (eV), multiplicity M, and the vertical transition energies, V.D.E (eV), from the anion to neutral clusters for Fe_nO_n ($n=1-5$) clusters. Experimental values for the E.A. are given in parenthesis. The arrows indicate the orientation of the atomic magnetic moment. The dark atoms are Fe atoms while those of the lighter shade are O sites.

electronic wave function is built from a linear combination of atomic orbitals that is further expressed as a linear combination of Gaussian wave functions centered at the atomic locations. The matrix elements of the Hamiltonian are computed via numerical integration over a carefully chosen mesh of points. The basis set[16] for Fe consisted of $7s$, $5p$, and $4d$ functions constructed from 20 bare Gaussians and that of O had $5s$, $4p$, and $3d$ functions constructed from 13 bare Gaussians. The basis sets were supplemented by $1d$ Gaussian. For details about the approach along with the details about the basis sets, the reader is referred to original papers. To find the ground state, several starting geometrical configurations were tried. In each case, the geometry was optimized by calculating the Hellmann-Feynman forces until the forces became smaller than a threshold value of 0.001 hartree/bohr. As we will show, the ground state of the oxidized cluster can be either ferromagnetic or antiferromagnetic in configuration. In principle, therefore, one should examine all possible magnetic states for all the geometrical arrangements. Our results at small sizes included these investigations. While the ground states at these sizes were ferrimagnetic, the corresponding binding energy per atom differed by less than 0.1 eV from the corresponding ferromagnetic configurations. Since the investigation of all possible ferrimagnetic configurations becomes computer intensive at larger sizes and since we are primarily interested in the variations of binding energies, we only investigated the ferromagnetic arrangements for clusters with more than 13 atoms. There are no experimental techniques to directly probe the geometrical arrangement of atoms as the clusters are too small for atomic microscopy. An alternate approach is to use negative ion photoelectron spectra.[18] Such spectra have been measured at small sizes and we have used this alternate approach to substantiate our findings for these cases.

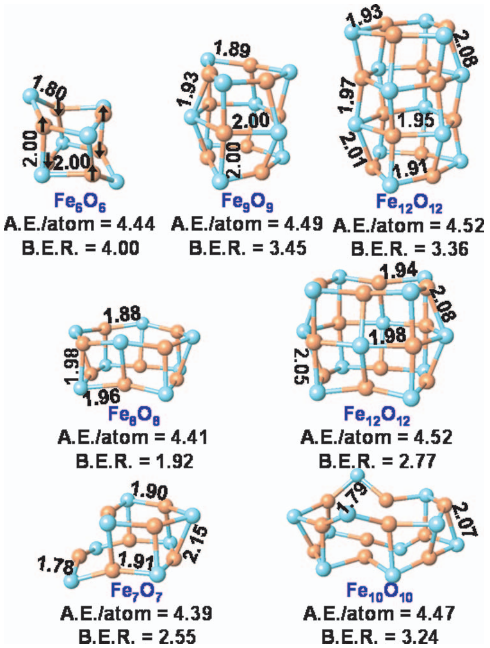

FIG. 2. (Color) Ground state geometries, A.E./atom (eV), and B.E.R. (eV) [Eq. (3)] of Fe_nO_n clusters for $n=6$, 7, 8, 9, 10, and 12.

Figure 1 shows the ground state geometries of Fe_nO_n clusters for $n=1$, 2, 3, 4, and 5. Also given are the atomization energies (A.E.) calculated using

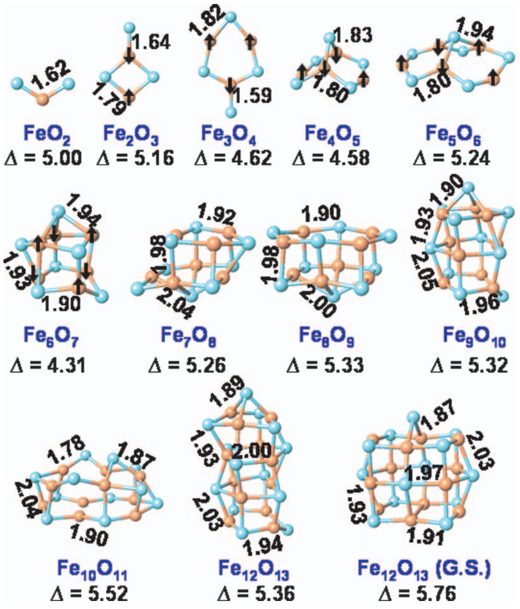

FIG. 3. (Color) Ground state geometries including bond lengths (Å) and binding energy of the additional O atom, Δ (eV), for Fe_nO_{n+1} ($n=1-10$, and 12) clusters. For $Fe_{12}O_{12}$, the figure shows the addition of O to both the isomers. The isomer marked G.S. is the ground state after the addition of O.

$$\text{A.E.} = nE(\text{Fe}) + mE(\text{O}) - E(\text{Fe}_n\text{O}_m), \tag{1}$$

representing the energy required to break the cluster into individual atoms. Here, $E(\text{Fe}_n\text{O}_m)$ is the total energy of the cluster, and $E(\text{Fe})$ and $E(\text{O})$ are the total energies of the Fe and O atoms, respectively. In the case of anionic clusters, the energy is calculated for breaking into neutral Fe and O atoms and an O^-. For FeO, the experimental data[19] and earlier calculations[20] exist. The calculated bond length of 1.61 Å, A.E. of 5.53 eV, ionization potential (I.P.) of 8.82 eV, and adiabatic electron affinity (A.E.A.) of 1.25 eV are comparable to the corresponding experimental values of 1.62 Å, 4.17 eV, 8.7 eV, and 1.50 eV, respectively.

The ground states for Fe_nO_n, $n=2-5$, are all open ring structures. This is really surprising since bulk FeO has a compact rock-salt structure. The previous studies[21] examined only compact structures. We, on the other hand, found the compact bulk-like geometries to be much higher in energy. As pointed out earlier, there is no microscopic or spectroscopic data to compare the calculated geometries. However, an alternate approach to indirectly probe the geometry, recently advocated by several authors,[18] is to combine theoretical studies with experimental data on negative ion photodetachment spectra.[22] In these experiments, one first generates the negative ions of the clusters to be probed. The extra electron in the negative ion is then detached by exposing the cluster to a laser beam of fixed frequency. The difference in the energy of the photon and the kinetic energy of the detached electron is then a measure of the energy required to go from the anion to the neutral cluster. Now suppose that the anion has a spin multiplicity of M. The neutral cluster obtained by detaching an electron will then have a spin multiplicity of $M \pm 1$ since the ejected electron could originate in the spin-up or -down manifold. Further, the neutral cluster of the given multiplicity can be in the ground or excited state of the same multiplicity. Generally, the transitions occur on a very short time scale and therefore are vertical; namely, the anion geometry does not relax during the transition. It is, however, possible to obtain an A.E.A. that can be compared with the calculated values. As the electronic structure is intimately linked to the geometry, an agreement between the calculated and experimental transitions and E.A. provides an indirect support that the calculated geometries should be correct. Such experimental spectra for Fe_2O_2, Fe_3O_3, and Fe_4O_4 have been measured by Wang and co-workers.[21] Here, we have carried out theoretical calculations on the anions of these clusters and Fig. 1 shows our calculated E.A. as well as lowest transitions from anions to neutrals. We first begin with the vertical transitions. For FeO, the experimental spectra exhibit transitions around 1.5 and 2.0 eV compared to predicted values of 1.3 and 2.2 eV, respectively. For Fe_2O_2, there is a peak around 1.5 eV compared to the calculated value of 1.3 eV. The case of Fe_3O_3 is interesting since there are no sharp peaks. Instead, one observes a broad region starting from around 2.0 eV. Our calculated transitions of 2.15 and 2.30 eV are within the experimental region. Finally, for Fe_4O_4, one again observes a broad peak starting around 2.5 eV and a minor peak around 3.0 eV consistent with our calculated values of 2.6 and 3.1 eV. In addition to the vertical transitions, we show in Fig. 1, the calculated and measured E.A. Note that the calculated values for Fe_nO_n ($n=2-4$) are within a few percent of the experiment. The close agreement again provides support that the calculated structures are the ground states.

A further confirmation of the stability of primary rings comes from a study of the fragmentation patterns of the clusters. When a cluster A_n is fragmented into A_{n-m} and A_m fragments,

$$A_n \rightarrow A_{n-m} + A_m, \tag{2}$$

the minimum energy corresponds to the path that generates most stable products. Favored fragmentation products therefore provide indirect evidence for stability. Such experiments[23] are available for Fe_nO_m clusters containing up to four Fe atoms. A comparison of the time-of-flight mass spectra data acquired by 118 and 193 nm ionization at low pulse energies suggests that the Fe_nO_n clusters with $n=2$, 3, and 5 are particularly stable and have high ionization potentials, as shown in Fig. 1. In addition to the geometrical shapes and the electronic bonding we also looked at the spin magnetic moments. In Fig. 1, we have marked the direction of the local spin moments at the various sites. Note that while the Fe sites have nonzero spin moments, the coupling is predominantly antiferromagnetic. We expect this trend to continue for extended structures. We would like to add that we have only examined collinear magnetic configurations. The antiferromagnetic coupling can sometimes lead to magnetic frustration that can result in noncollinear arrangements.[24] The close agreement with the negative ion photoelectron spectra, however, indicates that these effects are not significant in the present case.

The presence of stable rings raises interesting questions. As n increases, do the rings continue to grow or do the basic rings assemble to form extended structures? In the latter case, do they form planar structures or towers? How strong are the interactions between the rings in these extended structures and do the rings maintain their identity? Can one regard the $\text{Fe}_n\text{O}_{n+1}$ and $\text{Fe}_n\text{O}_{n+2}$ structures as rings joined by extra oxygen atoms? To answer these questions, we first examine Fe_nO_n structures for $n=6$, 7, 8, 9, 10, and 12. Figure 2 shows the ground state structures obtained by analyzing several possible arrangements. Note that for $n=6$, 8, and 10, the ground state corresponds to a tower built from 3×3, 4×4, and 5×5 rings. For $n=9$, the ground state is a tower structures built out of three stacked 3×3 rings. For $\text{Fe}_{12}\text{O}_{12}$, one can construct a tower by assembling four 3×3 or three 4×4 rings. We found that while the ground state corresponds to the tower built out of 4×4 rings, the tower built from 3×3 rings is only 0.01 eV higher in energy. Since this difference is outside the limit of accuracy of theoretical studies, the two structures can be considered to be degenerate. To further examine the nature of bonding in these towers, we calculated the binding energy between the rings (B.E.R.) by

$$\text{B.E.R.} = [xE(\text{Fe}_m\text{O}_m) - E(\text{Fe}_n\text{O}_n)]/(x-1), \tag{3}$$

where x is the number of rings of size m in a cluster of size n. These are marked in Fig. 2. A comparison of the binding energy in free rings and the B.E.R clearly indicates that the intra-ring interactions are stronger than the inter-ring interactions. In addition to the above clusters, we examined Fe_7O_7 that cannot be formed by rings of one kind. It is interesting that the ground state is now a stacking of 4×4 and 3×3 rings. The physical properties of the rings are also maintained in forming the towers. For example, the interatomic distances in rings are not too modified in going to towers.

While the towers are the most stable configurations for Fe_nO_n ($n<5$), preferred Fe sites in the rings can be coordinated to further stabilize the clusters. To examine it more closely, we first consider the location of an extra O atom in the elementary rings for $n=2$, 3, 4, and 5. These, along with the structure of other Fe_nO_{n+1} clusters, are shown in Fig. 3. First, note that the lowest energy configuration of Fe_2O_3 is an O atom located outside the central ring of Fe_2O_2. We also found that a structure wherein the two Fe sites are bound to a triad of O atoms forming a triangular by-pyramid is metastable.[25] The ground state Fe_3O_4 structure also prefers an O atom located outside the central Fe_3O_3 ring. The situation changes for higher sizes. For example, the ground state of Fe_4O_5 (shown in Fig. 2) is an O atom inserted in the Fe_4O_4 ring. Similarly, the structure of Fe_5O_6 inserts the O atom in the Fe_5O_5 ring. In Fig. 3 we show the gain in binding energy of the additional O in Fe_nO_{n+1} structures and one notices that it increases. As pointed out before, starting at Fe_6O_6, the elementary rings Fe_nO_n with $n=3$, 4, and 5 begin to stack, forming towers. We examined various locations of the additional O atom. As shown in Fig. 3, the most stable site corresponds to the O located at the axis of the ring, thus capping the hollow ring. This is reasonable as the inserted O can bind to multiple metal sites, thus stabilizing the structure. Note that the binding energy of the additional O for $Fe_{10}O_{10}$ is unusually large and is comparable to the binding energy of a FeO molecule. We believe that this increase in binding may be responsible for the dominant peaks of Fe_nO_{n+1} species starting at $n=10$. Further, since a tower has two ends, Fe_nO_{n+2} corresponds to the towers with caps on both the sides, forming the hollow drums. While the detailed results on such species will be presented later, note that Fe_8O_{10} drums would be ideal building blocks to assemble into bulk FeO lattice.

To conclude, we have demonstrated that while bulk FeO has a compact rock-salt structure, the ground state geometries of small Fe_nO_n clusters for $n=2$, 3, 4, and 5 are open rings. These rings are highly stable and assemble to form towers. The empty towers can however be decorated by O atoms to lead to hollow drums. We would like to point out that the progressions outlined here are not specific to iron oxide. For example, Castleman and co-workers[26] had speculated the possibility of a tower structure for $Mn_{12}O_{12}$ based on their fragmentation studies of Mn_nO_n clusters. Similarly, two of the authors of this paper had recently suggested[27] the possibility of fully saturated rings in some of the Cr_nO_{3n} clusters. It is our hope that the present investigations would stimulate more coordinated effort in the search of rings, towers, and drums in oxides of other materials. We are currently carrying out more detailed studies of the electronic, magnetic, and chemical properties of these new families.

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