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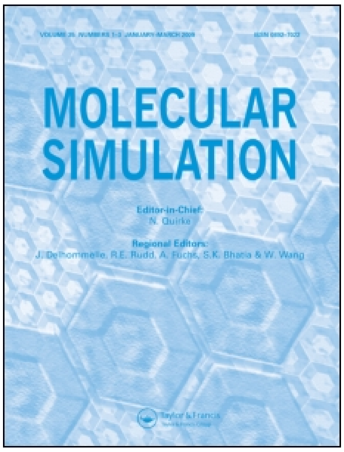

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Structure and Magnetism of Anion Iron Oxide Clusters

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Structure and Magnetism of Anion Iron Oxide Clusters $Fe_nO_m^-(n = 1, 2)$

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We have studied structural and magnetic properties in the anion iron oxide clusters, $FeO_m^-(m = 1 - 6)$ and $Fe_2O_m^-(m = 1 - 5)$, by means of first-principles molecular dynamics based on the density functional theory. The additional electron on the ground state neutral cluster was found to affect the geometry and magnetism of clusters. The vertical detachment energy (VDE) was estimated at the ground state geometry of anion clusters. A comparison with the experimental data indicates good agreement of tendency in the number of oxygen atoms.

Keywords: First-principles molecular dynamics; Car–Parrinello molecular dynamics; Iron oxide cluster; Electron affinity; Vertical detachment energy

INTRODUCTION

Magnetism should have a key role in various nanoscale transition metal clusters, because the intra- and inter-atomic exchange interaction energies are comparable to the chemical bonding energy variation contributed from valence electrons. Magnetic clusters are a candidate of magnetic nano-size material for the high density magnetic memory storage or the spintronics of semiconductors and are studied as model systems for active site component in a biochemical molecule. The reaction against oxygen or the functional with oxidation are interesting, however, for example, properties of the free standing iron oxide clusters have been scarcely studied with both theoretical and experimental approaches.

For small iron oxide clusters, which are negatively charged, photoelectron spectra were reported by Wang and his co-workers [1–3]. They had analyzed the electron affinity (EA) estimated at the onset of spectrum with respect to the binding energy and found that the EA of the oxide clusters with a given number of iron atoms, in general, increased with the number of oxygen atoms. The spectra show a variation among different stoichiometries of clusters, especially for FeO_m and Fe_2O_m. They suggested that the oxygen atom was sequentially added to the surface on the iron cluster core, in accordance with the linear increase of EA with respect to the number of oxygen atoms. They discussed possible atomic structures, but it is desirable to study the properties, based on an *ab initio* calculation.

We have previously studied the neutral iron oxide clusters [4]. In the previous work, the ground state geometry and magnetic structure were determined by using first principles molecular dynamics. The experimental data on the atomic structure and magnetic arrangement has been scarcely unknown. The magnetic moment of $(6.5 \pm 1)\ \mu_B$ Fe_2O was measured with the Stern–Gerlach type apparatus [5]. The value is in good agreement with the calculated value of $6.8\,\mu_B$, and the theoretical prediction indicates the isosceles triangle of atomic structure [4]. This result is essentially the same as the result of the previous *ab initio* approach [6]. In our previous calculation, the noncollinear magnetic clusters, which has a three-dimensional magnetic arrangement, was obtained as the ground state at Fe_3O_5 [4].

The atomic structure of charged clusters could be different from that of neutral clusters. The drastic changes in structure are expected to affect

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the photoelectron spectrum or the EA of clusters. To compare with the available experimental data of EA, in the present work, we report the ground state geometry and magnetic structure for the anion iron oxide clusters, $Fe_nO_m^-(n = 1, 2)$ and their vertical detachment energies (VDE) instead of EA. We discuss the dependence of VDE with respect to the number of oxygen atoms.

CALCULATION METHOD

We have used first principles molecular dynamics [7], which is based on the density functional theory [8,9] with ultra-soft pseudo potentials [10–12] and planewaves, to optimize the configuration of clusters. This scheme allows us to take the simultaneous optimization in both atomic and electronic degrees of freedom. The clusters were placed in a large cubic cell of side 20 a.u. with the periodic boundary condition. The energy cutoffs are 24 Ry or planewave expansion of electron wavefunctions at the Γ point and 250 Ry for the augmented electron density [11,12]. We used the generalized gradient approximation (called PW91) for the exchange-correlation energy [13]. To treat the metallic property that there are some degenerate states around the Fermi level, as in the calculation of neutral clusters, we introduced the additional freedom of partial occupations [14–16]. Consequently, the values presented for magnetization were obtained by integrating spin densities, resulting in non-integer value.

In pure iron clusters, there are ferromagnetic and antiferromagnetic interactions between magnetic moments on atoms [17,18]. Due to this fact, noncollinear magnetic structures could appear at stable - clusters or in the optimization process of atomic and electronic configurations. Therefore, we have used the scheme of noncollinear magnetism [17] as well as the usual spin polarized scheme for density functional calculations.

In those types of scheme, which take a planewave basis set with the periodic boundary condition, though the accurate calculation can be performed by increasing the energy cutoff, the approach to charged systems is not straightforward due to the inconvenience of solving the Poisson equation. In the present calculation, the contribution of uniform charge to the Hartree potential has been evaluated with the real space integration in the real cell.

RESULTS AND DISCUSSION

To check the accuracy of our scheme for charged clusters we collected results of iron dimer for VDE and ionization potential (IP) in Table I. In the present work, the VDE is estimated to be the total energy difference between the ground state anion and the neutral cluster having the same geometry. The IP is also calculated as the energy difference between the neutral ground state cluster and the ionized cluster having the same geometry. The convergence of VDE for cutoff energies is good and the increase of cutoff energy for wavefunction to 40 Ry result in the small change of 0.004 eV our calculated values for VDE are in good agreement with Castro's and Chrétien's values and for IP with the experimental values. Note that the agreement of LSDA's values with the experimental values may require an appropriate explanation, because experiences for DFT show that the GGA usually better describes energetics of the system, for example, cohesive energies, than the LSDA. The values recently calculated by Gutsev *et al.* with using the functional (the combination of Becke's exchange and Perdew–Wang's correlation, BPW91) shows a closer agreement with experimental value, but the reason have never been clarified [23]. The GGA adopted in the present work overestimated values of VDE by about 30% of the experimental value.

FeO_m^-

The series of clusters, $FeO_m^-(m = 1 - 4)$, has been theoretically studied by Gutsev *et al.* All of the ground state geometries for this series are essentially the same as those which were obtained in the previous work. In general, effects of additional electrons give longer bond lengths. The experimental work by Wu *et al.* implies that FeO_4^- contains the oxygen molecular unit, while the cluster obtained

TABLE I Vertical detachment energy for anion Fe_2^- and ionization potential for neutral Fe_2, compared with the previous calculations and the experimental data. The LSDA and GCA specify local spin density approximations [19,20] and gradient corrected approximations, respectively. For PP86 and BPW91, refer to the corresponding references

Method	*Present work*	*Castro et al. [21]*	*Chrétien et al. [22]*	*Gutsev et al. [23]*	*Exp.*
VDE LSDA	0.97	0.95			0.9*
VDE GCA	1.19	1.31	1.17†	0.94‡	
IP LSDA	6.34	7.21			6.3¶
IP GCA	6.26	7.00	7.14†	6.68‡	

*Ref. [24]. †PP86. ‡BPW91. ¶Ref. [25].

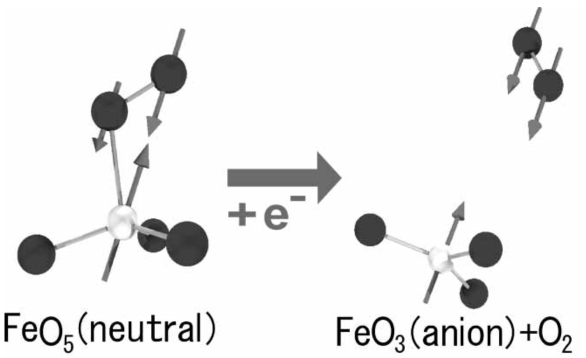

FIGURE 1 Cluster separation of FeO_5 by the additional electron.

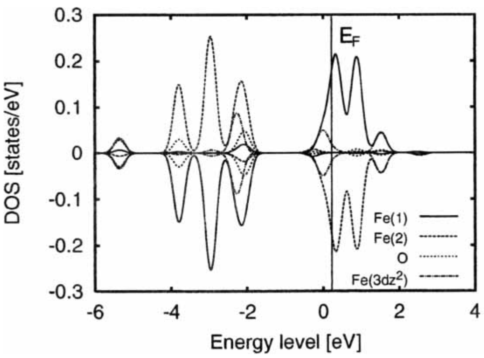

FIGURE 3 Electronic density of states in the ground state anion cluster, $(Fe_2O)^-$.

in the present work has no tight bond between O atoms.

The addition of an electron to FeO_5 and FeO_6 with the geometry of neutral cluster results in a molecular separation to an oxygen molecule and the anion cluster consisting of the other atoms. The schematic figure is shown for FeO_5 in Fig. 1. Note that the oxygen molecule separated is neutral and the resulting anion cluster has similar properties of the ground state for FeO_3^-. In our work no stable anion cluster for $m = 5$ and 6 has ever been obtained.

$Fe_2O_m^-$

The ground state geometry of anion clusters for Fe_2O changes drastically from that of the corresponding neutral cluster. The change is shown schematically in Fig. 2. The stable cluster of Fe_2O^- is antiferromagnetic, which is different from the ferromagnet in the neutral cluster. The ferromagnetic electronic structure in the neutral cluster shows that the additional electron occupies the *pd*-hybridized anti-bonding orbital. This occupation of electron drives the deformation to linear geometry. The anti-bonding hybridized state is pushed up above the Fermi level and the electron transfers to the non-bonding orbital of 3*d*-orbitals, which mainly consists of $3d(3z^2 - r^2)$ orbital. It may be important for stability of the anion cluster that the linear geometry induces the additional *pd*-hybridization as well decreases the energy loss from static coulomb repulsion among electrons. The density of states in Fe_2O^- is presented in Fig. 3, which clearly shows an exchange splitting of ~4 eV in each Fe atom. When we supposed the detached electron to be in the non-bonding 3*d*-orbitals at the Fermi level, the prominent peak in the photoelectron spectrum could be expected as in the experimental results [2].

While in the neutral cluster the direct exchange interaction between the magnetic moments favors the ferromagnet, the linear geometry, in which the iron atoms are separated by the O atom, with the electron occupation of 2*p* orbital on oxygen atom, induces the superexchange interaction, resulting in the convert to the antiferromagnetic arrangement.

For $Fe_2O_m^-(m = 2 - 5)$, the ground state geometries were obtained as the relaxed geometries of neutral cluster, which are shown in Fig. 4. We collected the bond distances and the bond angles in Table II. In high oxidization clusters, the Fe–Fe distance becomes longer and the Fe–O distances shorter. The bond lengths in these clusters are expanded from those in the respective neutral clusters.

For $Fe_2O_3^-$, we obtained two stable clusters. The ground state cluster has two bridge O atoms and one edge O atom with being the magnetization of 1.1 μ_B

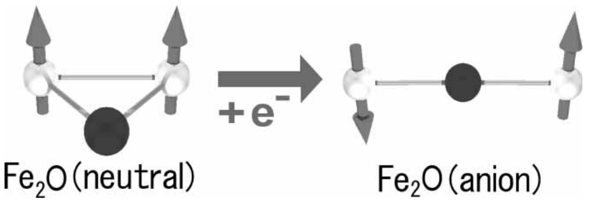

FIGURE 2 Deformation of the cluster Fe_2O by the additional electron.

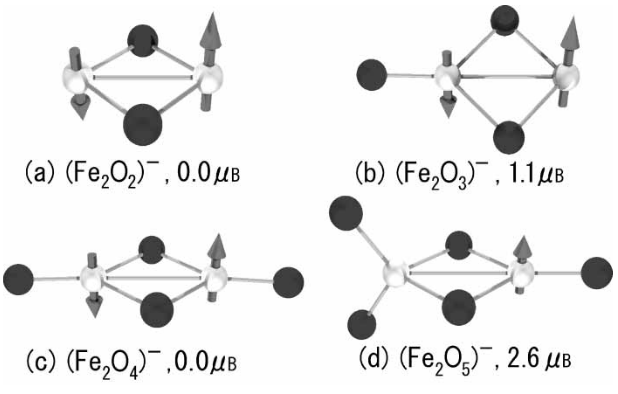
(a) $(Fe_2O_2)^-$, 0.0μ_B
(b) $(Fe_2O_3)^-$, 1.1μ_B
(c) $(Fe_2O_4)^-$, 0.0μ_B
(d) $(Fe_2O_5)^-$, 2.6 μ_B

FIGURE 4 The ground state geometry and magnetic configuration for the anion clusters, $Fe_2O_m^-(m = 2 - 5)$, with the magnetization in μ_B.

TABLE II Bond distances and bond angles in the stable clusters, $Fe_2O_m^-(m = 1 - 5)$. Fe(l) and Fe(r) specify the left and right Fe atoms and O(b) and O(e) the bridging and edging O atoms in each cluster of Fig. 4

$Fe_2O_m^-$	*Distance (Å) and angle (degree)*
$m = 1$	1.88 (Fe–O)
$m = 2$	2.48 (Fe–Fe), 1.87 (Fe–O)
$m = 3$	2.62 (Fe–Fe), 1.87 (Fe(r)–O(b)), 1.86 (Fe(l)–O(b)), 1.69 (Fe–O(e))
$m = 4$	2.67 (Fe–Fe), 1.84 (Fe–O(b)), 1.68 (Fe–O(e))
$m = 5$	2.72 (Fe–Fe), 1.80 (Fe(r)–O(b)), 1.81 (Fe(l)–O(b)), 1.61 (Fe(l)–O(e)), 1.65 (Fe(r)–O(e)), 112 (∠O(e)–Fe(l)–O(e))

and the other has three bridge O atoms with having the ferromagnetic magnetization of 8.9 μ_B. The latter is higher in energy by 1.3 eV. The obtained $Fe_2O_4^-$ has a planar structure, while in the neutral cluster the two edge O atoms are placed in trans-type (away from the plane formed by the other Fe_2O_2 unit).

The geometries for $Fe_2O_2^-$ and $Fe_2O_4^-$ correspond to the schematic drawing of possible structure by Wu *et al.* [2], however, the other clusters of series have a different geometry. In our simulation, for both anion and neutral, the cluster with three bridge O atoms, even if it was stable, always gave a higher total energy with respect to that of the ground state geometry.

Vertical Detachment Energy (VDE)

The VDE of the ground state geometry for $Fe_nO_m^-(n = 1, 2)$ is shown as a function of the number of O atoms in Fig. 5. The VDE, except at Fe_2O, increases with the number of O atoms, which results from the property of EA inherent in O atom. This tendency for the number of O atoms, although our values are always larger as in Fe_2^-, is in agreement with the experimental data [3].

The large VDE at Fe_2O^-, which is away from the above tendency, comes from the stability of linear geometry in the anion cluster. This increase at Fe_2O^- and the decrease at $Fe_2O_2^-$ well reproduces the experimental tendency [3]. At the clusters with the large numbers of O atoms, FeO_4^- and $Fe_2O_5^-$, the VDE shows a saturated behavior, which is also observed in the experiment.

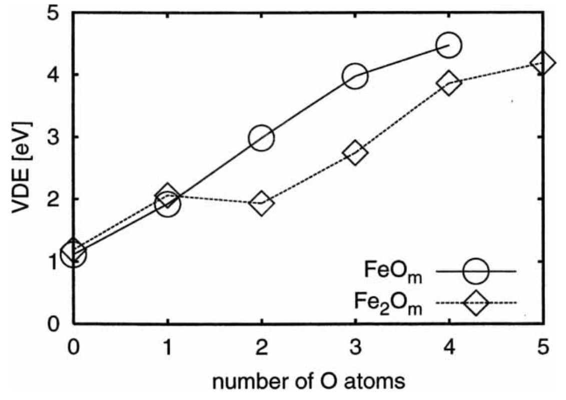

FIGURE 5 The vertical detachment energies of FeO_m^- and $Fe_2O_m^-$ clusters as a function of the number of O atoms.

SUMMARY

We have determined the ground state geometry and the magnetic arrangement for the anion iron clusters, $Fe_nO_m^-(n = 1, 2)$, which had been obtained in the gas phase experiment. We evaluated the VDEs and discussed the behavior with respect to the number of O atoms. The tendency for the number of O atoms, which was observed in the experiment, was reproduced well. It was found that the additional electron on the neutral clusters of FeO_5 and FeO_6 causes the separation of spin polarized oxygen molecule from the clusters. In the structural optimization, the ground state geometry of anion cluster, Fe_2O^- has the linear structure, while the neutral cluster is an isosceles triangle. This drastic change in geometry can be connected to the large value of VDE, which implies an agreement with experimental data deduced from the photoelectron spectra.

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