

Geometric and electronic structures of Fe_n^- ($n = 2\sim 8$) clusters

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Geometric and electronic structures of Fe_n^- ($n = 2\sim 8$) have been studied using a density-functional method. The most stable structure of Fe_3^- to Fe_8^- was equilateral triangle, tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, and D_{2d} symmetry structure, respectively. The calculated electron affinity (EA) of these clusters was in good agreement with their experimental values. Partial density of states (PDOS) indicate that those Fe clusters are ferromagnetic which is similar to the Fe bulk property.

Key words: metal cluster, density functional method, magnetic moment, electron affinity

1. INTRODUCTION

Small clusters consisting of up to a few hundred atoms often have physical and chemical properties different from those of bulk, exhibiting novel electronic, magnetic, optical and chemical behaviors [1, 2, 3]. The transition metal (TM) clusters are especially of interest for their magnetic moment. The magnetism of TM clusters such as Fe, Co and Ni has been widely studied so far because of their extraordinary magnetic moments. Among these transition metals, Fe clusters are attractive because its magnetic moment is very sensitive to its environment, e.g., its surface structure [4]. For this reason, we focus on Fe_n^- clusters as a representative of ferromagnetic clusters in the present study.

Experimentally, Billas et al. [5] reported that the magnetic moment of the Fe_n cluster is atomlike for the size up to 30 atoms and approaches the value of its bulk for the size increasing to 700 atoms. Although the magnetic property of the TM clusters is expected to change drastically with respect to the clusters size less than 30 atoms, the experimental data for this case has not been reported experimentally yet. On the other hand, theoretical calculations reported that neutral Fe clusters exhibit ferromagnetic properties for small size up to heptamers [6, 7, 8]. Unfortunately, no experiment has been done for the size-dependent magnetic property of the neutral TM clusters. Accordingly, it is necessary to examine the TM anion or cation clusters so as to compare their calculated results with experimental ones at the first stage, prior to discussing the neutral ones. In the present study,

we calculate Fe_n^- clusters and compare their ionization potential with experimental values of electron affinity (EA) for neutral clusters [9].

2. COMPUTATIONAL METHOD

We have performed geometry optimization for Fe_n^- ($n = 2\sim 8$) using a program package of Amsterdam Density-Functional (ADF) method [10]. The basis set for the cluster was constructed by triple- ζ Slater-type orbitals (STO). The $1s$, $2s$ and $2p$ atomic orbitals were treated under frozen core approximation, while the $3s$, $3p$, $3d$, $4s$ and $4p$ were treated as valence functions. We used VWN potential as a local part of the exchange and correlation potentials [11] and PW potential was used as gradient correction [12]. We performed spin unrestricted calculations ($2S = \alpha - \beta$) for all the clusters because the Fe has magnetic moment. We examined not only highly symmetric but also distorted structures in order to provide the freedom of spin states.

3. RESULTS AND DISCUSSION

3.1. Geometric structure

The most stable structure for Fe_n^- ($n = 2\sim 8$) obtained by ADF method is shown in Fig.1. Equilibrium bond length (R_e), total spin (S , where $2S = \alpha - \beta$), magnetic moment per atom (μ') and symmetry are also described in the figure. All clusters with different magnetic moments were examined because Fe metal indicates a ferromagnetic system. The R_e , S , and μ' of Fe_2^- were obtained to be 2.07 Å, 7/2, and 3.50 μ_B , respectively.

For Fe_3^- , we found it to be the equilateral triangle (D_{3h}) structure with $Re = 2.29 \text{ \AA}$, $S = 11/2$ and $\mu' = 3.67 \mu_B$. On the other hand, the most stable structure for the tetramer was the distorted-tetrahedron (D_{2d}) with $Re = 2.34 \sim 2.37 \text{ \AA}$, $S = 15/2$ and $\mu' = 3.75 \mu_B$. For the Fe_5^- pentamer, the most stable structure was the distorted-trigonal bipyramid (C_{2v}) with $Re = 2.31 \sim 2.62 \text{ \AA}$, $S = 17/2$ and $3.25 \sim 3.54 \mu_B$. For the hexamer, the most stable structure was found to be the distorted-octahedral structure (C_{4v}) with $Re = 2.32 \sim 2.56 \text{ \AA}$, $S = 19/2$ and $\mu' = 3.14 \sim 3.17 \mu_B$. Furthermore, the most stable structure for the Fe_7^- heptamer was the pentagonal bipyramid (D_{5h}) with $Re = 2.30 \sim 2.42 \text{ \AA}$, $S = 21/2$ and $\mu' = 2.95 \sim 3.12 \mu_B$. Finally, the most stable structure for the octamer was D_{2d} symmetry with $Re = 2.29 \sim 2.59 \text{ \AA}$, $S = 23/2$ and $\mu' = 2.85 \sim 2.90 \mu_B$. It is found from Fig. 1 that the average bond length of the clusters approached the bulk value of 2.48 \AA [13] when increasing their cluster size.

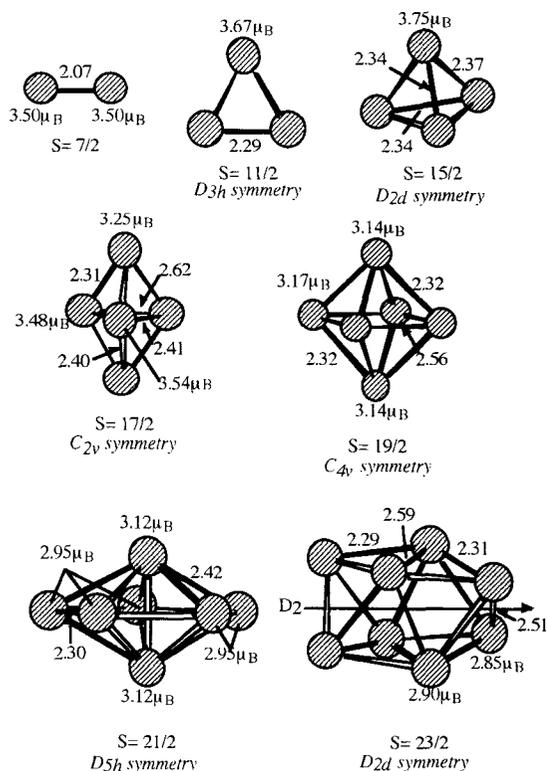


Fig. 1. The most stable structures for Fe_n^- clusters.

We next compare the results of Fig. 1 with those reported previously [6, 7]. Ballone and Jones [7] performed first-principle molecular dynamics simulations (Car-Parrinello method) for the Fe_n ($n = 1 \sim 7$) neutral clusters. The most stable structures for $Fe_3 \sim Fe_5$ and Fe_7 by their work are the same as those for $Fe_3^- \sim Fe_5^-$ and Fe_7^- by present work, respectively. The only exception is the hexamer of which the most stable structure of neutral species was capped-trigonal bipyramid. On the other hand, Castro reported the

most stable structures for the neutral clusters containing up to seven atoms, using density-functional theory [8]. The geometry of Fe_n clusters was similar to those for the corresponding anion clusters obtained in the present study. Magnetic properties of Fe_n^- cluster will be discussed in the next section.

3.2. Magnetic properties

All Fe_n^- clusters examined in the present study are ferromagnetic. Fig. 2 (a) shows the magnetic moment per atom (μ') as a function of cluster size n . The tetramer has the maximum value of $3.75 \mu_B$ among Fe_n^- clusters, but no "magnetic magic number" was found. Let us compare the magnetic moment of the Fe_n^- clusters with that of the neutral ones. Fig. 2 (b) shows the magnetic moment of the neutral clusters reported by Castro [8]. The magnitude of the magnetic moment for the neutral clusters is comparable to that for the anion clusters. While the neutral cluster has the maximum value of the magnetic moment at $n = 6$, the anion one has the maximum value at $n = 4$. In addition, it seems that the entire trend of the size-dependence of the magnetic moment for the anion cluster is opposite to that for the neutral one. Compared the magnetic moment of the neutral and anion clusters with that of $2.22 \mu_B$ for the bulk [14], both clusters have the magnetic moment greater than the bulk.

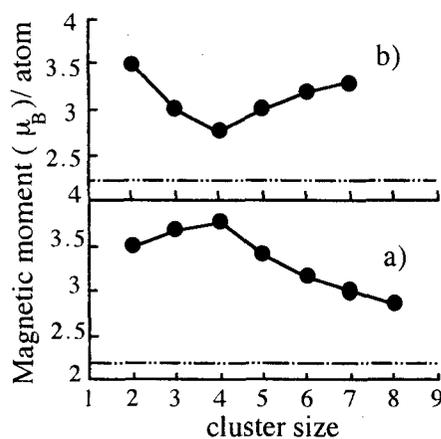


Fig. 2. Magnetic moment per atom of Fe_n clusters
a) Fe_n^- clusters, b) Fe_n clusters [8].

In order to clarify the s -, p - and d -contribution to the magnetic moment, we examined the partial density of states (PDOS) for the Fe_3^- to Fe_8^- clusters, as shown in Fig. 3. For all the Fe anion clusters examined here, the majority spin $3d$ band is completely filled with electrons, while the minority spin is one partially filled with electrons. This evidences the ferromagnetic property of the Fe anion clusters. In addition, it is

found that the DOS changes from the discrete to continuous level structure as the cluster size increases. We next discuss the nature of chemical bonding by analyzing the atomic orbital component. For the Fe_3^- , Fe_4^- and Fe_5^- clusters, the contribution of the sp -

components filled with the majority spin electrons are relatively large around the Fermi level. On the other hand, for Fe_6^- , Fe_7^- and Fe_8^- , the sp -components are located at an energy below the E_f .

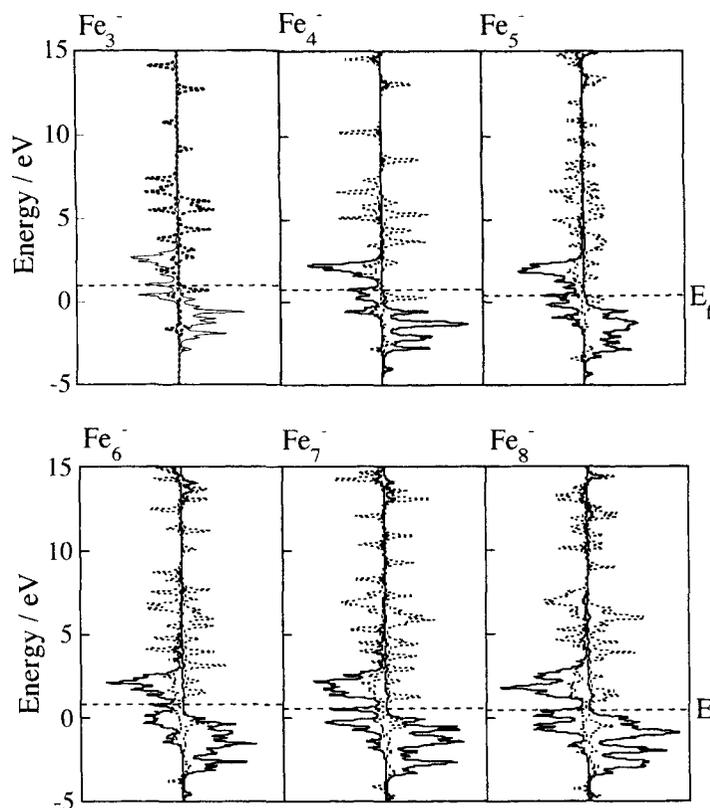


Fig. 3. Partial DOS of Fe_n^- ($n = 3-8$) clusters

Right: majority spin, left: minority spin.

Solid line: d -component, broken line: s, p -component and E_f is the Fermi level.

3.3. Electron Affinity

Since the EA of the neutral clusters is equivalent with IP of the anion clusters, we calculated the IP of the Fe_n^- clusters using the Slater's transition-state method [15] in which one-electron energy of the highest occupied molecular orbital was calculated by removing 0.5 nominal charge. The calculated value of EA was shown in Fig. 4 for the Fe anion clusters, together with the experimental values [9]. The agreement between the calculated and the experimental values is fairly good. This allows us to discuss the geometric and electronic structures of the Fe anion clusters. In order to examine the size-dependence of the electronic structure, the EA was plotted as a function of $n^{-1/3}$, as shown in Fig. 5. Where, the broken line was obtained by classical spherical conducting drop model

[16-20]. According to this model, the EA can be expressed as

$$EA = WF - \alpha(e^2/R), \quad (1)$$

where WF is the bulk work function (4.5 eV) for Fe, α is the slope parameter which is defined to be $5/8$, and e is the charge of an electron, and R is the cluster radius which is approximately the covalent radius of Fe metal (1.24 Å) times $n^{1/3}$. When decreasing the cluster size, i.e., the value of $n^{-1/3}$ approaches 0.62 (corresponding to $n \sim 4$), the EA obtained by the classical model becomes zero. In the present study, the calculated EA values for the Fe anion clusters are far from those obtained by the classical model. This indicates that the EA of the Fe anion clusters cannot be explained by the classical drop model. Namely, the anion clusters up to octamer

exhibit physical properties different from their bulk, though the electronic structure has a band-like character when the cluster size increases to $n = 8$.

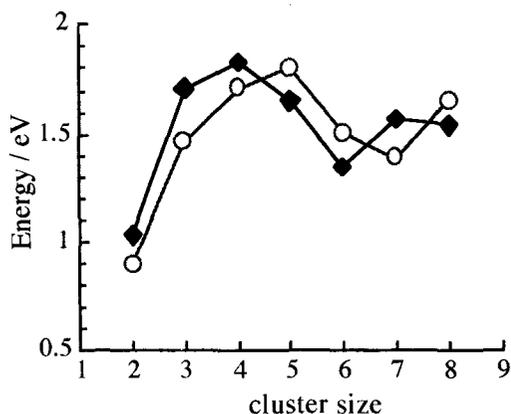


Fig.4. Calculated and experimental electron affinity of Fe_n^- clusters. The circles are the experimental results [9]. The squares are calculation (present work).

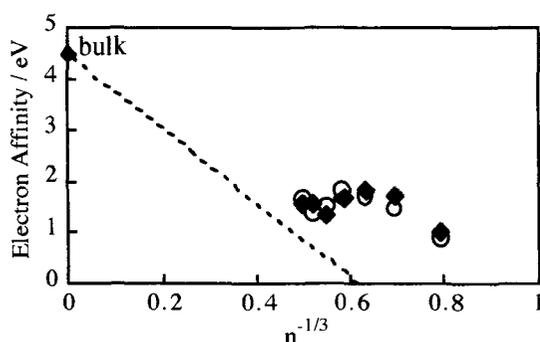


Fig.5. Electron affinity vs. $n^{-1/3}$ plots. The experimental values (open circle) are taken from ref.9. The broken line represents the prediction by spherical conducting drop model [16 - 20]. (See text)

4. CONCLUSION

We examined the geometric and electronic structures of Fe_n^- ($n = 2 \sim 8$) using density-functional calculations. The Fe_n^- clusters were found to be ferromagnetic but not different from its bulk properties. Calculated EA was in good agreement with the experimental value for all the Fe anion clusters.

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