First-principles calculation of magnetism of icosahedral Fe clusters*

Cheng Zhi-Da(程志达), Ling Tao(凌 涛), and Zhu Jing(朱 静)†

Beijing National Center for Electron Microscopy, Tsinghua University, Beijing 100084, *China*
Laboratory of Advanced Materials, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, *China*

(Received 9 March 2009; revised manuscript received 30 November 2009)

Icosahedral iron clusters are synthesized and characterized in our group by using experimental methods. But the measurements of magnetic properties still face difficulties: the sizes of the clusters and the amount of product. Therefore theoretical methods are employed to study these issues. In this paper, icosahedral iron clusters containing 13, 55, 147, 309 atoms are calculated by *ab initio* techniques. After the structural relaxation, the magnetism of the clusters is found to be similar to that of face centred cubic (FCC) iron with stronger ferromagnetism on the surface. But the central atom of each cluster is exceptional, which has a smaller magnetic moment. We also study the electronic structural properties in the clusters for a better explanation of the magnetism. It is suggested that in small clusters, the magnetic properties still depend on the local structural arrangement.

Keywords: ferromagnetism, iron, cluster, *ab initio*
PACC: 7115M, 7120C, 7550G, 7125W

1. Introduction

Magnetic properties of small transition metal particles were investigated intensively by both theoretical and experimental methods[1−11] to find properties and behaviours that are superior to those of bulk materials. In the information technology industry, small magnetic particles are of huge concern due to the strong relevance to ultrahigh density magnetic recording.

Generally speaking, magnetic properties of particles depend on their geometric structures and atomic configurations.[12,13] Therefore the structural information is important for the research of small magnetic particles or clusters. Experimental results of Sakurai *et al.* revealed the existence and the stability for icosahedral clusters containing tens of atoms.[3] Meanwhile, *ab initio* calculations of Rollmann *et al.* showed the competition between icosahedral structure and body-centred cubic isomers in small iron clusters.[1] Thanks to improvements in characterization methods like high resolution transmission electron microscope (HRTEM), direct observations of small clusters have been made easier. In our research group, synthesized iron clusters with icosahedral symmetry[11] have been successfully characterized with an FEI Titan 80-300 transmission electron microscope (TEM).

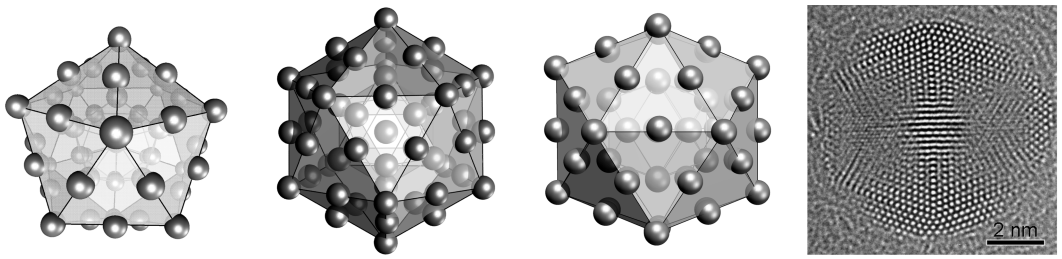
Also, the size dependence of magnetic properties has been researched by using molecular dynamics[8] and *ab initio* calculations.[1,2,5] The most mentioned difference of magnetic properties is the significantly improved magnetism and spin polarization in nanoclusters up to a few hundred atoms.

2. Experimental background

Several methods of preparing iron nanoclusters were reported.[3,11] In our group, the clusters were synthesized with a polyol reduction method.[11] High resolution Cs-corrected TEM images in Fig. 1(d) show the icosahedral symmetry and the corresponding shapes. Previous theoretical results also predicted that iron clusters with high symmetries and shell structures (containing up to 671 atoms) had the stability order icosahedral > body centred cubic (BCC) > decahedral > FCC.[13]

Although the accurate observation of the high resolution electronic microscopy can be achieved, the measurement of local magnetic properties of the clusters still faces many difficulties: the very small size the low amount of the product, and the variable sizes of synthesized clusters. Because the magnetism is of a short-range interaction, those difficulties are unlikely to overcome. Fortunately, intrinsic properties of the clusters still can be studied in theoretical frameworks, one of which is the *ab initio* method.

*Project supported by National Natural Science Foundation of China (Grant No. 50671053).
†Corresponding author. E-mail: jzhu@mail.tsinghua.edu.cn
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(a) (b) (c) (d)

Fig. 1. Structures of icosahedral clusters, where theoretical atomic arrangements display different intrinsic symmetries, i.e. (a) 5-fold (b) 3-fold (c) 2-fold and (d) 2-fold (an experimental image by Cs-corrected TEM).

Although *ab initio* method does not hold for studying clusters as big as our experimental products, it can provide accurate information about structural, energetic and magnetic properties for many common systems including iron. So we construct a model for small cluster, which is applicable to the experimental product but feasible enough for our calculation so as to obtain common and instructional conclusions about the magnetism of icosahedral iron clusters.

3. Theoretical model and method

The model of icosahedral iron cluster is generated from geometric shells. In the very beginning there is one atom in the centre. Then according to the icosahedral symmetry, 12 vertices are added and a smallest icosahedral cluster containing 13 atoms is formed. Larger clusters generally follow the same shell-by-shell modeling by adding not only vertices but also surface atoms. The number of atoms in a perfect icosahedral cluster is given by the following expression:

$$N = (10n^3 + 15n^2 + 11n + 3)/3, \tag{1}$$

which yields

$$N = 13, 55, 147, 309, \ldots. \tag{2}$$

The calculations are performed in the framework of density functional theory (DFT) by the linear combination of atomic orbital (LCAO) method as implemented in the SIESTA package.[15] It is a standard density-functional program with using norm-conserving pseudopotentials and a uniform real-space grid to represent the valence charge density. In our work, The Perdew–Burke–Ernzerhof (PBE) framework under the generalized gradient approximation (GGA) scheme is used to represent the exchange correlation interaction.

The parameters similar to those in Ref. [5] are adopted in our calculations. We use a double-zeta singly polarized basis set with 15 orbits per atom and an energy shift of 100 meV in our calculation. The pseudopotential is generated automatically for the [Ar] 3d64s2 configuration with a pseudo core radius of 0.7 Bohr atomic radius. The mesh cutoff parameter for real space integration is set to be 180 Ry and the k-grid cutoff radius parameter is 14 Å (1 Å=0.1 nm). Sufficient vacuum space between the neighbouring clusters ($\sim$ 20 Å) has been chosen to avoid the interference effects.

Due to computation limits, our calculations are applied to clusters containing 13, 55, 147 and 309 iron atoms separately. Fully structural relaxations have been carried out to obtain reasonable results. Every cluster is first shaped into perfect icosahedral symmetry with identical atom distances, and then the structure is scaled proportionally so as to find an estimated lattice parameter by finding a minimum energy. Finally, the molecular dynamics optimization under the SIESTA program is performed. With the two step procedure, we are able to speed up the relaxation and achieve a high accuracy at the same time.

4. Results

4.1. Structure

As an example, cluster containing 55 iron atoms is shown in Figs. 1(a)–1(c). The 5-fold, 3-fold and 2-fold symmetries are demonstrated respectively. And the Cs-corrected HRTEM image (d) shows a larger cluster observed in the 2-fold symmetry.

The ideal icosahedral iron clusters in our model are not stable because the atomic forces are not balanced. In the molecular dynamic structural relaxation, the criterion of equilibrium cluster structure

is set to be the value less than 0.04 eV/Å in atomic force. After a procedure of seeking minimal energy, the atomic arrangements are changed and the model becomes more practical. Distances between each atom and the central atom are summarized in Fig 2. Atomic positions are shifted after the relaxation especially for the atoms on the surfaces: $d_{\mathrm{i-surface}} < d_{\mathrm{i-inner}} < d_{\mathrm{bulk-FCC}}$, where i denotes icosahedral cluster. It is suggested that surface atoms are pulled to the centre and other atoms are changed correspondingly. An obvious explanation is that metallic bonds only pull surface atoms from one direction. Then the attraction will be balanced with atomic repulsion which increases as the distance decreases. This trend is also proved from quantitative results. Our calculation shows that in bulk FCC iron the distance between neighbouring atoms is 2.60 Å, while in icosahedral clusters the distances are dramatically small: they range from 2.40 Å to 2.51 Å.

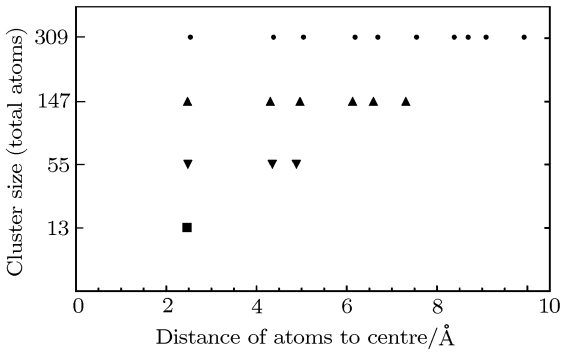


Fig. 2. Atomic distances after structural relaxation, where surface atoms are obviously pulled to the centre.

However, values we derived should be compared under the same calculation framework. It is a well-known systematic error of GGA scheme that the calculated lattice parameters are larger than experimental results overall. For example, the calculated lattice parameter of FCC iron is $a = 3.67$ Å compared with experimental value $a = 3.56$ Å. So the theoretical results above should be amended before being compared with experimental results

4.2. Atomic magnetic moments

Magnetism of the clusters is a major part in this study. Our calculations have already been spin-polarized at the beginning of the relaxation; therefore the magnetic properties are determined simultaneously with the structural properties. We summarize averaged atomic magnetic moments in icosahedral iron clusters as well as common bulk iron (BCC and FCC structures) in Table 1. In general, icosahedral clusters in our calculations generally have the following magnetic properties except the smallest cluster:

(a) the central atom has the weakest ferromagnetism (1.80–1.90 μ_{B}); (b) the surface atoms have stronger ferromagnetism (2.98–3.25 μ_{B}); (c) other atoms are similar to those of bulk FCC iron (average value is 2.62 μ_{B} which is close to FCC value 2.64 μ_{B}).

In Table 1, the size dependence of average magnetic moment in clusters shows a descending trend as size increases, and the converging limit is the FCC bulk. The ratio of usual atoms (surface atoms and centre atom) to total atoms decreases as the clusters grow larger and the clusters will eventually behave like FCC iron clusters.

Table 1. Average magnetic moment of icosahedral iron cluster and bulk iron.

size	average magnetic moment (μ_{B}) of atoms with the same distance to centre (central atom to surface atom)											total
13	2.91	3.54										3.49
55	1.90	2.62	3.19	3.19								3.04
147	1.87	2.51	2.63	2.62	3.25	3.14	3.07					2.91
309	1.80	2.49	2.58	2.65	2.59	2.65	2.70	3.11	3.06	3.00	2.98	2.84
FCC												2.64
BCC												2.47

4.3. Electronic structures

Magnetic properties are also strongly related to electronic structures, which is also essential for researching the material. In our study, detailed electronic structures are compared so as to find out the specific characteristics in icosahedral iron clusters.

We calculate the densities of states (DOSs) of d electrons as shown in Fig. 3, since the magnetism is mostly introduced by 3d electrons in iron. Atoms in 3 different clusters with different sizes and in 2 different common bulk structures are represented, respectively. In each subfigure, spin-up states and spin-down states are separated by the horizontal x-axis. The position and the intensity of energy level give an explanation of the magnetic moments in the atoms at first. The difference between spin-up states and spin-down states spontaneously causes an unbalanced charge distribution, thus magnetic moments are introduced into iron atoms.

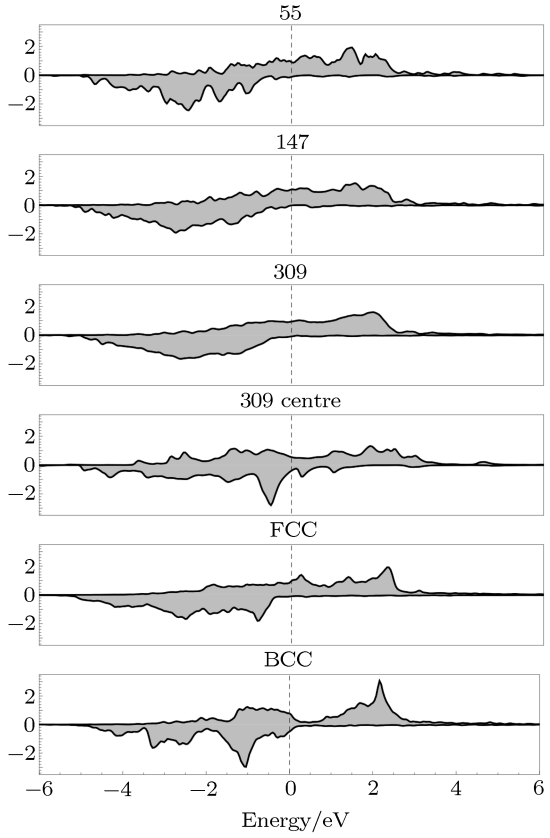


Fig. 3. Curves for density of states for d electrons versus energy in different types of atoms. Fermi energy ($E_{\rm F}$) in the system is set to be zero point of energy (dot line). Horizontal axis separates two spin states (up and down) of electrons. Densities in clusters are averaged.

The DOS of clusters is an average value, so it can reflect the comprehensive properties. There is much in common in different icosahedral clusters, i.e. the three clusters are all alike in shape of DOS, and the positions of some typical peaks are also comparable. Compared with bulk BCC iron, these clusters have many characteristics of FCC iron. A visible neck-shaped structure appears above Fermi level in BCC iron, but it is not found in FCC iron and icosahedral clusters. Also, there is a minor peak at around 3 eV in FCC iron and clusters, and the peak does not appear in BCC structure. These attributes make sense because the atomic arrangement in each facet of icosahedral cluster is of FCC actually. But electronic structures of their central atoms are still different. Take the central atom of cluster containing 309 atoms for an example, the shape of DOS deviates much from averaged density of cluster. The electronic structure affects occupancy of electrons, and then the magnetic moment is changed dramatically.

4.4. Spin density

Spin density of cluster containing 309 iron atoms is visualized in Fig. 4 viewed from a cross-section of the cluster (also the plane of reflection symmetry). Spin density is an informative method of discovering properties of the icosahedral cluster as a combination of atom arrangement and electronic distribution in real space.

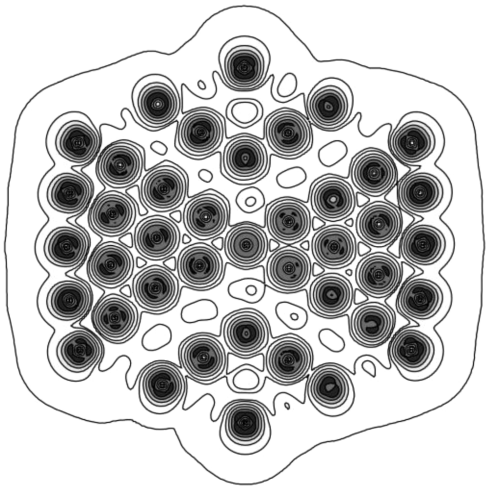


Fig. 4. Spin density of icosahedral iron cluster containing 309 atoms viewed from cross-section (also the plane of reflection symmetry).

Some details about atomic position are revealed schematically: atoms on the surface arrange in an curve instead of a straight line after structural relaxation, because surface atoms tend to avoid sharp edges and vertices. The spin densities of surface atoms increase obviously due to the weaker atomic and electronic interactions on the external side of surface. The central atom is also interesting to be noticed because the spin density is unusually low, and the neighbouring atoms are slightly affected. As a matter of fact, we can divide an icosahedron into twenty tetrahedrons

sharing one vertex, thus the centre. Atomic arrangement is of FCC in each tetrahedron, so most of the atoms behave like those in bulk FCC iron. But the centre is shared by all tetrahedrons, the symmetries near the atom are greatly different and the properties vary as a result

5. Conclusion

We calculate icosahedral clusters with full structural optimization by *ab initio* method. There are some common limitations: a) the clusters in the model only contain up to several hundred atoms, due to the high computation cost; b) only ground state properties are obtained because the temperature in calculations could only be zero Kelvin. Those limitations should be overcome by the development of newer theoretical methods, but we construct a reasonable model and obtain intrinsic properties, especially magnetic properties of the clusters as follows.

(a) Lattice parameters in clusters are smaller than those in bulk metal, $d_{\mathrm{i-surface}} < d_{\mathrm{i-inner}} < d_{\mathrm{bulk-FCC}}$ (i- for icosahedral cluster), reflecting the balance between atomic repulsion and metallic bond. The surfaces of clusters are curved to reduce surface energy.

(b) Icosahedral iron clusters have ferromagnetism like FCC iron. Size dependence of magnetism shows a descending trend as size increases, and the converging limit is the FCC bulk.

(c) Central atoms in clusters have smaller magnetic moments and different electronic structures resulted from the usual local environment and atomic arrangements.

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