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Structures and Magnetic Properties of Al-Doped Fe_n (n = 2-7) Clusters: A DFT Study

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The structures and magnetic properties of aluminum doped Fe_n (n = 2-7) clusters have been systematically studied at the BPW91 level in density-functional theory (DFT). Calculated results show that an Al impurity does not change the ground-state structure of small iron cluster and prefers to occupy surface site bonding with iron atoms as many as possible. The total magnetic moments of $Fe_{n-1}Al$ clusters is smaller than those of corresponding iron clusters due to the antiferromagnetic coupling between Fe and Al. The natural population and natural electron configurations are performed to analyze the main reason of the total magnetic moments decreased.

Key Words: Density functional theory, BPW91 method, $Fe_{n-1}Al$ cluster, Magnetic moment.

INTRODUCTION

Transition-metal clusters are a subject of particular interest due to the strong environment dependence of their magnetic properties and their possible applications in magnetic recording and storage technologies. However, physical and chemical properties of transition-metal clusters show remarkable size-dependent variations that cannot be explained by the shell model of s valence electrons due to the existence of *d* electrons, which presents a tremendous challenge to both experimental and theoretical investigations on transition-metal clusters[1]. Recently, with the appearance of the DFT theory which has the ability to directly explore and assign cluster geometries and discriminate between possible isomers, some meaningful improvements have been achieved in the property studies of not only transition-metal atoms[2-6] but also mixed clusters including transition-metal atoms[7-15].

Recently, the interest in studying the Al-doped iron clusters has grown rapidly since Pithawalla *et al.*[16] found the magnetic property of FeAl nano-particles that is different from ordered compounds. Reddy *et al.*[17] have performed density-functional calculations on the electronic structures and magnetic properties of $Fe_{1-x}Al_x$ (0 ≤ x

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≤ 0.5) for various Al concentrations by modelling the bulk phase with a 15-atom cluster and found the transfer of Al 3*p* electrons into the minority 3*d* orbital of Fe has a profound effect on the magnetic properties of Fe-Al clusters. Subsequently, Reddy *et al.*[18] obtained the structures and magnetic properties of $(FeAl)_n$ (n ≤ 6) clusters and found the geometric arrangement of clusters are different from the bulk ordering and dominated by Fe-Fe clustering. In addition, Dieguez *et al.*[19] and Das *et al.*[20] also studied the Fe-rich cluster using molecular dynamics simulations based on EAM and density functional theory.

Although the progress in studying the magnetic properties of Fe-rich clusters has been made, the reports on the evolution of cluster properties with the cluster size are few. Motivated by the above and the potential technological application of Fe-Al alloy, we choose one Al atom as impurity to dope small iron clusters and study the evolution of the geometrical arrangement of $Fe_{n-1}Al$ (n = 2-7) clusters with the cluster size. The key objective is to explore the interactional mechanism of impurity atom with the host clusters and how this would affect the magnetic behaviour of iron clusters.

COMPUTIONAL METHOD

All geometry optimizations without symmetry constrains are performed with the functional of Becke for exchange[21] and correlation described by Perdew and Wang[22] as implemented with Gaussian 98 program package[23]. In the optimization process, all possible configurations and spin multiplicities are considered and searched unbiasedly. Moreover, the optimized structures are further verified by frequency calculations (no negative frequency).

In terms of basis sets, the Lanl2dz basis sets[24] and the 6-31G(d) basis sets[25] are selected to describe Fe atoms and Al atoms, respectively. Those basis sets combined with the BPW91 method result in bond lengths of 2.01 Å and 2.49 Å for Fe_2 and Al_2, respectively which are in agreement with the corresponding experimental values of 2.02 Å[26] and 2.47 Å[27], respectively. In addition, we also evaluate the ground state of Fe-Al dimer, the calculated bond length is found to be 2.42 Å in coincidence with that of Reddy *et al.*[18]. Good agreement between theoretical and experimental values indicates that the present computational method and basis sets are viable.

However, the mixed basis sets overestimate energies due to basis set superposition error (BSSE). The best method eliminating the error is to choose the big all-electron basis sets such as 6-311++G (2d, 2p) to calculate the $Fe_{n-1}Al$ (n = 2-7) clusters, but the all-electron basis sets are much more computationally demanding. To solve this problem, single-point BPW91/6-311++G (2d, 2p) calculations are performed for all the structures based on the geometries obtained from the BPW91/Lanl2dz/6-31G(d) optimizations. As seen in Table-1, the energies obtained by single-point calculation for Al-doped Fe_n (n = 2-4) are very close to those obtained by the fully optimizations with a minor discrepancy not more than 0.001. Clearly, the solution designed for the calculation of iron aluminides clusters is feasible.

TABLE-1
COMPARISON OF TOTAL ENERGIES/A.U. CALCULATED AT BPW91/6-311++G (2d, 2p) AND BPW91/ Lanl2dz/6-31G (d)//BPW91/6-311++G (2d, 2p) LEVEL

Cluster	BPW91/6-311++G (2d, 2p)	BPW91/Lanl2dz/6-31G (d)//BPW91/6-311++G (2d, 2p)
Fe_2	-2527.572916	-2527.572838
FeAl	-1506.186494	-1506.186488
Fe_3	3791.404042	-3791.403855
Fe_2Al	-2770.024610	-2770.024448
Fe_4	-5055.258685	-5055.258674
Fe_3Al	-4033.881359	-4033.881350

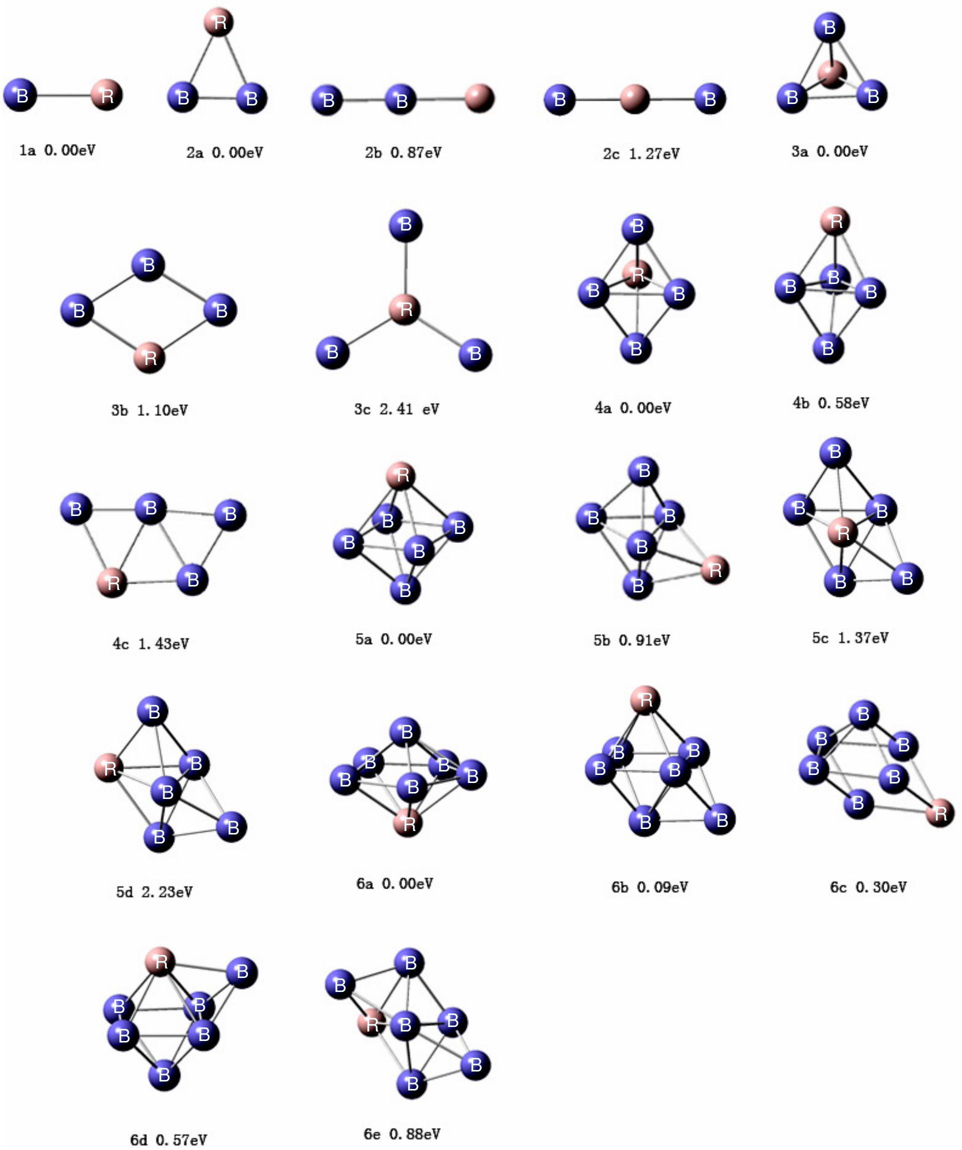
RESULTS AND DISCUSSION

Equilibrium structure: The optimized stable structures of $Fe_{n-1}Al$ (n = 2-7) clusters are shown in Fig. 1. For pure Fe_n clusters, all possible stable structures have been reported in recent work[2], which will not be presented for comparison in this paper. There are three possible isomers for Fe_2Al, the lowest-energy structure is an isosceles triangle. Another two isomers are linear-chain structures shown in Fig. 1.2b and 2c, of which the Al atom occupying a terminal position is 0.40 eV lower in energy than that of taking a central position. Does it mean the iron atoms being easier to go together?

The Al-doped Fe_4 cluster forms an equilateral triangle and the Al atom caps the surface resulting in a tetrahedral configuration, which is the first 3D configuration among the $Fe_{n-1}Al$ clusters, as shown in Fig. 1.3a. This is the ground state which is low in energy a planar rhombus by 1.10 eV. The structure 3c which iron atoms are segregated by one Al atom completely obtains the worst stability. It becomes evident that the Fe atoms tend to be gathered together.

For Fe_4Al, the lowest-energy structure is a trigonal bipyramids which the Al atom is in the rectangular base and bonds with four Fe atoms. Another stable geometry that the Al atom occupies the apex of the trigonal bipyramid and bonds with three Fe atoms is 0.58 eV higher in energy than the ground state. The ground-state structure for Fe_5Al is the same rectangular bipyramid as that of Fe_6 cluster. Other three stable configurations (5b, 5c and 5d) are represented that the cap atom or the side atom of the capped trigonal bipyramid is replaced by an Al atom, respectively. Fig. 1 shows that 5b structure is 0.46 eV and 1.32 eV more stable than 5c and 5d, respectively, while the structure 5d with four Fe-Al bonds is energetically less favourable than 5c with 5 Fe-Al bonds by 0.86 eV. For Fe_7Al, it can be seen from Fig. 1 that the structure 6c with three Fe-Al bonds is 0.21 eV less stable than 6b that Al atom bonds with four Fe atom.

To summarize, the Al-doped Fe_n clusters have similar ground-state structures to those of the corresponding pure Fe clusters. In all the $Fe_{n-1}Al$ clusters, the Al atom prefers to occupy the surface position. Most importantly, it can be concluded



1a 0.00eV 2a 0.00eV 2b 0.87eV 2c 1.27eV 3a 0.00eV

3b 1.10eV 3c 2.41 eV 4a 0.00eV 4b 0.58eV

4c 1.43eV 5a 0.00eV 5b 0.91eV 5c 1.37eV

5d 2.23eV 6a 0.00eV 6b 0.09eV 6c 0.30eV

6d 0.57eV 6e 0.88eV

Fig. 1. Low-energy isomers for $Fe_{n-1}Al$ (n = 2-7) clusters at the BPW91 level. The B = blue and R = red balls represent iron atoms and aluminium atoms, respectively. The number beside the structure is relative energies (in eV) with respect to that of the corresponding lowest-energy isomers.

that the Fe atoms tend to be gathered together, yielding a maximum of Fe-Fe bonds and the Al atom seem to be located around a Fe core with a maximum of Fe-Al bonds.

Magnetic and electronic properties: Based on the lowest-energy structures, the total magnetic moments of $Fe_{n-1}Al$ clusters are computed and the corresponding results are presented in Table-2 and for comparison, the total magnetic moments of Fe_n are also shown. The total magnetic moments of $Fe_{n-1}Al$ clusters increase with the cluster size, but from Table-2, it can be seen that the doping of an Al atom results in the decrease of the total magnetic moments of corresponding pure iron clusters. Table-2 also shows the local magnetic moments of Fe_n and $Fe_{n-1}Al$ clusters. The local magnetic moments at the Fe site are found to be positive, while the Al atom always exhibits a negative local moment. It is indicated that the local magnetic moment of Al atom is antiferromagnetically coupled to those of the surrounding Fe atoms in agreement with the original experiment[28] as well as the theoretical results earlier[17,18, 20]. It should be noted that an increase of Fe-Al coordination means a decreasing coordination of its own kind for Fe. Therefore, the doping of an Al atom will necessarily decrease the total magnetic moments of Fe_n clusters.

TABLE-2
LOCAL AND TOTAL MAGNETIC MOMENTS OF Fe_n AND $Fe_{n-1}Al$ CLUSTERS

Cluster	Local magnetic moment (μ_B)	Total magnetic moment (μ_B)	Cluster	Local magnetic moment (μ_B)	Total magnetic moment (μ_B)
Fe_2	1 Fe 3.000000 2 Fe 3.000000	6	FeAl	1 Fe 3.419697 2 Al -0.419697	3.0
Fe_3	1 Fe 3.588970 2 Fe 3.378931 3 Fe 3.032099	10	Fe_2Al	1 Al -0.663299 2 Fe 2.831998 3 Fe 2.831301	5.0
Fe_4	1 Fe 3.001754 2 Fe 2.999340 3 Fe 2.999524 4 Fe 2.999383	12	Fe_3Al	1 Fe 3.582008 2 Fe 3.582007 3 Al 0.254136 4 Fe 3.581849	11
Fe_5	1 Fe 3.033828 2 Fe 3.213158 3 Fe 3.269928 4 Fe 3.213160 5 Fe 3.269927	16	Fe_4Al	1 Fe 3.165678 2 Fe 3.396365 3 Fe 3.396263 4 Al -0.123948 5 Fe 3.165642	13
Fe_6	1 Fe 3.334029 2 Fe 3.334047 3 Fe 3.334056 4 Fe 3.334068 5 Fe 3.331900 6 Fe 3.331900	20	Fe_5Al	1 Al -0.570887 2 Fe 3.088133 3 Fe 3.177999 4 Fe 3.087945 5 Fe 3.177824 6 Fe 3.038986	15
Fe_7	1 Fe 3.157347 2 Fe 3.157331 3 Fe 3.144320 4 Fe 3.018197 5 Fe 3.144252 6 Fe 3.173602 7 Fe 3.204950	22	Fe_6Al	1 Fe 2.856145 2 Fe 2.913131 3 Fe 2.913169 4 Fe 2.880690 5 Fe 2.845940 6 Fe 2.880211 7 Al -0.289285	17

To further understand the interaction between Fe and Al, natural population analysis (NPA) and natural electron configurations are performed and the corresponding results are summarized in Table-3. For FeAl cluster, the charges of Fe are negative while the charges of Al are positive, which implies the electrons transfer from Al to Fe. The electronic configuration of the Fe atom and Al atom is $3d^6 4s^2$ and $3s^2 3p^1$, respectively. However, the natural electron configurations is $3d^{6.74} 4s^{1.35}$ for Fe atom and $3s^{1.95} 3p^{0.92}$ for Al atom in FeAl cluster, which indicates the electrons captured by the 3d orbitals of Fe is from 4s electrons of Fe and 3s, 3p electrons of Al.

TABLE-3
NATURAL POPULATION AND NATURAL ELECTRON
CONFIGURATION FOR $Fe_{n-1}Al$ CLUSTERS

Cluster	Atom	Natural population	Natural electron configuration
FeAl	1Fe	-0.11509	$4s^{1.35}3d^{6.74}4p^{0.01}5s^{0.01}4d^{0.01}$
	2Al	0.11509	$3s^{1.95}3p^{0.92}3d^{0.01}$
Fe_2Al	1Al	-0.11418	$3s^{1.94}3p^{1.16}4s^{0.01}$
	2Fe	0.05624	$4s^{0.99}3d^{6.90}4p^{0.04}5s^{0.01}4d^{0.01}$
	3Fe	0.05794	$4s^{0.99}3d^{6.90}4p^{0.04}5s^{0.01}4d^{0.01}$
Fe_3Al	1 Fe	0.11581	$4s^{1.00}3d^{6.80}4p^{0.07}5s^{0.01}4d^{0.01}$
	2 Fe	0.11581	$4s^{1.00}3d^{6.80}4p^{0.07}5s^{0.01}4d^{0.01}$
	3 Al	-0.34719	$3s^{1.70}3p^{1.63}4s^{0.01}3d^{0.01}4p^{0.01}$
	4 Fe	0.11557	$4s^{1.01}3d^{6.80}4p^{0.07}5s^{0.01}4d^{0.01}$
Fe_4Al	1 Fe	0.14228	$4s^{0.93}3d^{6.87}4p^{0.05}5s^{0.01}4d^{0.01}$
	2 Fe	0.08863	$4s^{0.94}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
	3 Fe	0.08804	$4s^{0.94}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
	4Al	-0.46106	$3s^{1.77}3p^{1.67}4S^{0.01}3d^{0.01}4p^{0.01}$
	5 Fe	0.14211	$4s^{0.93}3d^{6.87}4p^{0.05}5s^{0.01}4d^{0.01}$
Fe_5Al	1Al	-0.33480	$3s^{1.74}3p^{1.58}3d^{0.01}4p^{0.01}$
	2 Fe	-0.01412	$4s^{0.90}3d^{7.05}4p^{0.06}5s^{0.01}5p^{0.01}$
	3 Fe	0.13355	$4s^{0.90}3d^{6.91}4p^{0.05}5s^{0.01}5p^{0.01}$
	4 Fe	-0.01469	$4s^{0.90}3d^{7.05}4p^{0.06}5s^{0.01}5p^{0.01}$
	5 Fe	0.13859	$4s^{0.90}3d^{6.90}4p^{0.05}5s^{0.01}5p^{0.01}$
	6 Fe	0.09147	$4s^{0.92}3d^{6.92}4p^{0.06}5s^{0.01}5p^{0.01}$
Fe_6Al	1 Fe	0.05904	$4s^{0.81}3d^{7.04}4p^{0.08}4d^{0.01}5p^{0.06}$
	2 Fe	0.09944	$4s^{0.80}3d^{7.04}4p^{0.05}4d^{0.01}$
	3 Fe	0.09916	$4s^{0.80}3d^{7.04}4p^{0.05}4d^{0.01}$
	4 Fe	0.09109	$4s^{0.80}3d^{7.06}4p^{0.04}4d^{0.01}$
	5 Fe	0.08593	$4s^{0.78}3d^{7.08}4p^{0.05}4d^{0.01}$
	6 Fe	0.08679	$4s^{0.80}3d^{7.06}4p^{0.04}4d^{0.01}$
	7 Al	-0.52145	$3s^{1.64}3p^{1.86}3d^{0.01}4p^{0.01}$

For $Fe_{n-1}Al$ (n = 2-7), the charge on Al atom are always negative, indicating that there is an obvious electron transfer from Fe atoms to Al atom. The natural electron configurations reveal that the electrons occupy the 3d orbitals of Fe is about 7.0, while 4s electrons is smaller than 1.0, indicating 3d electrons captured are less than 4s electrons lost. In addition, Table-3 also shows that the electrons of 3p orbital captured are more than the electrons of 3s orbital lost, which indicates some 4s electrons are transferred to 3p orbital of Al atom. Clearly, the hybridization between Fe-4s and Al-3p also brings out.

In a word, the doping of Al atom decreases the total magnetic moments of Fe_n clusters. With the exception of the hybridization within Fe atom and Al atom, the electrons of 4s orbital of Fe are transferred to 3p orbital of Al for the Fe-riched clusters. Since the total magnetic moments of $Fe_{n-1}Al$ clusters are located at Fe site, the hybridization between Fe-4s and Al-3p results in the decrease of 4s electrons, while the decrease of 4s electrons cannot but decrease the total magnetic moments of $Fe_{n-1}Al$ clusters. As the number of Al atom increases, there are some 3s electrons and 3p electrons of Al transferred to 3d orbitals of Fe atoms. Due to more than 5 electrons occupy 3d orbitals, therefore, the more the electrons are transferred to 3d orbitals, the more the total magnetic moments at Fe site decrease, which indicate the hybridization between Al-3s, Al-3p and Fe-3d results in the decrease of the total magnetic moments. Reddy *et al.*[17] found the transfer of Al 3p electrons into the minority 3d orbital of Fe has a profound effect on the magnetic properties of Fe-Al clusters, differentiating from our calculated results, we look forward to be verified by experiments methods and advanced theoretical studies.

Conclusion

To summarize, the structures and magnetic properties of $Fe_{n-1}Al$ (n = 2-7) clusters have been studied by the density functional method. The calculated results suggest the following conclusion.

(i) The mixed basis sets combined with single-point calculations greatly reduce the computational efforts and improve calculated quality. (ii) Calculated results show that the ground state structures of Fe_n clusters does not change upon the substitution of Al atom in an iron atom. In all small $Fe_{n-1}Al$ clusters, the Fe atoms tend to be gathered, yielding a maximum of Fe-Fe bonds and the aluminum atom is located around a Fe core with a maximum of Fe-Al bonds. (iii) The coupling between the moments localized at Fe and Al sites is found to be antiferromagnetic in agreement with original experimental values as well as theoretical results, which is the main reason on the doping of an Al atom decreasing the total magnetic moments of Fe_n clusters. (iv) The natural population and natural electronic configurations show the hybridization between Fe-4s and Al-3p results in the decrease of the total magnetic moments for Fe-riched clusters. As the number of Al atom increases, the total magnetic moments depend on the hybridization between Al-3s, Al-3p and Fe-3d.

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