Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Structure, magnetic moments and growth strategies of the Fe$_n$Zr (n = 1–6) clusters

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ARTICLE INFO

ABSTRACT

The geometries, magnetic moments and growth strategies of the Fe$_n$Zr (n = 1–6) clusters have been studied using all-electron density functional theory. The results reveal that the lowest-energy Fe$_n$Zr (n = 1–6) clusters can be achieved by insteading one Fe atom with a doped Zr atom in the lowest-energy structures of Fe$_N$ (N = 2–7). Fe$_n$Zr clusters are more likely to form the dense accumulation structure than the Fe$_n$ clusters. By the analysis of the differences of the total binding energies, it can find that Fe$_5$Zr cluster possess higher stability than the other considered Fe$_n$Zr clusters. Local peaks of HOMO–LUMO gap curve are found at n = 1, 6, meaning that the chemical reactivity of the two clusters is worse. Fe$_3$Zr and Fe$_6$Zr clusters have larger magnetic moments than other concerned Fe$_n$Zr (n = 1–6) clusters. The small Fe$_n$Zr clusters are almost acquired by small Fe$_{n-1}$Zr clusters which adsorbed a Fe atom at lower temperature except for Fe$_2$ + FeZr not Fe + Fe$_2$Zr to compose Fe$_3$Zr.

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1. Introduction

Transition metal clusters (TMCs) have attracted more attention for their unique magnetic features [1]. Binary TMCs have been massively studied by experimental and theoretical techniques [2], and the Fe-based metal clusters are the most promising magnetic materials [2]. Zirconium is an essential metal in nuclear industry [3]. Amorphous Fe–Zr alloys have attracted much interest and debate during the past decade [4]. Zirconium can refine the austenite grain of steel. Zirconium also reduces the strain aging phenomenon and improves the toughness of steel and so on. To study the evolution mechanism of the texture from the atomic level, we will concern Fe$_n$Zr (n = 1–6) clusters. A further attention is the relation between the Fe$_n$Zr cluster structures and magnetic properties. All these physical properties are correlated with the electronic structure of the alloy [5]. TMCs have more complicated electronic structures than the homo-nuclear clusters. The physical and chemical properties of TMCs are also transformed with the cluster size [3]. The understanding and control of the grain micro-structure of poly-crystalline materials are technological important [6]. Fe–Zr clusters have paid more attention to nano-crystalline thin films.

Binary XY clusters, with X, $Y \in$ {Fe, Co, Ni, Mn}, have been implemented by first principle within density functional theory (DFT) [2]. The all-electron density functional method (DMol^3) is an adequately accurate and efficient procedure for clusters [7]. So far, the central issue of TMCs research is mainly on the 3d transition metal, the 4d metal clusters are relatively less mentioned. In the present work, we select the Zr atom as an impurity and investigate the geometries, magnetic moments, and growth strategies of the Fe$_n$Zr (n = 1–6) clusters. It is very meaningful to analyze the other 4d transition metal doping to iron clusters.

2. Computational details

To acquire the initial structures of the Fe$_n$Zr clusters, we replaced a Zr atom on each possible site of various iron nano-clusters studied previously [7,8]. All the hypothetical initial structures must be geometric optimized [2]. Our calculations were executed using the spin polarized DFT implemented in the DMol^3 package [9,10] within the generalized gradient approximation (GGA) using BLYP functional [11,12]. The double numerical polarization (DNP) basis set [9] was chosen. All of these have been adopted in previous calculations [1,2]. In the geometry optimization processes, the energy gradient and atomic displacement converged to within 1×10^{-5} Hartree/Bohr and 5×10^{-3} Å, respectively. Corresponding to a total energy convergence of

1×10^{-5} Hartree, the charge density in the self-consistent iterations converged to within 1×10^{-6} e/Å³. Mülliken population analysis was adopted to acquire the atomic charge and magnetic moments of the clusters, respectively [13,14].

The average binding energy $E_b(n)$ was defined

$$E_b(n) = [nE(\text{Fe}) + E(\text{Zr}) - E(\text{Fe}_n\text{Zr})]/(n+1) \qquad (1)$$

where n is the number of Fe atoms. $E(\text{Fe})$ and $E(\text{Zr})$ are the single atom energies of the Fe and Zr atoms. $E(\text{Fe}_n\text{Zr})$ is the total energy of the lowest-energy structure for the Fe_nZr cluster.

The relative stability of the Fe_nZr clusters can be better understood by calculating the second-order difference of cluster energies $\Delta^2 E$ [15]

$$\Delta^2 E_n = E_{n+1} + E_{n-1} - 2E_n \qquad (2)$$

where E_{n+1}, E_{n-1} and E_n represent the binding energy of Fe_{n+1}Zr, Fe_{n-1}Zr and Fe_nZr, respectively.

To understand the growth strategies, in this study only $\text{Fe}_m\text{Zr} + \text{Fe}_{n-m} \rightarrow \text{Fe}_n\text{Zr}$ is considered to the lowest-energy structures of Fe_nZr ($n = 1$–6). The reaction energy ΔE was defined

$$\Delta E = [(E_m + E_{n-m}) - E_n]/(n+1) \qquad (3)$$

3. Results and discussion

3.1. Structures of Fe$_n$Zr clusters

For comparison, the lowest-energy structures for the pure Fe_N ($N = 2$–7) clusters, the lowest-energy structures and some typical stable isomers for each Fe_nZr cluster are shown in Fig. 1. Comparing the Fe_nZr ($n = 1$–6) structures with the lowest-energy structures of Fe_N ($N = 2$–7), it shows that the lowest-energy structures of Fe_nZr clusters which usually have higher dense accumulation configuration can be obtained by simple replacing a Fe atom of the most stable structures of Fe_N by the Zr impurity atom. Although the atomic radius and ionic radius of Zr are both slightly larger than that of the Fe, but 4d electron configuration of Zr which make it has higher dense packing character [3]. Due to the 4d orbitals character of the zirconium atoms, only two electrons occupying the 4d orbitals, which are prefer to produce the anti-bond orbital [3]. It causes the band structure for Fe–Zr alloys is different from Ni–Zr alloys [16].

Fig. 2 shows that the Zr replacing how to effect on the configurations of the Fe_N ($N = 2$–7) isomers. For Fe_3Zr, the default planar
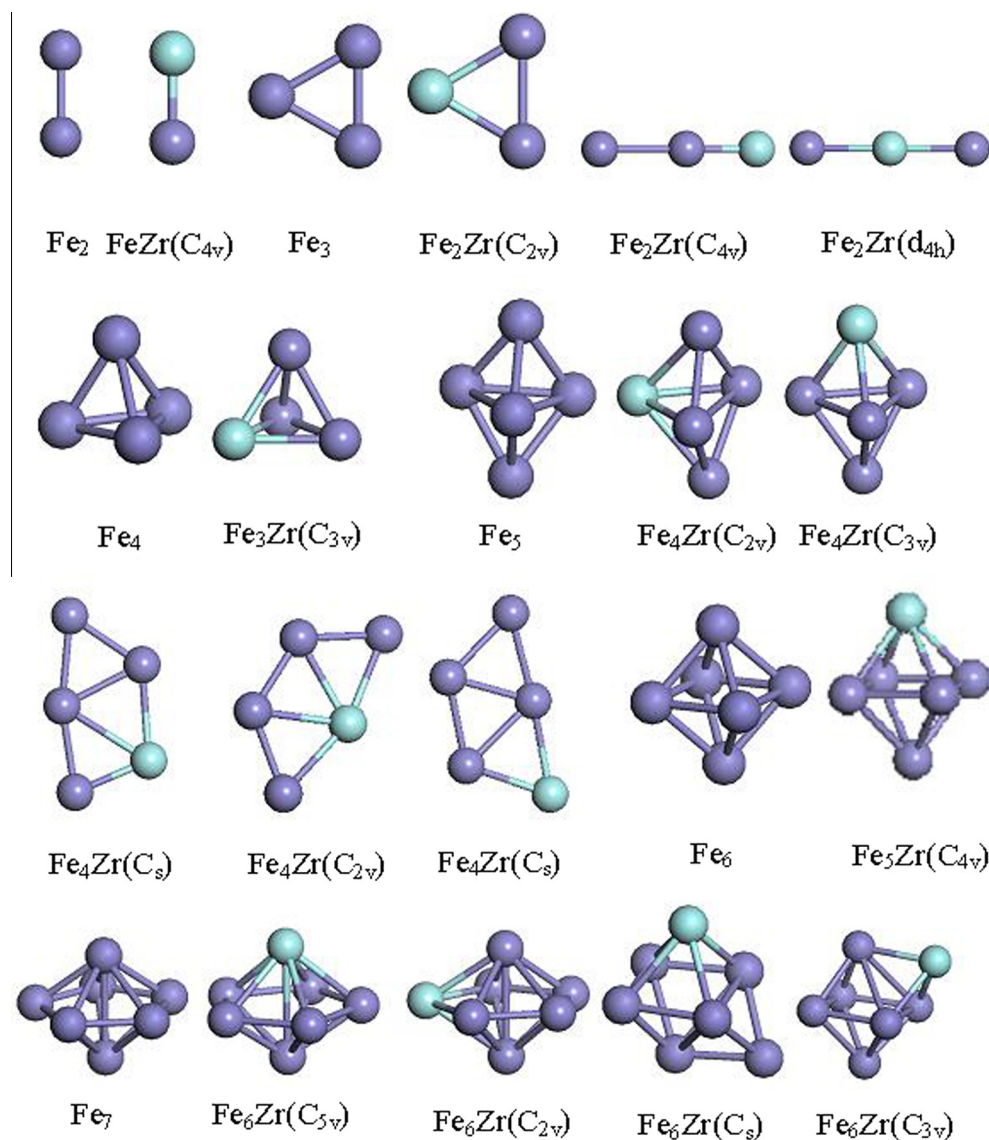

Fig. 1. The pure Fe$_N$ (N = 2–7) clusters and the lowest-energy configurations and lowlying isomers of Fe$_n$Zr (n = 1–6) clusters (gray ball: Fe atom, and sky ball: Zr atom).