



Electronic structure and stability of metal–carbon nanoparticles with Cr, Mn, Fe and W impurities



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ABSTRACT

Theoretical modeling of the effect of Cr, Mn and W atoms substituting iron sites on the electronic structure of the most stable isomers of some Fe_xC_y clusters as well as of the fragments of Fe_3C and M_{23}C_6 ($\text{M} = \text{Cr, Mn, Fe, W}$) crystal carbides lattice was carried out using the DFT based Dmol³ method. Our calculations predict the most preferable impurity positions, magnetic moments on metal atoms as well as the stability of binary and ternary clusters. We demonstrated that in the cases of systems containing 3d-atoms the interactions between M4s, 4p and C2p orbitals correlate with the variation of stability, whereas for the W–C bonding this correlation was obtained for the interaction between W5d and C2p states.

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1. Introduction

The binary M_xC_y clusters may be obtained by the defragmentation of solid-phase metal carbides and by the laser vaporization of the metal and cooling in acetylene. The use of latter technology led to the discovery of the so-called metallo-carbohedrenes (metcars), such as Ti_8C_{12} [1] with anomalously high stability and geometrical structures, which considerably differ from the fragments of the crystal lattices. The knowledge of stability and electronic structure of the Fe_xC_y nanoparticles is important to better understand the properties of steels and composite materials. In experimental work of Pilgrim and Duncan [2], the distribution of cationic Fe_xC_y^+ particles had been obtained. According to these results, the smallest observed cluster had Fe_5C_6 composition and a small relative abundance. The most abundant Fe_xC_y^+ species had (7,8), (8,12) and (12,12) (x,y) content.

Theoretical modeling of the electronic structure of small Fe_xC_y and Fe_xC_y^+ metcars [3–5] showed that the ferromagnetic (FM) ordering was preferable in the majority of ground isomers of the investigated species. Our investigations of the Fe_xC_y nanoparticles containing from 5 to 15 atoms [5] did not confirm the earlier results [6] that the fragments of crystal lattice of iron carbides are the best starting geometries to achieve the most stable isolated binary clusters. Moreover, we had obtained that the construction

of binary Me_xC_y particles by the addition of atoms “one by one” (corresponding to the vaporization – cooling technologies) led to the more stable objects. Our “binomial” scheme for the generation of stable isomers for binary particles, as well as the same DMol³ method were also used by Xu et al. [7] to find all possible geometries for the Fe_3O_3^+ cluster. The DMol³ method was also used by Ma et al. [8] to predict the structures and magnetic moments of FeC_N and Fe_2C_N clusters; however, the way for selection of initial structures converging to the most stable isomers in this work is not clear.

It is well-known that d-impurities may strongly affect the stability of transition metal carbides and the creep properties of steels [9–10]. In the present paper, we study the influence of chromium, manganese, iron and tungsten impurities on the stability and magnetic properties of the three types of nano-sized systems: (1) Fe_5C_6 , Fe_6C_6 , Fe_7C_8 metcars; (2) Fe_5C_6 and Fe_6C_6 fragments of the Fe_3C crystal lattice; (3) M_8C_6 fragments of the M_{23}C_6 carbides lattice ($\text{M} = \text{Cr, Mn, Fe, W}$).

2. Objects of calculations

Earlier in our investigations of the electronic structure of small iron – carbon clusters [3–5], the “binomial” scheme for the generation of all stable isomers was suggested. A shortcoming of this method is the rapid multiplication of isomers as the number of atoms increases [3,4]. However, the analysis of the parentage of the ground geometries for FeC_2 , Fe_2C , FeC_3 , Fe_3C , Fe_2C_2 and Fe_2C_3

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showed that in all cases the most stable isomer Fe_xC_y was obtained from the most stable configurations of both “preceding” particles $\text{Fe}_{x-1}\text{C}_y$ and $\text{Fe}_x\text{C}_{y-1}$ by the addition of Fe or C atoms, respectively. Thus, to find the ground-state for any Fe_xC_y cluster one needs to consider only the ground-states of all previous compositions. The two paths of each cluster generation give one a possibility for the verification of the results. In the present paper, we consider the ground isomers of the three metcars reported earlier [5]: (1) Fe_5C_6 – the smallest experimentally observed composition [2] with the FM ordering of metal atoms spin moments ($S_{\Sigma\text{Me}} = 15.3 \mu_B$, since the magnetic moments lie primarily on the metal atoms; the total spin moment S_{tot} of the cluster was equal to $16 \mu_B$); (2) Fe_6C_6 cluster in which the spin moments of two metal atoms had the opposite direction to those of the four other Fe atoms ($S_{\Sigma\text{Me}} = 6.9 \mu_B$, $S_{\text{tot}} = 7 \mu_B$); (3) Fe_7C_8 – the most abundant composition [2] with the FM ordering of magnetic moments ($S_{\Sigma\text{Me}} = 20.8 \mu_B$, $S_{\text{tot}} = 22 \mu_B$). The shapes of these clusters are shown in Fig. 1.

The other two types of clusters considered in the present paper were the small fragments of crystal lattice of the most stable solid-phase carbides Fe_3C (cementite) and M_{23}C_6 ($M = \text{Cr}, \text{Mn}, \text{Fe}, \text{W}$). It is evident that the stoichiometry of crystal fragments containing hundreds or thousands atoms will be close to (3,1) or (23,6); however, the small Fe_xC_y fragments of the crystal lattice could be of the various compositions. We considered several types of the Fe_3C crystal fragments of Fe_5C_6 and Fe_6C_6 compositions with initial atomic coordinates corresponding to the parameters of Fe_3C lattice reported in Ref. [12]. These initial structures were subjected to geometry optimization, leading to the new equilibrium geometries corresponding to the isolated clusters. In general, the achieved equilibrium structure corresponds to the minimum of binding energy E_b (which is sometimes called the “total bond energy” or the “atomization energy”). The E_b of a neutral system is defined as $E_b = E_{\text{tot}} - E_{\text{sum}}$, where E_{tot} is the total energy of the system and E_{sum} is the sum of the total energies of all isolated neutral atoms in the system. Due to geometry relaxation, the binding energy of each cluster noticeably decreased and the structure became more compact. The most stable structures for these two compositions were used as the objects for the investigations of $\text{Cr} \rightarrow \text{Fe}$ and $\text{Mn} \rightarrow \text{Fe}$ substitutions. The shapes of these clusters are shown in Fig. 2. Note that the states with $S_{\text{tot}} = 0$ were obtained for both particles; however, the Fe_5C_6 cluster converged to the nonmagnetic state (NM), i.e. the spin moments of all atoms were equal to zero, whereas the anti-ferromagnetic (AFM) ordering was realized with the equal spin moments of “up” and “down” orientations in the Fe_6C_6 cluster. As mentioned above, the stability of several binary Me_xC_y metcars investigated in Ref. [5] was greater than that of the fragments of cementite lattice with the same composition. In the present cases of Fe_5C_6 and Fe_6C_6 particles, the absolute values of binding energy of both metcars were greater than those of the corresponding crystal fragments by ~ 5 eV.

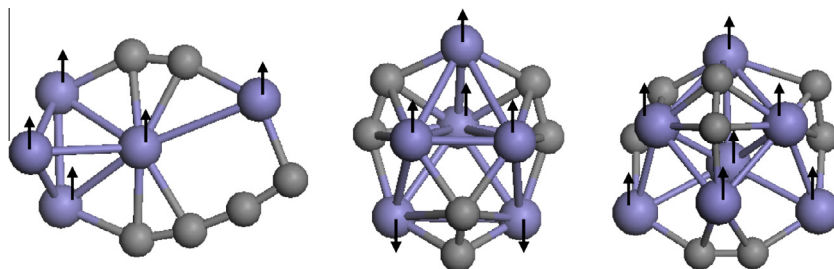


Fig. 1. Geometrical structures of the ground-state isomers of Fe_5C_6 (left), Fe_6C_6 (center) and Fe_7C_8 (right) particles, the arrows “↑” and “↓” correspond to “up” and “down” orientations of metal atoms spin moments.

The M_{23}C_6 carbides crystallize in the space group $\text{Fm}\bar{3}m$ ($Z = 4$) and contain four nonequivalent metal types: M1 (4a), M2 (8c), M3 (32f) and M4 (48h), and the carbon atoms are in (24e) site. The lattice parameters of M_{23}C_6 follow the ion radii of d -metal M decreasing from Cr to Fe and increasing from Cr to W [13,14]. We considered several types of M_{23}C_6 crystal fragments containing all types of nonequivalent metal sites and the various numbers of atoms (from 14 to 30). The initial structures with the atomic positions corresponding to the lattice parameters of M_{23}C_6 [13,14] were subjected to geometry optimization, leading to the new equilibrium geometries. Since the absolute value of binding energy for the M_xC_y clusters gradually increases with increasing number of atoms, for the evaluation of relative stability of the nanoparticles with various sizes it is more reasonable to compare the binding energy per atom $E_{xy} = |E_b|/(x+y)$ [5]. The analysis of these specific energies showed that for the lattice fragments containing M1, M2 and M4 atoms the values of E_{xy} were in the range of 2–3 eV/atom, while in the case of M3, the maximum value of E_{xy} (more than 4 eV/atom) was obtained for the Cr_8C_6 , Mn_8C_6 , Fe_8C_6 and W_8C_6 clusters with O_h point symmetry and the equivalent positions of all metal and all carbon atoms. The shape of these particles is shown in Fig. 2. This result is in agreement with the band structure calculations of solid-phase M_{23}C_6 carbides [11], where the substitution of M3 site was found the most unfavorable. Because we searched for the most stable clusters, in further investigations the M_8C_6 particles ($M = \text{Cr}, \text{Mn}, \text{Fe}, \text{W}$) were used as the matrixes for the metal \rightarrow metal substitutions. It should be noted that the R_{M-M} distances in these clusters followed the same trend as in the solid carbides: $R_{\text{Cr-Cr}} = 2.51 \text{ \AA}$, $R_{\text{Mn-Mn}} = 2.50 \text{ \AA}$, $R_{\text{Fe-Fe}} = 2.41 \text{ \AA}$ (2.51 \AA , 2.45 \AA and 2.43 \AA in the Cr_{23}C_6 , Mn_{23}C_6 and Fe_{23}C_6 , respectively). The FM magnetic ordering was obtained for all of these species: Cr_8C_6 ($S_{\Sigma\text{Me}} = 10.4 \mu_B$, $S_{\text{tot}} = 10 \mu_B$), Mn_8C_6 ($S_{\Sigma\text{Me}} = 24.2 \mu_B$, $S_{\text{tot}} = 23 \mu_B$), Fe_8C_6 ($S_{\Sigma\text{Me}} = 17.3 \mu_B$, $S_{\text{tot}} = 17 \mu_B$) and W_8C_6 ($S_{\Sigma\text{Me}} = 7.4 \mu_B$, $S_{\text{tot}} = 7 \mu_B$). As seen, the spin moments of tungsten atoms were considerably less than those of the 3d-metals, and the direction of magnetic moments of the carbon atoms was opposite to those of the metal atoms.

3. Computational methods

Geometry optimization of all clusters was performed using the DMol³ method [15] with double numerical atomic basis set with polarization functions (“dnp”). The generalized gradient approximation (GGA) in the “PBE” form [16] was used in all calculations. Calculations of the clusters containing tungsten were performed in the scalar relativistic approximation [17]. The scalar relativistic approach allows one to include in the calculations almost all relativistic effects except the spin-orbit interaction. The role of the latter in electronic structure of the lead hexacyanoferrate containing iron atoms was investigated in our paper [18]. As found, the spin-orbit splitting of the Fe3d states, which forms the magnetic

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