Fe–Co magnetic nanoclusters by density functional theory calculations

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**ABSTRACT**

We present density functional theory results referring to the structural, electronic and magnetic properties of 13, 55, 147 and 309 Fe–Co (magnetic–magnetic) icosahedral nanoclusters (ICO) comparing with our previous results on Fe–Cu (magnetic–nonmagnetic). It came out that the Fe atoms always favour the edge surface sites exhibiting higher average magnetic moment (MM) for Fe and FeCo ICOs than FeCu while the local Fe MM is greater for FeCu12 and Fe6Cu49 ones. This is due to the strong hybridisation of Fe 3d–Co 3d states, while in Fe–Cu the Fe spin down states are restricted close to fermi without been affected by the corresponding Cu states. These results could be used for the design of environmental sustainable smart magnetic alloys.

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**Introduction**

Transition metal clusters and coatings are interesting since their structural, electronic and magnetic properties depend on their size and composition, rendering them suitable candidates for various potential applications. In particular, the magnetic moment (MM) of Fe clusters with less than 100 atoms is around 3μB much higher than the corresponding 2.2μB bulk value while it decays as a function of clusters’ size towards the bulk values [1–5]. Similar behaviour was also found by density functional theory (DFT) calculations when mixing Fe with a non-magnetic element like Cu in 13, 55, 147 and 309 magic numbered ICO clusters [6]. It is found that the local Fe MM of the FeCu12 is almost double than the bulk Fe while the Fe (111) triangle face in Cu49Fe6, Cu137Fe10 and Cu294Fe15 MM (2.7μB) converges faster to the Fe monolayer (ML) on Cu(111) (2.3–2.7μB) than the Fe at edge positions which nevertheless exhibit the highest local MM (3.1μB) [6]. These DFT data agree with experimental studies that the Fe/Cu(111) MM stands within the large ICOs and the bulk MM values [6–10]. Indeed, when growing Fe thin films on non-magnetic substrates like Cu results in an fcc tetragonal distorted (fct) structure depending on the film thickness showing higher local Fe MM up to 2.5–2.7μB on Cu(100) and 3.3μB on Cu(111) than the Fe bcc (2.1–2.15μB) [7–10]. To this end, experiments on Fe ultrathin ferromagnetic (FM) fcc tetragonal distorted film grown on magnetic fcc Co(100) coherently produced on non-magnetic fcc Cu(100), showed similar structural and thickness dependent magnetic properties [11–14]. The thinnest (up to 4ML) Fe film’s MM is 3.0μB on Co(100) and 2.8μB on Cu(100) while between 5 and 10 ML they drop to 1.1 and 0.8μB, respectively [14]. However, the study of Fe’s MM on fcc-like Co(111) on Cu(111) to our knowledge is still lacking although the Fe on Cu(111) reveals higher MM than Fe growing on Cu(100) [7–14].

Concerning the nanoclusters, theoretical DFT calculations on large ICOs (up to 400 atoms) to our knowledge are limited in pure (e.g. Co, Fe and Ni) [3,4,5,15], Co–Mn (13, 55 atoms) [16] and Fe–Cu (13, 55, 147 and 309) [6] nanoclusters. It came out that as the size of the cluster increases, the clusters’ MM decreases to the corresponding bulk value; the cluster’s core atom MM approaches faster the bulk MM than the cluster’s surface MM [3–6]. Experimental results show that Ni clusters’ MM with more than 300 atoms approach the bulk limit more rapidly than the Co and Fe MM clusters which need more than 500 atoms to converge [2]. Moreover, Fe55 shows an antiferromagnetic (AFM) coupling between the central atom and first shell’s atoms while the Fe147 MM oscillates between the shells from antiferromagnetic to ferromagnetic [4]. On the contrary, Co55 and Co147 maintain a ferromagnetic behaviour like Co13 [4,5]. Concerning the electronic properties, the clusters up to 55 atoms (Fe, Co, Ni and Fe–Cu) display half metallic character in the sense that HOMO–LUMO energy gap is very small for minority spin as compared to that for majority-spin component while the 147 and 309 icosahedra show metallic nature [4,6]. Nevertheless, studies concerning the electronic and structural properties of clusters having Fe and magnetic element substitutions like Co and sizes higher than 13 atoms, e.g. icosahedral 55, 147 and 309 to our knowledge are absent.

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The transition metal clusters with less than 20 atom have been widely studied with ab initio calculations [17–26]. DFT revealed that the icosahedral Fe13 exhibits the highest MM 3.38 μB among all 3d and 4d transition 13 and 23 atom metal clusters [15] while for Co13 and Cu13 hcp-like structures are favoured [19]. Moreover, it is found that in Fe12X, (X = Al and 3d element) the local spin MM of a substituent atom decreases with respect to that substituted iron atom except for the case of surface Mn atom where the local MM is 4.6 μB [24,25]. Similarly, in ferromagnetic (CoxFe1−x)N (N = 5, 13), although the local MM of both Co and Fe atoms is slight enhanced as the Co concentration increases, the average MM decreases since Co atoms have one less d hole [17]. Interestingly, when doping non-magnetic element clusters like Cu13 with Fe, the local Fe MM becomes almost double than the Fe bcc due to its partially filled 3d shell although antiferromagnetic alignment is found between the Cu and Fe MM [6,26].

In this work, we present a systematic study of Fe–Co icosahedral clusters aiming to reveal the electronic and magnetic properties as well as the evolution of MM towards the FeCo thinnest film on Cu(111) which could be considered as an infinite cluster’s surface side system. The comparison with the local Fe MM of the Fe–Cu clusters and thin films is also provided using our previous SIESTA calculations [6] and the calculated average clusters’ MM in order to understand the influence of a magnetic (Co) and non-magnetic (Cu) substitution in Fe.

**Computational details**

We performed DFT calculations within the general gradient density approximation of Perdew and Wang [27] using the SIESTA [28]. For all elements, the core electrons were replaced by norm-conserving pseudopotentials in the fully nonlocal Kleinman Bylander [29] form and the basis set was a linear combination of numerical atomic orbitals constructed from the eigenstates of the atomic pseudopotentials [30].

For the 13-atom cluster we considered the boundary Fe12Co and Co12Fe cases. For the 55-atom we perform a detail configuration investigation, taken into account the energetically favoured Fe sites, the triangle (111) facets and the edge positions, aiming to depict the system with the highest MM and to compare our data with the Fe-Cu nanoclusters’ results. All the understudy 55-atom configurations are in Figure 1 in the next session. In line with the FeCu case, we choose the triangle and edge configuration for the 147 and the 309 clusters. For cases we used a box with vacuum twice as large as the size of the nanocluster in order to avoid periodic images interactions while no – periodic boundary conditions were applied.

The surfaces consist of a (3 × 3 × 2) Cu(111) unit cell supercell resulting in six atomic layers with nine atoms. We consider the cases of Fe monolayer on Cu(111), Fe/Co atomic layers on Cu(111), Co/Fe on Cu(111) and mix FeCo on Cu(111) thin films. We applied in-plane periodic boundary conditions and a 9 × 9 × 1 k-point mesh. The vacuum spacing is equal to the length of the supercell along [111] direction while the three atomic layers were fixed in order to mimic the bulk behaviour. For the geometry optimisation, the structure is considered fully relaxed when the magnitude of forces on the atoms was smaller than 0.005 eV Å⁻¹. The cluster’s binding energies (Eb) were calculated by subtracting from the clusters total energy the corresponding equal number of Fe and Co atomic energies.

**Results and discussion**

**Structural and magnetic properties**

Aiming to reveal the MM moment evolution as the size of the cluster increases towards (111) thin films and the taken into account the ICO favoured structure of the larger Fe and Co clusters as well as its (111)-like facet which shows the highest MM we adopt for all nanoclusters, even for the tiny 13-atom. Consequently, we started with the smallest 13 atom FeCo cluster and we consider the boundary cases of Fe12Co (Eb is equal to −3.25 and −3.27 eV when Fe is a core atom) and Co12Fe (−3.34 and −3.33 eV for Fe core atom). We found that Co always like to be core atom in line with previous DFT on Fe12Co [24] while the most stable is the Co12Fe. The total MM is higher in the Fe-rich cluster Fe12Co (43.2 μB), having the biggest local MM on the Fe shell atom of Co12Fe (3.1 μB). The Co core atom exhibits always the lowest MM (1.8 μB). These results are in line with our previous calculations on Cu12Fe clusters were the local MM was higher at the Fe shell atom [6]. On the contrary, the Cu12Fe cluster shows antiferromagnetic behaviour between Cu and Fe atoms while in the case of Fe–Co we always observe ferromagnetic behaviour. The Eb of the Fe13 (−3.24 eV) stands within the previous DFT data ranging from −3.07 to −4.43 eV [17], the total MM is 44.1 μB (2.6 μB/atom) in line with 44 μB [17] while the Fe shell atoms show higher MM (3.1 μB). In addition, the Co13 (−3.33 eV) is compared to binding energies ranging from −3.26 up to −5.14 eV [17] and the local MM at the shell atoms (2.1 μB) and at the core (1.9 μB) are higher than the bulk value (1.7 μB) in line with previous DFT calculations [4,15,17].

The next magic number for icosahedral clusters is the 55. For these FeCo there are several configurations depending on the Fe composition depicted in Figure 1. Starting with the pure Co55 and Fe55 icosahedral clusters we found the total MM at 103 and
150 \mu_B\) respectively, in line with 105 and 150\mu_B of [24]. Co_{55} shows a FM behaviour between all cluster’s atoms while Fe_{55} displays AFM coupling between core and first shell’s atoms. Firstly, we substitute a Fe atom in all available sites of Co_{55} (core, first and surface shell) as presented in Figure 1. It came out that the Co_{55}Fe energetically favoured configuration is the one with Fe atom at the clusters’ surface which also shows the highest local MM (2.99\mu_B) compared to the other cases. The Co surface atoms of Cu_{54}Fe local MM varies from 1.84 to 1.87\mu_B while the core Co atom has on the average 1.6\mu_B that is smaller than the Co bcc (1.7\mu_B). This Fe atom’s higher local MM at the surface was also found for the Cu_{49}Fe case [6]. Furthermore, we study several configurations in the Co_{49}Fe_{6} clusters by substituting six Co atoms with Fe atoms: (a) at the cluster’s edge (−4.163 eV), (b) side (covering one surface side triangle, −4.159 eV) and (c) the half 1st shell positions (−4.157 eV) revealing the Edge Co_{49}Fe_{6} as the energetically favoured. In addition, the Edge Co_{49}Fe_{6} exhibits the highest local Fe MM (2.92\mu_B) compared to the Side (2.87\mu_B) and 1st shell’s (2.50\mu_B) configurations in line with the Cu_{49}Fe cases [6]. For the Co_{49}Fe_{6} clusters, the Co surface atoms show local MM up to 1.87\mu_B which decreases at the 1st shell (average 1.70\mu_B) and drops at the Co core atom (1.5–1.6\mu_B) in values lower than the Co bcc while the total cluster MM is around 106–108\mu_B. The next composition was the Co_{43}Fe_{12} where Fe atoms substitute: (a) all surface edge sites (−4.117 eV) or (b) all the 1st shell positions (−4.126 eV) in line with Co_{49}Fe_{6}, which show again that the Fe located at the edges is the energetically favoured configuration with great Fe local MM (2.91\mu_B). In the Co_{43}Fe_{12} cases, the Co local MM decreases even more at the first shell (1.05\mu_B) while the core atom retains 1.65\mu_B. Finally, the Co_{137}Fe_{10} where Fe covers the cluster’s surface (−4.368 eV) is favoured against the Fe_{55} (−3.823 eV) showing higher local Fe MM (2.76\mu_B) in line with Cu_{13}Fe_{42} case [6]. Summarising, we found that in 55 Co–Fe clusters the binding energy decreases as the Fe composition increases while the highest value for the local Fe MM is at the surface edge. For all cases, the Co and Fe reveal FM behaviour while the Cu and Fe clusters show AFM character.

For the 147 clusters, we focused on the Co_{135}Fe_{12} edge configuration having Fe at the edge surface sites and the Co_{137}Fe_{10} where Fe atoms cover the surface triangle side. The edge Co_{135}Fe_{12} (−4.41 eV) is energetically favoured against the Co_{137}Fe_{10} (−4.25 eV).

**Figure 1.** Co–Fe icosahedral 55 atom clusters along with the corresponding local MM and the binding energy. Blue (dark) and red (light) spheres stand for the Co and Fe atoms.
For the Co$_{135}$Fe$_{12}$ the total MM is 294μB while the Fe local MM is 3.00 and 1.82μB for Co surface atoms. The Co$_{137}$Fe$_{10}$ triangle case displays greater total MM of 335μB but lower Fe local MM of 2.89μB and higher Co local MM 1.90μB compared to the edge Co$_{135}$Fe$_{12}$ case. Finally, the Fe and Co atoms reveal FM behaviour in both Co$_{135}$Fe$_{12}$ and Co$_{137}$Fe$_{10}$ clusters.

Electronic density of states (EDOS)
Chemical reactivity of metallic clusters depends on the EDOS close to the Fermi level. In this section, we present the total and partial EDOS for the selective cases of (a) Co$_{12}$Fe, (b) Co$_{49}$Fe$_{6}$, Co$_{135}$Fe$_{12}$ when Fe occupies the Edge surface sites and (c) the Fe on Co MLs grown on Cu(111), Figure 2. The first column

**Figure 2.** EDOS: (a) Co$_{12}$Fe, (b) Co$_{49}$Fe$_{6}$ and (c) Fe/Co ML on Cu(111). The spin up and spin down highest occupied wavefunctions are depicted for Co$_{12}$Fe and Co$_{49}$Fe$_{6}$. Black, red, blue and green lines stand for the total, s, p and d electrons' contributions, respectively.
corresponds to the Co partial and clusters total EDOS while the second column stands for the Fe partial EDOS. The molecular-like Co$_{12}$Fe EDOSs of both Co and Fe show more localised states which are broadened and become wider as the size of the cluster increases approaching band characteristics of the films on Cu(111). In addition, for all cases the spin majority shows different behaviour than the spin minority revealing the electronic origin of the MM. Both Co and Fe states stand from $-6 \text{ eV}$ up to the fermi level while the highest occupation is due to the 3$d$ electrons rather than the sp. Focusing on the Co$_{12}$Fe EDOS, both Co and Fe spin up 3$d$ states are more localised than the spin down while the spin down state around $-0.5 \text{ eV}$ and around $-2 \text{ eV}$ exist in both atoms indicating their enhanced hybridisation. At the fermi level, both $d$ and $p$ orbitals contribute in the spin up states while the spin down states is basically occupied by the $d$ electrons of both atoms. The Co$_{12}$Fe total EDOS in the inset of Co EDOS clearly shows the different spin up and spin down electron occupation. Comparing with the Cu$_{12}$Fe EDOS, the more visible difference is the almost empty occupation of the Fe 3$d$ spin down states, showing only a pronounced state around $-0.3 \text{ eV}$ [6]. In the Co$_{49}$Fe$_{6}$ EDOS the spin up Co 3$d$ states are wider while the Fe exhibits a pronounced 3$d$ occupation around $-2 \text{ eV}$. The Co$_{49}$Fe$_{6}$ spin down 3$d$ EDOS exhibits states from $-4 \text{ eV}$ up to the fermi which gradually increase their occupation while the Fe 3$d$ states are basically located from $-2$ to $-1 \text{ eV}$ showing a pseudo gap at the fermi level. The total Co$_{49}$Fe$_{6}$ EDOS follows as expected mainly the Co partial EDOS while similar characteristics shows the Co$_{135}$Fe$_{12}$ total spin up EDOSs although more pronounced. In the Co$_{135}$Fe$_{12}$ total spin down EDOSs the pseudogap at the fermi level is partially filled due to the Co 3$d$ spin down states. Interestingly, the Co(111) ML on Cu(111) reveals similar Co and Fe spin up states with the Co$_{49}$Fe$_{6}$ having only higher occupation around $-1 \text{ eV}$. In the spin down both Co and Fe 3$d$ states appears around $-2 \text{ eV}$ and at the fermi level while the spin up fermi level occupancy is almost absent. In the total EDOS CoFe thin film on Cu(111) the Cu states are dominant and therefore the high occupation of the states mainly below $-3.5 \text{ eV}$ is observed.

**MM**

In Figure 3, we present the average total MM (a) for the basic under study cases as well as the local Fe MM (b) aiming to reveal the size dependence and the system with the highest values of MM. In Figure 3(a), we observe that the highest average MM stands for the Fe$_{13}$ while the Fe-Cu clusters reveal the lowest average MM due to the AFM behaviour and the almost absent MM at the Cu atoms (dashed line and open symbols are taken from our LSDA – DFT calculations [6]). The Fe–Co clusters saw higher MM than the pure Co$_{13}$ and Co$_{55}$ as well as the Co bcc suggesting the improved MM upon Fe substitution with small MM difference between the 55 and 147 triangle and edge configurations. Turning on the local Fe MM, Figure 3(b), we observe that the Co$_{12}$Fe, Co$_{49}$Fe$_{6}$ and Co$_{135}$Fe$_{12}$ clusters show higher Fe MM than the pure Fe clusters, Fe fcc and Fe bcc, showing similar MM values for the Edge and triangle cases. In addition, all the Fe–Co clusters reveal

![Figure 3](image-url)
bigger Fe MM compare to the Fe ML on Co or Cu(111) surface. Finally, it should be noted that Fe local MM is equivalent between the clean Cu(111) and the Co/Cu(111) once Fe remains as the outermost surface layer.

**Conclusions**

In this work, we present DFT calculations on Fe–Co and compare our data with Fe–Cu clusters and thin films aiming to understand the influence of Fe in magnetic or non-magnetic systems. It came out that both Co and Cu atoms always favour the core cluster’s site while the Fe atoms the edge surface sites. Fe–Co and Fe–Cu clusters reveal the Edge configuration as the one with the highest Fe local MM. In addition, the Fe12Co shows the greatest MM that converges towards the fcc FeCo (111) thin film as the size of the cluster increases. For all cluster sizes, the Co and Fe reveal FM behaviour while the Cu and Fe clusters show AFM character. The electronic properties reveal that the Fe 3d states are strongly hybridise with the Co 3d for both spin up and spin down EDOS while in the Fe–Cu clusters the Fe partial 3d spin down EDOS is saturated close to the fermi level. The Co12Fe and Co49Fe6 clusters reveal a pseudogap at the fermi level in the spin minority that is altered in the case of Co135Fe12 and Fe/Co/Cu(111). Concluding, the FM Fe–Co clusters or Fe coating of Co/Cu(111) are suggested as the best candidate for Fe-based systems with equivalent total and local Fe MM compared to the corresponding Fe–Cu systems. These results might be used for the design of magnetic devices with tune magnetic properties.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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