# Role of Ga-doping in iron–gallium alloy clusters*

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The structural and magnetic properties of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$; $n = 13$, $m = 0 \sim 3$) alloy clusters have been studied using density functional theory. The substitutional doping is favourable for small clusters with up to six atoms at low Ga concentration and substitutional Ga atoms in 13-atom clusters prefer surface sites. The Ga-doping generally could reduce the energetic stability but enhance the electronic stability of Fe clusters, along with a decrease of the local magnetic moments of Fe atoms around Ga dopants. These findings provide a microscopic insight into Fe–Ga alloys which are well-known magnetostriction materials.

**Keywords:** iron–gallium alloy clusters, density functional theory, stability, magnetic properties

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## 1. Introduction

Alloy clusters have attracted considerable interest in recent years, mainly due to their novel electronic and magnetic properties which are quite different from those of bulk materials.[1−3] For example, a recent Stern–Gerlach deflection experiment showed that the average magnetic moments of Co–Mn alloy clusters are remarkably enhanced with increasing Mn concentration, in contrast to the bulk behaviour.[4] In practice, more and more applications have implemented this kind of nanostructure and their great advantages have been clearly demonstrated as well. Benefiting from the large surface-to-volume ratio, alloy clusters could exhibit special chemical activity and thus great potential in the heterocatalysis.[3] Alloy clusters may also be suitable for the reversible hydrogen storage,[5] spintronics devices,[6] and optical devices.[7] One of the most important aspects is that various properties of these alloy clusters are dependent on the cluster size, composition and even other factors controllable by current experimental techniques.[8−12] This feature is especially advantageous to the development of new functional materials by self-assembling alloy clusters, just like the synthesis of ferromagnetic FePt nanocrystal superlattices.[13]

In this work, we will focus on the Fe–Ga alloy clusters for the following reasons: It is well known that the nonmagnetic gallium can be doped into the Fe lattice and the formed Fe–Ga alloys have attractive magnetic properties, such as large room temperature magnetostriction coefficients at a low saturating field.[14,15] In practice, Fe–Ga alloys are regarded as important candidates for magnetostrictive devices like acoustic sensors[16] and vibrators.[17] Though a lot of experimental and theoretical investigations have been preformed,[18−24] the origin of the enhanced magnetostriction in Fe–Ga alloys is not very clear so far. In fact, Fe–Ga alloys are believed to have complicated internal structures[23,24] beyond the simple theoretical models.[18,19,22] Thus, the investigation of Fe–Ga alloy clusters could be particularly helpful in understanding the Fe–Ga interaction in various local environments.[20] Moreover, it is also interesting to make an attempt to check if there are some novel properties and new potential applications for Fe–Ga alloy clusters. From a more fundamental viewpoint, as the main group element just next to the 3d tran-

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sition metal elements in the periodic table, the Ga atom has similar atomic radius to the Fe atom, which should be favourable for the formation of alloy clusters. In addition, Fe–Al clusters were found to exhibit diverse magnetic behaviour dependent on the Al concentration,[25] and then novel magnetic properties could be anticipated for Fe–Ga alloy clusters in a natural manner. However, to our best knowledge, there is still a lack of understanding of Fe–Ga alloy clusters and thus a detailed theoretical analysis is highly desirable.

This article is organized as follows. Section 2 presents a brief description of the computational methodology. Section 3 presents the main results and related discussions about geometrical structures, stabilities and magnetic properties of some Fe–Ga clusters. In detail, small $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) clusters are discussed in Subsection 3.1 to reveal the early evolution stage of the Fe–Ga clusters, based on a systematic analysis of a large set of initial geometries and possible electronic configurations. Then in Subsection 3.2, $Fe_{13-m}Ga_m$ ($m = 0 \sim 3$) clusters are studied based on the Ga substitution in the icosahedral (ICO) isomer of the $Fe_{13}$ cluster with a core-shell structure. They correspond to the case of multiple Ga atoms distributed in host Fe atoms and may be used as a starting point to understand bulk Fe–Ga alloys because of their core-shell structure and a higher average coordination number. In the next, the binding energy and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are discussed in Subsection 3.3, to disclose the Ga doping effect on the cluster stability. A detailed analysis is performed on magnetic properties of Fe–Ga clusters in Subsection 3.4. Finally, a summary of the whole work is given in Section 4.

## 2. Method and computational details

For clusters with less than $10^3$ atoms, the density functional theory (DFT) is usually an efficient and accurate technique to investigate their geometries, energetics and various properties. In this work, all calculations are preformed using the DMol$^3$ package[26] within the DFT framework. The spin-polarized Perdew–Wang (PW91)[27] functional based on the generalized gradient approximation (GGA) is employed to take into account the exchange and correlation effects of electrons. In the self-consistent field (SCF) calculation, the double numerical plus polarization basis set is used to expand the electronic wavefunction. Note that this basis set is at the same level of accuracy as the well-known 6-31G$*$ basis set. Moreover, the multipolar fitting up to octupole is chosen for both charge density and Columbic potential and a fine integration grid is also adopted. The geometry optimization without any symmetry restriction is followed by a frequency calculation to examine if the optimized low-lying isomers is stable. Additionally, a set of tight convergence thresholds is chosen: The density in the SCF calculation should converge within $1\times10^{-6}$ a.u. and the energy variation, force and displacement of the geometrical optimization are less than $1\times10^{-7}$ a.u., $1\times10^{-4}$ a.u., and $1\times10^{-3}$ a.u., respectively.

## 3. Results and discussions

### 3.1. Small $Fe_{n-m}Ga_m$ clusters ($n = 3 \sim 6$, $m = 0 \sim 2$)

For these small clusters, it is feasible to perform an extensive search by considering various initial geometries, as well as all possible collinear magnetic couplings for each geometry. The low-lying isomers of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) clusters are shown in Fig. 1. The calculated ground state of $Fe_3$ cluster has an acute triangle structure and the total magnetic moment of this isomer is 10 $\mu_B$. The most stable isomers of $Fe_4$, $Fe_5$ and $Fe_6$ have the pyramid, trigonal bi-pyramid and distorted octahedron structures respectively and their total magnetic moments are 14, 18 and 20 $\mu_B$ respectively. Note that our results agree well with some previous DFT-GGA results,[28–31] though in the literature results were usually found to rely on the computational methods and even technical details of the calculations.[30,32]

It is found that the mono-doped clusters $Fe_{n-1}Ga$ has the similar geometrical framework like the pristine $Fe_n$ cluster for $n$ between 3 and 6, though the Fe–Ga bond length is quite a lot larger than the corresponding Fe–Fe bond length. For example, the Fe–Ga bond length in $Fe_5Ga$ is about 11% longer than the Fe–Fe bond length in $Fe_6$. However, after doping with two Ga atoms, only the largest cluster, $Fe_4Ga_2$, can still keep the ground state morphology of the corresponding pristine Fe cluster. This implies that the substitutional doping is preferred for small clusters at low Ga concentration. Another remarkable feature of the ground states in Fig. 1 is that Ga atoms are always located at the outmost shell of the alloy cluster, i.e., no low-lying isomers with a Ga atom fully encapsulated in Fe atoms could be found.

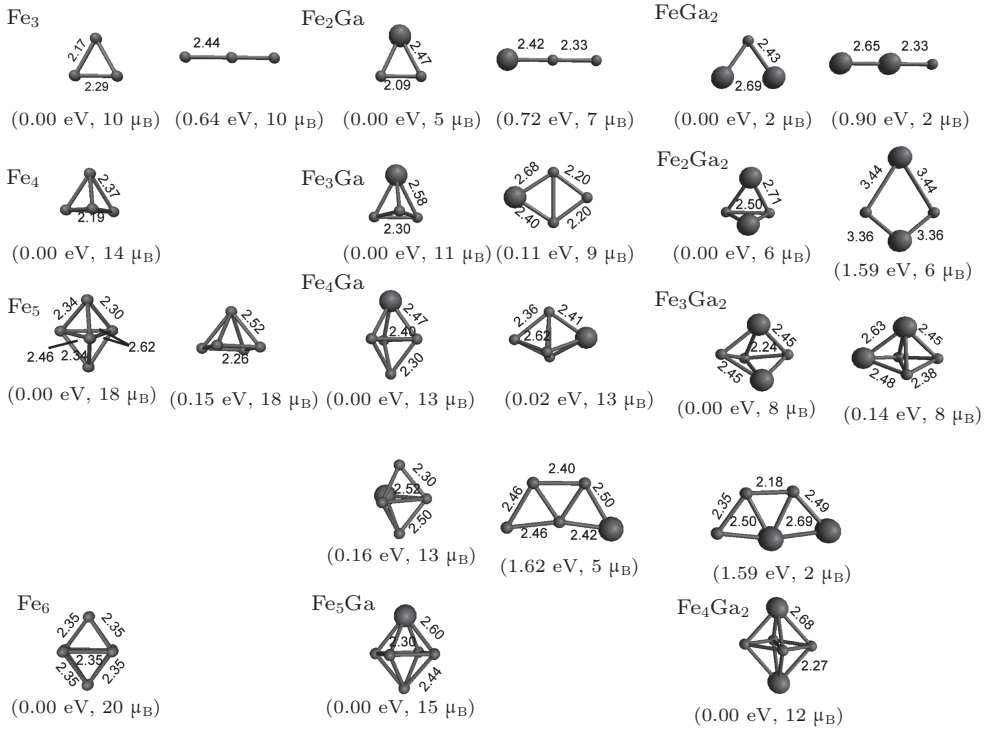



**Fig. 1.** Geometrical structures of low-lying isomers of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) clusters. Note that the Fe and Ga atoms are depicted with small and large balls respectively. The bond lengths (in Å, 1 Å=0.1 nm) are depicted. The first and second values under each isomer are its energy relative to the ground state and total magnetic moment.

### 3.2. $Fe_{13-m}Ga_m$ clusters ($m = 0 \sim 3$): substitutionally doped $Fe_{13}$

A larger cluster model with reasonable doping concentration should be more informative for understanding realistic Fe–Ga alloy clusters. In general, the atomic interaction in larger alloy clusters should be more complicated and various doping behaviours (for example, Ga atoms are segregated or mixed in Fe host atoms) can be more clearly demonstrated in larger alloy clusters. Different from these smaller clusters discussed in Subsection 3.1, larger clusters with core-shell structures could be more close to metal nanoparticles synthesized in experiments.[33] Typically, the 13-atom system should be a good candidate because $Fe_{13}$ has high stability[34] and is widely used as a doping model. For instance, Dunlap[35] performed an early theoretical study for the case that the central atom of the ICO $Fe_{13}$ cluster was replaced by various dopant atoms. It is shown that magnetic properties of these clusters have been influenced by the chemical doping evidently.

In the past, the perfect ICO isomer with $I_h$ symmetry was deemed as the most stable $Fe_{13}$ cluster, but the distorted ICO isomer is found to be more stable finally.[36] However, to reduce the possible choices of initial coordinates, the ICO isomer is adopted as the starting point of the substitutional doping but the symmetrical restriction is disabled during the optimization. Because it is practically difficult to determine the global minimum of such large clusters with complicated magnetic coupling from first principles calculations, a simplified strategy is necessary. Furthermore, typical magnetic coupling schemes are taken into account for each initial coordinate.

As shown in Fig. 2, in the ground state and other low-lying isomers of every doped cluster, Ga atoms strongly prefer to stay at the surface sites instead of the cluster center, similar to the small clusters discussed in Subsection 3.1. In addition, for $Fe_{13-m}Ga_m$ ($m = 1 \sim 3$) clusters with varied Ga concentrations (7.7 %, 15.4 % and 23.1 % for $m = 1 \sim 3$), the most stable isomer is about 2 eV more favourable than the lowest isomer with a central Ga atom. All these facts indicate that the central substitution is energetically unfavourable for the Ga doping in comparison with the substitution on the surface. On the other hand, for the ground state of the $Fe_{11}Ga_2$, two Ga atoms are located at the second nearest vertex sites and two surface Fe atoms are shared between the Ga atoms. The isomer with Ga atoms at the nearest surface sites is about 0.14 eV higher in energy than the ground state and the isomer with two Ga atoms at the opposite vertex sites of an icosahedron is about 0.39 eV higher in energy than the ground state. Moreover, similar Ga distribution is found in the ground state of $Fe_{10}Ga_3$.

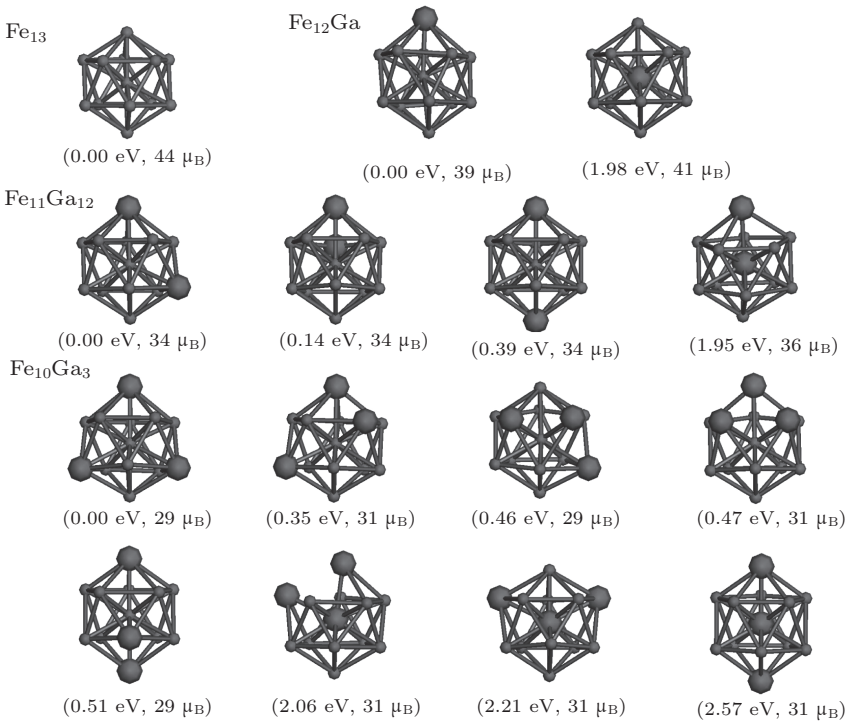



**Fig. 2.** Geometrical structures of $Fe_{13-m}Ga_m$ ($m = 0 \sim 3$) clusters from the substitutionally doped ICO $Fe_{13}$ cluster. The energy relative to the ground state and the total magnetic moment are also given.

For 13-atom systems, the average nearest Fe–Ga distances in $Fe_{13-m}Ga_m$ are 2.64, 2.61, and 2.61 Å for $m = 1$, 2, and 3, respectively, which are still larger than the average nearest Fe–Fe distance in $Fe_{13}$ (about 2.51 Å). However, different from these smaller clusters, some Fe–Ga bonds may be shorter than the corresponding Fe–Fe bond in $Fe_{13}$.

It is important to understand the effect of the Ga–Ga interaction in these clusters doped with two or three Ga atoms. In general, the distance between neighboring Ga atoms could be used to roughly estimate their interatomic interaction qualitatively. Interestingly, there is a clear transition of Ga–Ga distance with increasing cluster size: for small clusters, i.e., $FeGa_2$, $Fe_2Ga_2$, and $Fe_3Ga_2$, the Ga–Ga distances are 2.69, 2.71, and 2.96 Å respectively, which are all less than 3 Å. Then the Ga–Ga distance will increase to above 4 Å for larger clusters suddenly. In detail, the Ga–Ga distances are 4.07 and 4.34 Å in $Fe_4Ga_2$ and $Fe_{11}Ga_2$ and Ga–Ga distances in $Fe_{10}Ga_3$ are about 4.4 Å. These results may suggest that quite different Ga–Ga interactions are present in smaller and larger clusters. Note that $Ga_2$, $Ga_3$, and $Ga_4$ clusters have the Ga–Ga bond lengths of 2.46, 2.55, and 2.63 Å respectively,[37] while the experimental Ga–Ga bond length in the monoclinic-phase is about 2.484 Å.[38] Thus, the Ga–Ga distance in small clusters like $Fe_nGa_2$ ($n = 1 \sim 3$) is close to the Ga–Ga bond length in Ga clusters[37] and bulk,[38] and it may imply that the Ga–Ga interaction is like a stretched Ga–Ga bond in these alloy clusters. On the other hand, the sudden increase of the Ga–Ga distance in larger clusters suggests that there is no direct Ga–Ga interaction.

## 3.3. Binding energy and HOMO–LUMO gap

The binding energy is a central quantity to characterize the energetic stability of a cluster. Generally speaking, the cluster with larger average binding energy (i.e., the binding energy divided by the total amount of Fe and Ga atoms) tends to be more stable against the thermal dissociation. Figure 3(a) shows two distinct features of the average binding energy. First, for all series (i.e., $Fe_n$, $Fe_{n-1}Ga$, or $Fe_{n-2}Ga_2$), the average binding energy increases with the cluster size monotonically, which could be rationalized as the result of increasing average coordination. In fact, similar behaviour was observed in pristine Fe clusters[39] and some other alloy clusters.[40,41] Secondly, for these clusters of the same size, the average binding energy decreases with increasing Ga concentration except the $Fe_4Ga$. Therefore, it is clear that the Ga-doping can

weaken the energetic stability of Fe clusters. This is also in agreement with the fact that the average binding energies of Ga clusters[37] are quite less than those of Fe clusters. We also performed another useful examination. For diatomic clusters $Fe_2$, $Ga_2$ and FeGa, the bond lengths are 2.00, 2.46, and 2.47 Å respectively and the binding energies are 3.65, 1.58, and 3.09 eV respectively. Clearly, the Fe–Fe interaction is stronger than the Fe–Ga interaction and the Ga–Ga interaction is the weakest. By the way, it is reasonable that Ga atoms prefer surface sites because less Fe–Fe bonds will be broken like that.

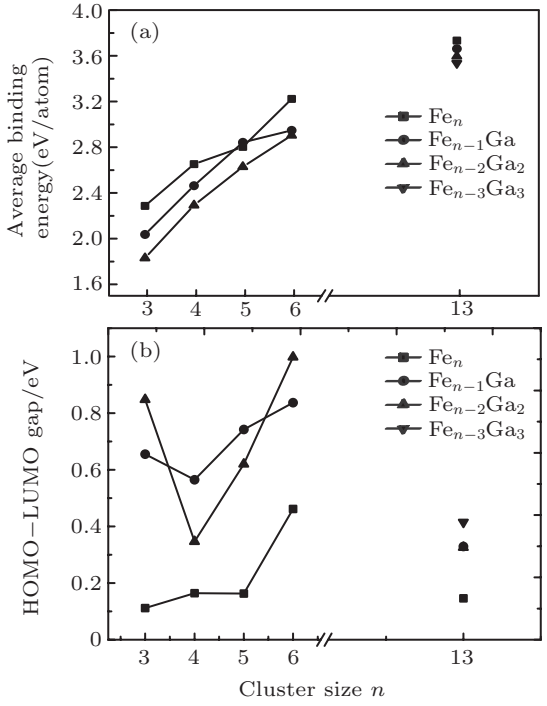



**Fig. 3.** (a) Average binding energies and (b) HOMO–LUMO gaps of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) and $Fe_{13-m}Ga_m$ ($m = 0 \sim 3$) clusters.

The HOMO–LUMO gap (HLG) is an important parameter for evaluating the electronic stability of a cluster. Namely, clusters with larger HLG tend to demand more energy for the electron excitation from an occupied orbital to an empty orbital. Apparently figure 3(b) shows that the Ga-doping could increase the HLG of Fe clusters by about 0.2 eV $\sim$ 0.7 eV and thus could enhance their electronic stabilities. For the 13-atom system, the order of HLGs is $Fe_{10}Ga_3$ > $Fe_{12}Ga \simeq Fe_{11}Ga_2 > Fe_{13}$. Nevertheless, there is no monotonous relation between the HLG and the Ga concentration in Fe–Ga alloy clusters, which is consistent with the fact that the HLG is sensitive to many factors such as the cluster size and morphology.

## 3.4. Magnetic properties

Alloy clusters containing transition metal atoms like Fe, as well as the assembled materials by these alloy clusters, are usually expected to exhibit novel magnetic properties due to the confinement size and reduced dimensionality. Furthermore, flexible magnetic properties may be achieved by controlling the morphology, composition, or ordering.[11,42,43] In order to fully understand the effects of Ga-doping, magnetic properties of the ground states presented in Figs. 1 and 2 are discussed and analysed detailedly in the following.

As shown in Fig. 4(a), total magnetic moments of pristine Fe clusters and Fe–Ga alloy clusters increase with the growing number of Fe atoms. For small clusters with no more than six atoms, there exists an approximately linear relation between the total magnetic moment and the amount of Fe atoms inside. For 13-atom clusters, the total magnetic moment will be decreased by 5 $\mu_B$ after every Ga-doping, then an exact linear behaviour is shown. These results may suggest that the magnetic moments of Fe–Ga alloy clusters are mainly contributed from Fe atoms. This is mainly because the Fe atom has a partially filled 3d shell but the Ga atom has a completely filled 3d shell deeply below the 4s and the 4p shells. The influence of Ga dopant atoms on the magnetic properties is further shown in Fig. 4(b), where the average magnetic moment of Fe atom (i.e., the total magnetic moment divided by the number of Fe atoms) is given as a function of the number of Ga atoms. For the clusters with the same total number of atoms, the magnetic moment per Fe atom tends to decrease with increasing Ga concentration, except $Fe_3Ga$. On the other hand, from both experiments[44,45] and first principles calculations,[46] the Ga doping was found to play a delicate role in Fe–Ga alloys with varied Ga concentrations and phases. For example, Aldred found that the magnetic moment per Fe atom in Fe–Ga alloys could be enhanced at low Ga concentration and then decreased when the Ga concentration was above about 14%.[44] Although the results for clusters are not fully identical to those of experiments and other theoretical calculations for bulk alloys, it is interesting to note that the Fe–Ga clusters studied in this work could especially provide some microscopic information in the doping zone, then it could be helpful to the understanding of the heterogeneity of Fe–Ga alloys.

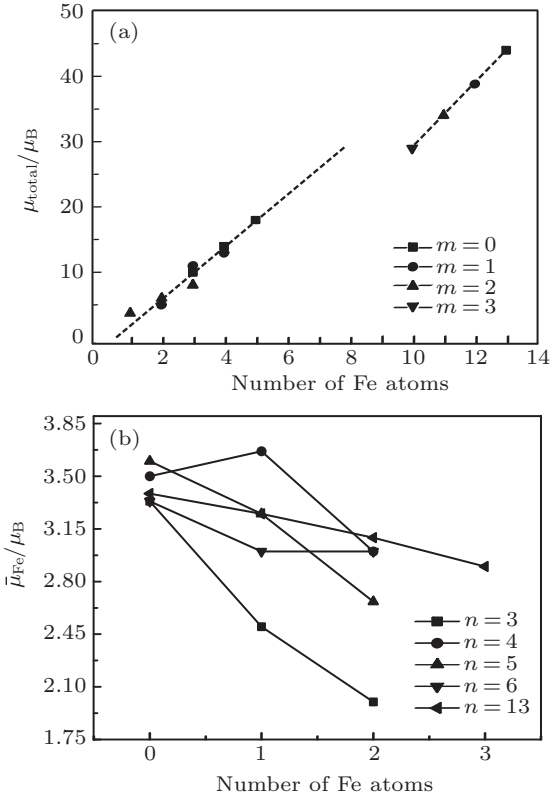



**Fig. 4.** (a) Total magnetic moments $\mu_{\rm total}$ of ground states of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$; $n = 13$, $m = 0 \sim 3$) clusters as a function of the number of Fe atoms. Note that the lines are plotted to show the linear dependence. (b) The average magnetic moment per Fe atom $\bar{\mu}_{\rm Fe}$ as a function of the number of Ga atoms.

Next, both Hirshfeld population analysis (HPA)[47] and Mulliken population analysis (MPA)[48] are performed on the charge density and the spin density for the ground states of Fe–Ga alloy clusters. Note that the HPA is believed to be prior to the MPA since the latter has been deemed as a method strongly sensitive to the basis set.[49] Usually, each Ga atom should lose a small amount of electrons (less than 0.05 e) to the Fe host atoms according to the HPA results. Moreover, the HPA demonstrates that the total magnetic moment is mostly contributed by Fe atoms, but local magnetic moments of Ga atoms could play a minor role sometimes. In addition, the MPA also yields the same conclusion that local magnetic moments of Fe atoms are contributed by the Fe-3d components. For Ga atoms, their local magnetic moments are mainly contributed from Ga-4p components and the Ga-3d is nearly unaffected in these clusters.

To clarify the magnetic coupling in Fe–Ga alloy clusters, the spatial distribution of local magnetic moments of small $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) and large $Fe_{13-m}Ga_m$ ($m = 0 \sim 3$) clusters are presented in Figs. 5(a) and 5(b) respectively. Clearly all Fe atoms in the clusters have parallel magnetic moments (i.e., the ferromagnetic coupling). The top Fe atom of the $Fe_4$ cluster has the largest local magnetic moment of 3.74 $\mu_{\rm B}$, while the central Fe atom of the $Fe_{10}Ga_3$ cluster has the smallest moment of 2.28 $\mu_{\rm B}$. On the other hand, in all Fe–Ga alloy clusters except $Fe_3Ga$, the noticeable local magnetic moments of Ga atoms (the absolute value is larger than 0.1 $\mu_{\rm B}$) are antiparallel to those of Fe atoms. For $Fe_2Ga$ and $FeGa_2$, the Ga atoms even have the local magnetic moment of nearly 0.5 $\mu_{\rm B}$. For 13-atom clusters shown in Fig. 5(b), the trend of local magnetic moments of Ga atoms with increasing doping concentration is also interesting. In the mono-doped $Fe_{12}Ga$, Ga has the magnetic moment of 0.08 $\mu_{\rm B}$ parallel to the magnetic moments of Fe; in $Fe_{11}Ga_2$, the local magnetic moments of Ga atoms are reduced to nearly zero; in $Fe_{10}Ga_3$, Ga atoms have the magnetic moments antiparallel to the magnetic moments of Fe and the absolute values are 0.08, 0.08, and 0.02 $\mu_{\rm B}$, respectively.

In all Fe–Ga alloy clusters except $Fe_3Ga$, there is also a common reduction effect of the Ga-doping on local magnetic moments of neighbouring Fe atoms, that is, Fe atoms around Ga dopants have smaller local magnetic moments than those at the corresponding sites in pristine Fe clusters. Especially, the local magnetic moments of Fe atoms in 13-atom systems decrease monotonically with increasing Ga concentration. For example, the local magnetic moment of the central Fe atom decreases from 2.69 $\mu_{\rm B}$ to 2.57 $\mu_{\rm B}$ after the first Ga-doping and then to 2.44 $\mu_{\rm B}$ and 2.28 $\mu_{\rm B}$ with the second and the third Ga-dopings. Moreover, for surface Fe atoms with two neighbouring Ga atoms, their local magnetic moments will decrease to around 3 $\mu_{\rm B}$. For $Fe_3Ga$, corresponding to its exceptional behaviour shown in Fig. 4(b), local magnetic moments of all atoms are coupled ferromagnetically and local magnetic moments of the two Fe atoms are enhanced. In a word, the Ga-doping can induce comprehensive changes of magnetic characteristics of Fe–Ga alloy clusters (especially those Fe atoms nearby the dopants), implying that magnetic properties of Fe–Ga alloys are sensitive to the concentration and distribution of Ga dopants.

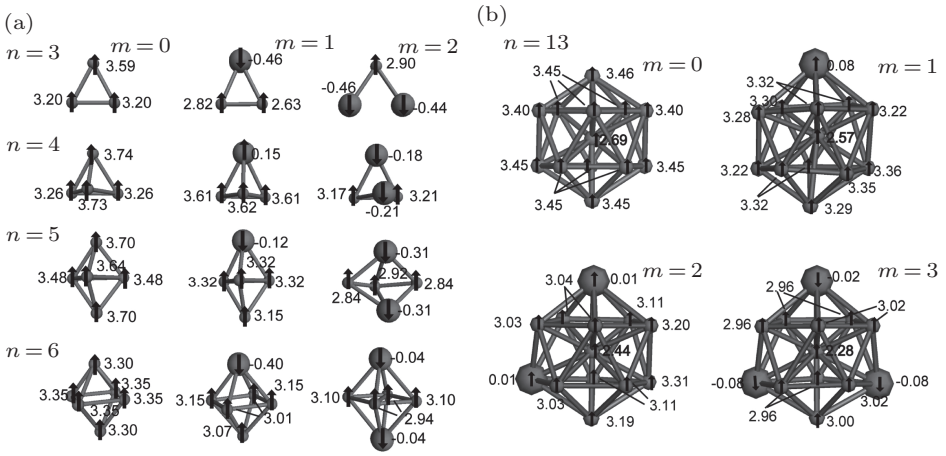



**Fig. 5.** Local magnetic moments of ground states of (a) $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$) and (b) $Fe_{13-m}Ga_m$ ($m = 0 \sim 3$) clusters. Note that the arrow and the value on the atom denote, respectively, the direction and absolute value of local magnetic moment of the atom.

# 4. Summary

In summary, we have systematically investigated geometrical structures, stabilities and magnetic properties of $Fe_{n-m}Ga_m$ ($n = 3 \sim 6$, $m = 0 \sim 2$ and $n = 13$, $m = 0 \sim 3$) clusters using the DFT method. For smaller clusters with no more than six atoms, the substitutional doping is favourable at low Ga concentration. For substitutionally doped $Fe_{13}$ clusters with up to three Ga atoms, the surface sites instead of the cluster center are favourable for Ga dopants. For the Fe–Ga clusters with two or three Ga atoms, the Ga–Ga interaction is revealed to be dependent on the cluster size. Overall, the Ga-doping will reduce the average binding energies of Fe clusters gradually but increase their HOMO–LUMO gaps. The magnetic moments of Fe–Ga alloy clusters are mainly contributed from the Fe-3d components and the Ga-4p could play a minor role sometimes. The local magnetic moments of all Fe atoms are ferromagnetically coupled. Importantly, the Ga-doping also has significant effects on the magnetic properties. For most clusters, the magnetic moment per Fe atom decreases with increasing Ga concentration. In detail, Ga atoms not only diminish the local magnetic moments of neighbouring Fe atoms in comparison with the pristine Fe clusters, but also contribute to some noticeable magnetic moments antiparallel to the magnetic moments of Fe atoms.

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