

Binary Nanoalloy Clusters: A Case Study for FeCr Clusters.

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A study of Fe_xCr_y binary nanoalloy clusters is carried out for sizes $n=x+y=13$ and 55 , the first two closed shell structures. While for $n=13$, various compositions like $x=12$ and $y=1$; $x=11$ and $y=2$; $x=10$ and $y=3$; $x=1$ and $y=12$ are studied, for the larger size ($n=55$) the morphology of a Fe-rich cluster ($\text{Fe}_{42}\text{Cr}_{13}$) and a Cr-rich cluster ($\text{Fe}_{13}\text{Cr}_{42}$) are analysed. The potential energy surface of the nanoalloys are scanned thoroughly using an evolutionary genetic algorithm in conjunction with a density functional theory based first principles method and the most stable clusters are picked up for every size and composition. A definite hierarchy in Cr-Cr, Fe-Cr and Fe-Fe bonding strengths is seen to determine the stability of the clusters. Cr-Cr bonding is promoted over Fe-Cr bonding which in turn is preferred over Fe-Fe bonding in the nanoalloy systems.

PACS numbers:

I. INTRODUCTION

In this work we intend to develop an *ab initio* based method to study the morphology of technologically viable nanoalloys. These nanoalloy clusters can form the building units to synthesize various functional materials with tailor-made characteristics.¹ It is noteworthy that the electronic, magnetic, structural, optical, chemical and thermodynamic properties of such alloy clusters change drastically with a slight change in size or composition.^{2,3} But in alloy clusters, due to the possibility of a large number of homotops for various geometric structures, the study becomes both interesting and challenging. The term homotops was coined by Julius Jellinek⁴. This refers to alloy clusters of kind A_xB_y , with the total number of atoms ($x+y$) same and the composition (x/y) also same. These nanoalloys also have the same structural geometry. The only difference between these homotops lies in the arrangement of the A and B species within the geometrical structure. However, this mere difference in arrangement of A and B species can lead to remarkably different magnetic and chemical properties in nano systems unlike bulk. This has been earlier seen by us for a study on Mn-Co nanoalloy clusters⁵. Through the current study we intend to devise a methodology to investigate various geometrical and magnetic isomers as well as homotops for nanoalloy clusters of various compositions and sizes to determine the stable magneto-geometric structure for the required size and composition.

The particular nanoalloy cluster we intend to study in the present work is Fe_xCr_y clusters, with total number of atoms, $x+y=13$ and 55 . The reason for choosing these sizes is, when the total number of atoms in a cluster is 13 , 55 , 147 and so on then they form closed-shell structure of exceptionally high stability and unique properties. Such clusters are thus also referred to as “magic clusters”.⁶ These so-called “magic clusters” have total number of atoms $n=(10s^3+15s^2+11s+3)/3=13,55,147,309,561$ and so on, where the symbol ‘s’ indicates the number of closed

shells that constitute the geometrical structure of the cluster.

The reason for choosing the constituent species of our nanoalloy to be Fe and Cr lies not only in the technological importance of Fe-Cr alloy but also in the magnetic nature of the atoms. Technologically speaking, Fe-Cr alloy based ferritic steel is in high demand in recent times as structural materials for fission and fusion reactors.^{7,8} Speaking about the magnetic nature of the constituent species, while Fe-Fe interaction is known to be ferromagnetic in bulk⁹, both Fe-Cr^{10,11} and Cr-Cr¹² interactions are well established to be antiferromagnetic. Thus it would be interesting to see the resultant magnetogeometric structure of FeCr nanoalloys as a result of these competing magnetic interactions. Another important factor that is going to determine the structure of the nanoalloy is the relative strength of the Fe-Fe, Fe-Cr and Cr-Cr bonds. The cluster for every size and composition is going to orient itself in an arrangement where the bond strength is maximized.

Before studying the Fe-Cr nanoalloy cluster, let us take a look into the pure Fe and pure Cr clusters. Fe_{13} clusters exhibit an icosahedral structure with a total magnetic moment of $44 \mu_B$. The system is ferromagnetic.¹ Fe_{55} clusters also exhibit icosahedral structure with a total magnetic moment of $105 \mu_B$. Antiferromagnetic alignment between the central atom and its first nearest neighbours is preferred¹. Fe_5 clusters exhibit noncollinear magnetic ordering in the bipyramidal structure.¹⁴

Generally, antiferromagnetic exchange interactions, as present between Cr ions, result in collinear antiferromagnetic configurations or non-collinear ordering in case the system has magnetogeometric frustration.¹⁵ However, Cr_3 has a collinear antiferromagnetic distorted triangular structure.¹⁴ Previous studies done on small Fe-Cr clusters show that the two lowest energy isomers of Fe_2Cr_4 exhibit distorted octahedral geometry but collinear spin ordering.¹⁶

II. METHODOLOGY

In order to scan the complex potential energy surface of binary nano-alloys we use the genetic evolutionary algorithm in combination with a density functional theory (DFT) based pseudopotential plane wave method for structural optimisation as implemented in Vienna Ab initio Simulation Package.^{17–19} We have chosen the projector augmented wave method,²⁰ and used the Perdew-Bruke-Ernzerhof exchange-correlation functional²¹ for the spin-polarized generalized gradient correction. The wave functions are again expanded in a plane wave basis set and reciprocal space integrations are carried out at the Γ point. Symmetry unrestricted optimizations (of both geometry and spin) are performed using the conjugate gradient and quasi-Newtonian methods until all the force components are less than a threshold value of 0.005 eV/Å. Simple cubic supercells are used with periodic boundary conditions, and it is made sure that two neighboring clusters are separated by at least 10 Å vacuum space. This ensures that the interaction of a cluster with its periodic image is negligible. The genetic algorithm that we use is the implementation in Universal Structure Predictor: Evolutionary Xtallography (USPEX).²² Though this method has proved to be hugely successful in predicting the crystal structure of bulk systems²³, applying it for predicting structures for crystals (which has no periodic symmetry) is a relatively new endeavour. The structures in the first generation were chosen to be icosahedral, cuboctahedral and anticuboctahedral guided by previous studies.¹ In the subsequent generations the structures were generated employing heredity operations, permutations and random production.

In order to get a quantitative understanding of the strengths of the Cr-Cr, Fe-Fe and Fe-Cr bonds, we have computed the crystal orbital Hamiltonian population (COHP) as implemented in the Vienna Ab initio Simulation Package (VASP)^{17,18} in conjunction with Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER)²⁵. The COHP and the integrated COHP (ICOHP) provides us information about the nature of a specific bond between a pairs of atoms and the integrated value of the strength of such interactions respectively. This gives a quantitative measure of bonding.

III. RESULTS AND DISCUSSIONS

A. Fe_xCr_y clusters: $x+y=13$

In this section we shall present results on Fe_xCr_y clusters with $x=12$ and $y=1$; $x=11$ and $y=2$; $x=10$ and $y=3$; $x=1$ and $y=12$. For a given size we have tuned the composition to investigate the effect of making the system Fe-rich and Cr-rich, as well as to study the evolution of structure with change in the number of Cr-Cr, Fe-Cr and Fe-Fe bonds in the system.

In Fig. 1, we see that the stable solution for $\text{Fe}_{12}\text{Cr}_1$ is

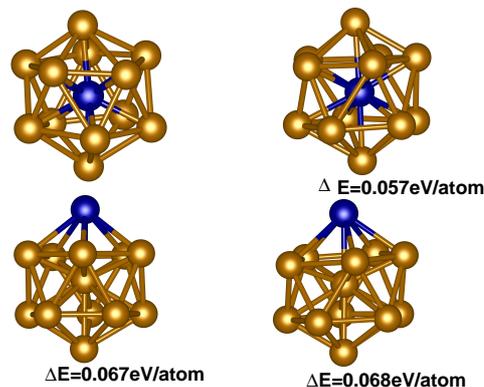


FIG. 1: The Cr atom is shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_{12}\text{Cr}_1$, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solution the Cr atom is antiferromagnetically coupled to all the Fe atoms.

one in which the Cr atom sits at the center of the icosahedral structure, thus maximizing the number of Fe-Cr bonds (reducing the number of Fe-Fe bonds). This indicates that Fe-Cr bonds might be preferred over Fe-Fe bonds in Fe-Cr nanoalloys. The reason for this will be investigated in details later in the present work. The isomers with Fe sitting at the center of the icosahedron are seen to be much higher in energy (0.067eV/atom) and thus are unstable. In order to investigate the extent of instability that maximizing Fe-Fe bonds at the cost of Fe-Cr bonds can have on a Fe-Cr nano system we have estimated the segregation energy as shown in Fig. 2. The calculation of the segregation energy is done in accordance with the prescription given in the paper by Wang and Johnson²⁴. It is seen that the energy cost to remove a Cr ion from the center to apical position of a icosahedron is 0.87eV. This again reconfirms that Fe-Cr bonds are stronger than Fe-Fe bonds.

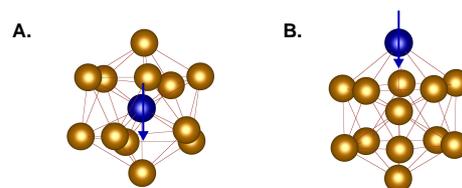


FIG. 2: A calculation of the energy cost to remove a Cr ion from the center of the icosahedron (position where Fe-Cr bonds are maximised) to apex position (without structural relaxation) in $\text{Fe}_{12}\text{Cr}_1$ stable structure: $\Delta E_{SEG} = E_B - E_A = 0.87\text{eV}$. This is a measure of how unstable a nanoalloy becomes when Fe-Fe bonds are maximised in the system by decreasing the number of Fe-Cr bonds.

We also tried to calculate the energy required to flip the spin of the Cr atom so that it is ferromagnetically coupled to the Fe atoms. But it is very difficult to stabilize the structure with Cr atom ferromagnetically coupled to Fe

atoms.

Next, we calculated the Crystal Orbital Hamiltonian Population (COHP) and Energy integrated value of COHP (ICOHP) for $\text{Fe}_{12}\text{Cr}_1$. This will give a numerical estimate of the strengths of the Fe-Fe and Fe-Cr bonds. In the Table I ICOHP $_{\uparrow}$ and ICOHP $_{\downarrow}$ depict the energy integrated value of COHP for the ‘up’ and ‘down’ spin channels respectively. Thus, ICOHP = ICOHP $_{\uparrow}$ + ICOHP $_{\downarrow}$. As is clear from the Table, the bond strength decreases with increase in bondlength. However, for a given distance between the atoms, the strength of the Fe-Cr bonds in general is greater than that of Fe-Fe bond. Thus the system prefers to maximize Fe-Cr bonds rather than forming Fe-Fe bonds.

Next we study $\text{Fe}_{11}\text{Cr}_2$ clusters. It is interesting to see what happens when Cr-Cr bonds also play a crucial role in determining the system structure. It is seen

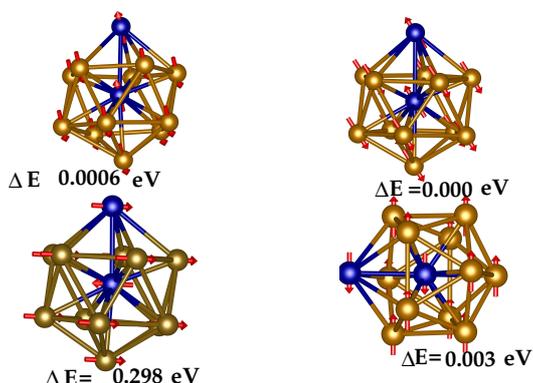


FIG. 3: The Cr atoms are shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_{11}\text{Cr}_2$ system, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solution, both the Cr atoms are antiferromagnetically coupled to all the Fe atoms (spin direction of atoms indicated by red arrows).

from Fig. 3 that the $\text{Fe}_{11}\text{Cr}_2$ system prefers to form Cr-Cr bonds. This fact is further emphasized from Fig. 4, where it is seen that for $\text{Fe}_{10}\text{Cr}_3$ clusters the three Cr atoms always prefer to be nearest neighbours of each other. For $\text{Fe}_{10}\text{Cr}_3$ clusters, the very interesting phenomena of magneto-geometric frustration is seen from Fig. 4, where the three Cr atoms form an isosceles triangle due to strong antiferromagnetic interaction between the Cr atoms. The observed trend in preference in bond formation continues for $\text{Fe}_1\text{Cr}_{12}$ clusters as seen from Fig. 5. Here also it is seen that the system prefers to maximize Cr-Cr bonds rather than Fe-Cr bonds in the stable state. Thus the Fe atom never occupies the center of the icosahedron for stable solutions. Thus we conclude that the hierarchy of the preference of interatomic bonding is as follows: the Cr-Cr bonds are preferred over the Fe-Cr bonds which in turn are favoured over the Fe-Fe bonds in Fe-Cr binary nano-alloys. The underlying reason for this

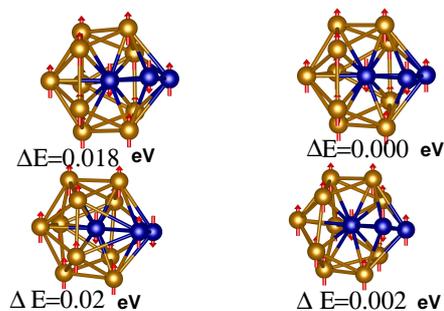


FIG. 4: The Cr atoms are shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_{10}\text{Cr}_3$ system, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solutions, the three Cr atoms form an isosceles triangle due to magnetic frustration (spin direction of atoms indicated by red arrows).

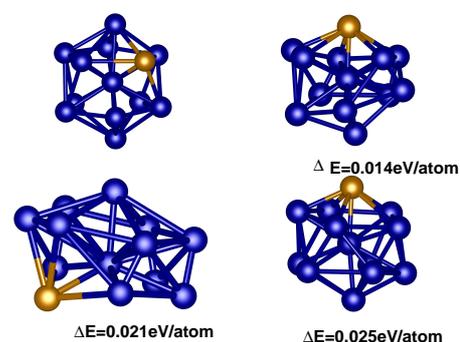


FIG. 5: The Cr atoms are shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_1\text{Cr}_{12}$ system, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solutions, the Cr-Cr bonds are maximized at the cost of Fe-Fe bonds.

hierarchy of preference lies in the relative bond strengths of Fe-Fe, Fe-Cr and Cr-Cr bonds, as discussed earlier.

B. $\text{Fe}_{42}\text{Cr}_{13}$ and $\text{Fe}_{13}\text{Cr}_{42}$ nanoalloys

Next, we study Fe_xCr_y clusters, with $x+y=55$, the next closed shell structure. For this system, we report two compositions, namely $\text{Fe}_{42}\text{Cr}_{13}$ and $\text{Fe}_{13}\text{Cr}_{42}$ nanoalloys.

It is seen, from Fig. 6, that the Cr atoms in $\text{Fe}_{42}\text{Cr}_{13}$ systems, tend to cluster together to form the core of the double shelled icosahedra. Thus, in the process the number of Cr-Cr bonds are maximized. This is expected from our earlier discussion on small Fe-Cr clusters, where it is seen that Cr-Cr bonds are the most preferred bonds in these nano alloys.

It is seen, from Fig. 7, that the Fe atoms in $\text{Fe}_{13}\text{Cr}_{42}$ systems, do not cluster together. Rather they get distributed in such a way that it seems the system promotes

TABLE I: A study of the Integrated Crystal Orbital Hamiltonian Population for the majority and minority spin-channels (depicted by ICOHP_↑ and ICOHP_↓) for the various Fe-Cr bonds and Fe-Fe bond in the Fe₁₂Cr₁ system.

Atom1	Atom2	Dist (in Å)	ICOHP _↑ (in eV)	ICOHP _↓ (in eV)	ICOHP (in eV)
Cr	Fe1	2.39	-0.515	-0.572	-1.087
Cr	Fe2	2.43	-0.487	-0.466	-0.953
Cr	Fe3	2.35	-0.545	-0.626	-1.171
Cr	Fe4	2.34	-0.566	-0.646	-1.212
Cr	Fe5	2.39	-0.522	-0.553	-1.075
Cr	Fe6	2.37	-0.532	-0.579	-1.111
Cr	Fe7	2.38	-0.517	-0.573	-1.09
Cr	Fe8	2.37	-0.533	-0.580	-1.113
Cr	Fe9	2.34	-0.567	-0.650	-1.217
Cr	Fe10	2.43	-0.490	-0.471	-0.961
Cr	Fe11	2.39	-0.515	-0.541	-1.056
Cr	Fe12	2.35	-0.542	-0.619	-1.161
Fe1	Fe2	2.37	-0.156	-0.836	-0.992

Fe-Cr bonds over Fe-Fe bonds. This is also expected from our earlier discussion on small Fe-Cr clusters, where it is seen that Fe-Cr bonds are promoted more than Fe-Fe bonds due to relative strengths of these bonds in the nano alloy systems.

IV. SUMMARY AND CONCLUSIONS

In this paper we have studied Fe-Cr clusters of sizes 13 and 55- the first two closed shell structures. We have used a combination of genetic evolutionary algorithm and first principle Density Functional Theory based method to scan the extensive potential energy surface for binary nanoalloy system and picked up the most stable structures for each size and composition. For small Fe-Cr clusters we have studied various compositions. For all the compositions it is seen that Cr-Cr bonds are promoted over Fe-Cr bonds which in turn are preferred over Fe-Fe bonds in this cluster. The reason for this hierarchy in

bonding preference is the relative strength of the Cr-Cr, Fe-Cr and Fe-Fe bonds as indicated by Integrated Crystal Orbital Hamiltonian Population calculations. This trend in hierarchy in bonding is seen to continue for larger Fe-Cr clusters, namely 55 sized clusters with compositions : Fe₄₂Cr₁₃ and Fe₁₃Cr₄₂ . While Cr atoms cluster together in Fe-rich nanoalloys to maximize Cr-Cr bonds at the cost of Fe-Cr bonds; Fe atoms never cluster in Cr-rich nanosystems in order to promote Fe-Cr bonds over Fe-Fe bonds. These interesting dynamics in bonding determine the morphology of technologically important binary nanoalloy systems.

Acknowledgments

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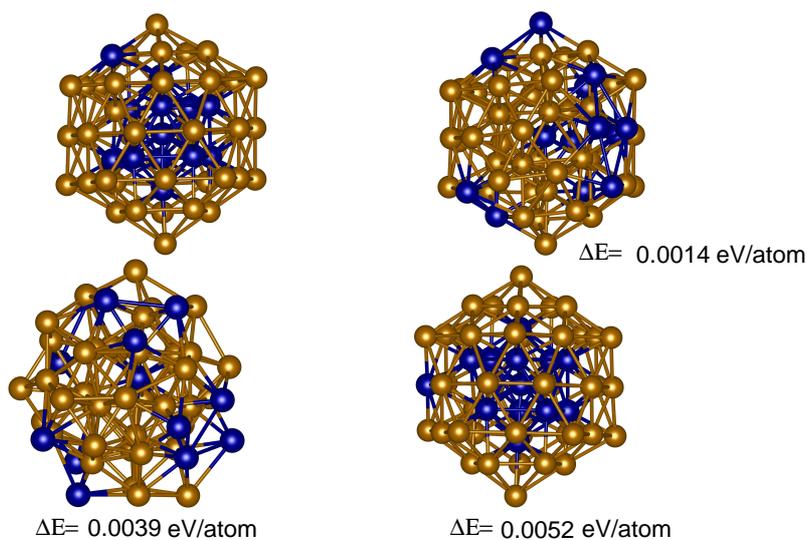


FIG. 6: The Cr atoms are shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_{42}\text{Cr}_{13}$ system, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solutions, the Cr atoms tend to cluster together to maximize the number of Cr-Cr bonds.

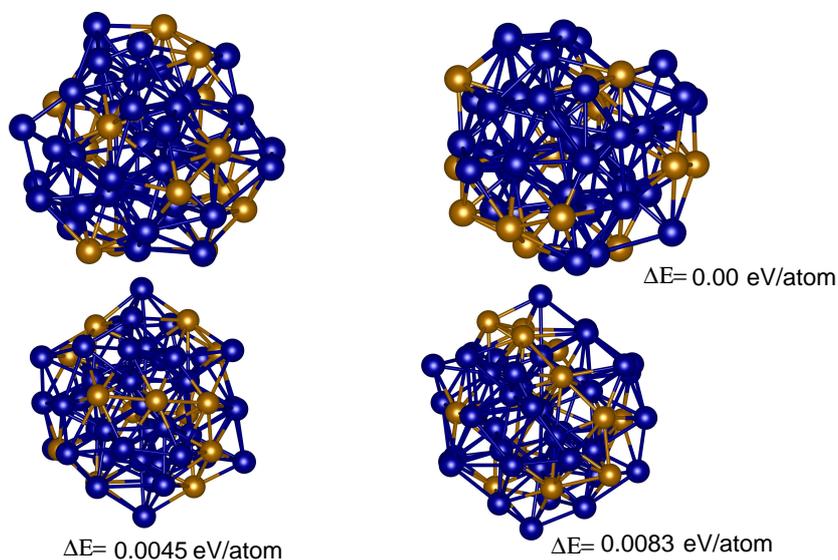


FIG. 7: The Cr atoms are shown in blue while the Fe atoms are shown in golden. Apart from the most stable solution for $\text{Fe}_{13}\text{Cr}_{42}$ system, the first three isomers are shown with their difference in energy from the ground state quoted (in eV/atom). Here, in the stable solutions, the Fe atoms never cluster together in order to reduce the number of Fe-Fe bonds.

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