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Ultra-small Cd@NiAg and Cr@NiAg nano-clusters with enhanced mixing

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ABSTRACT
Structural, mixing vs segregation, and electronic properties of Cd-doped and Cr-doped ultrasmall NiAg nanoclusters have been analyzed here using first principles density functional theory based electronic structure calculations. The optimized structures of the doped clusters assume a core-shell-like structural pattern, similar to that of the undoped NiAg clusters. Both the dopings induce an enhanced mixing trend keeping intact the core-shell structural pattern of the host NiAg nanoclusters. Between the two types of dopings, the Cr-doping appears more effective for providing enhanced mixing of the NiAg clusters. Enhanced orbital hybridization for the doped NiAg clusters plays an important role in increasing the mixing trend. In the present work, we use a new formulation of mixing energy for such ternary nanoclusters to assess the merit of the doped binary NiAg nanoclusters compared to a similar doping in the associated monometallic nanoclusters of same size. This analysis indicates that the Cd-doping indeed is efficient for enhancing the mixing of the NiAg nanoclusters, while the Cr-doping would be more favorable for the monometallic Ni-cluster compared to the binary NiAg nanocluster of similar size.

I. INTRODUCTION
Synthesizing functional ternary nanoalloys with controllable compositions and morphological shapes has been of immense research interest during the last decade for enhancing catalytic activity as well as selectivity in the field of fuel cells, and reducing the cost of catalysts, compared to the associated bimetallic as well as monometallic counterparts of similar size. For example, the ternary PtMM' catalysts (M, M' = Fe, Co, Ni, Ir) exhibit enhanced electrocatalytic activities and stability in comparison with pure Pt and the binary PtM or PtM' counterparts. Likewise, the ternary Pt@AgPd nanoparticles exhibit a superior catalytic activity toward Oxygen Reduction Reaction (ORR). An extraordinary electrocatalytic activity for ORR has also been reported for the Pt@AuCu trimetallic core-shell nanostructures, while the Au@CuPt trimetallic nanoparticle is a promising catalyst for both ORR and methanol oxidation reactions. A superior electrocatalytic activity for ethanol oxidation has been shown by a core-shell Cu@PdCo nanocatalyst. The primary objective of these works was to minimize the usage of precious noble metals such as Pt, Pd, and Au while retaining the high catalytic activity compared to the monometallic nanoclusters of the associated noble metal. On the other hand, the reported quantitative analysis of the mixing trend in the case of the ternary nanoalloys by the first principles Density Functional Theory (DFT) study, however, is not sufficient enough to acquire an appreciable understanding before starting synthesis at a laboratory. The reported results are mostly related to the analysis of their optimized structure. In the present work, we focus on transition metal doped ultrasmall binary NiAg nanoclusters and try to rationalize their mixing trend. The two dopant elements are partially filled 3d transition metal Cr-atoms in one case and filled 4d transition metal Cd-atoms in another case.

Regarding doping, the previous first principles studies focused mostly on “doping” in a monometallic system for engineering its properties. The doping in a binary system and quantification of the mixing trend for more insights using DFT calculations are obviously a step forward in this direction. The analysis of the present work is also useful for any ternary nanoparticle in general, where the element having the least content could be considered as a dopant in the binary system of other two elements having
relatively larger contents. Furthermore, the analysis of the present work could also be generalized to assess the mixing trend for quaternary nanoalloys compared to the associated ternary or binary nanoalloys.

Ag nanoparticles have received increasing research interest for their unique optical, electrical, thermal, and biological properties. Consequently, the Ag nanoparticles are useful for many potential applications such as electronic, antimicrobial, and biomedical products. Ag nanoparticles have also been used for environmental treatments such as air, water, and surface disinfection. The magnetic Ni nanoparticles are also very useful for their applications in spintronics devices and catalysis. The binary NiAg nanoclusters usually combine both the merits of the nanostructures of their two constituent species. Furthermore, the alloys of Ag and Ni have important applications such as sensors, catalysis, electrical contacts, and switches for their optical and magneto-optical properties. The AgNi nanoalloy has also been utilized as shape-memory alloys for medical applications.

A crucial issue with the binary NiAg system is that its two constituent species, Ni and Ag, are associated with a large atomic size mismatch (~14%). Therefore, the binary NiAg system has a large miscibility gap with a solid solution of Ni in Ag ~ 0.1 at. % even at 750 °C. Consequently, to release the internal strain arising from the size mismatch, all larger sized NiAg nanoclusters having compositions around the bulk miscibility gap region usually adopt a core-shell-like structural pattern with the more cohesive, smaller sized Ni atoms at the core and bigger sized Ag atoms at the surface due to their lower surface energy. Note that a bulk of experimental works also confirm a clear core-shell structural pattern for the NiAg nanoalloys energetically as well as kinetically. Due to the trend of immiscibility between the two species, Ni and Ag, it has been a great challenge to synthesize stable NiAg nanoalloys. In a recent work, a complete mixing between Ag and Ni atoms, however, has been predicted for smaller nanoparticles (dimension of ~7 nm). The driving factors for retaining a single phase microstructure around this smaller size are (1) a high surface curvature at smaller sizes that enhances solid solubility and (2) a decrease in the driving force for nucleation and growth of any second phase within such a smaller particle.

With the purpose of enhancing the mixing trend of the NiAg nanocluster, we substitutionally doped 13-atom sized binary Ni$_x$Ag$_{13-x}$ clusters with a Cd or a Cr atom in place of an Ag atom (doping concentration of ~7.7 at. %) for every possible composition between the two atomic species of the host cluster. Note that either dopant atom has a grossly similar electronic configuration with that of one constituent species of the host system, i.e., partially filled 3d elements (Cr and Ni) in cases of the Cd-doped NiAg clusters and filled 4d elements (Cd and Ag) in cases of the Cd-doped NiAg clusters. In the present work, using DFT based spin-polarized electronic structure calculations, we have performed a detailed analysis of structural, mixing, and electronic properties for the doped NiAg clusters of either class. We find that both classes of the doped NiAg clusters adopt a core-shell-like structural pattern as similar to the undoped Ni$_x$Ag$_{13-x}$ clusters. Interestingly, the Cd-doped clusters prefer to adopt an open disordered structural pattern more like the Ag-rich undoped NiAg clusters, while the Cr-doped clusters prefer a clear compact icosahedral structural pattern.

Both types of dopings are associated with an enhanced orbital hybridization among the constituting atoms, which provides an increasing mixing trend for the doped NiAg clusters compared to the undoped counterpart having equal Ni concentration. Our analysis of the mixing energy also indicates that both types of dopings would be preferred for enhanced mixing of the NiAg nanoclusters. However, our further analysis of the mixing energy shows that the Cd-doping in the binary NiAg cluster is indeed preferred, while the Cr-doping would be more preferred for the monoatomic Ni$_{13}$ cluster.

II. COMPUTATIONAL DETAILS

Spin-polarized first principles calculations reported in this study were performed using DFT within the framework of the pseudopotential plane wave method, as implemented in the Vienna Ab initio Simulation Package (VASP). 3d as well as 4s electrons for the transition metal Ni and Cr atoms and 4d as well as 5s electrons for the late transition metal Ag and Cd atoms were treated as the valence electrons. The interaction between the valence electrons and the ion core has been described by the projected augmented wave (PAW) pseudopotential while exchange correlation energy functional was considered under the framework of the generalized gradient approximation (GGA) as formulated by Perdew, Burke, and Ernzerhof (PBE). Energy cut-off for plane wave expansion was set to 400 eV. The convergence of the energies with respect to the cut-off value was checked. Furthermore, for the cluster calculations, a simple cubic supercell was used with the periodic boundary conditions, where two neighboring clusters were kept separated by around 12 Å vacuum space. The large cell-size essentially makes the interaction between cluster images negligible. Reciprocal space integrations were carried out at the Γ point.

The determination of equilibrium structure possessing the minimum energy is challenging due to the presence of many homotopes out of various possible distributions of the three species of atoms within a given morphology, which give many possible isomers within a small energy range. We have adopted the simulated annealing approach as implemented in the VASP code. We used thermodynamically motivated ab initio Born-Oppenheimer molecular dynamics (MD)-based simulated annealing to explore the potential energy surface. The MD calculations used in the present work are the same as used in our previous work for the undoped Ni$_x$Ag$_{13-x}$ clusters. The derived structures out of the MD calculations have further been reoptimized using the symmetry unrestricted zero temperature relaxation technique using conjugate gradient and quasi-Newtonian methods until the maximum force component and the energy difference between two consecutive self-consistent cycles were less than a threshold value of 0.001 eV/Å and 0.0001 eV, respectively. While spin-orbit interaction has been considered in the noncollinear calculations, all the possible spin multiplicities for each structure have been considered in the collinear calculations to attend the overall minimum energy structure (MES) with an optimal magnetic configuration.

III. RESULTS AND DISCUSSIONS

A. Optimized structures

Figure 1 shows our calculated optimized structures of the minimum energy for both types of doped clusters. It should be mentioned...
here that a cubic closed packed (CCP) structure had been reported as the MES for the Ni$_{13}$ cluster in our recent work.$^{11}$ Such a structural pattern has also been seen for the Ni-rich binary NiAg cluster of total 13 atoms. In the present work, we find that similar structural geometry having the CCP pattern continues to hold for the Ni-rich Cd-doped NiAg clusters. We note that coupled pentagonal rings formed by the constituting atoms start to appear first in the optimized structure of the CdNi$_{6}$Ag$_{6}$ cluster and it continues to persist for the optimized structures of all the subsequent Cd-doped Ag-rich NiAg clusters. It is seen from Fig. 1 that the dopant Cd-atom always prefers to position at the least coordinated site because of its weak trend toward bonding due to its filled valence atomic orbitals. It is also seen that the constituting Ag atoms occupy the less coordinated sites of the optimized structures, while the Ni atoms prefer to stay clubbed together and occupy the higher coordinated sites of the optimized structure. Our analysis of the radial distribution function$^{42}$ for the optimized structures of the Cd-doped NiAg clusters reveals that the Ni-atoms tend to stay closer to the center of the cluster, while the dopant Cd atom as well as the constituent Ag atoms like to stay away from the center of the cluster. So, similar to the undoped NiAg clusters, a trend toward adopting a core-shell-like structural pattern is indicated for the Cd-doped NiAg clusters.

For the Cr-doped NiAg clusters, each system adopts a compact icosahedral structure with the smaller sized Cr-atom at the center, and all the constituting Ni and Ag atoms of the host system prefer to stay at the surface of the icosahedron. Therefore, unlike the case of Cd-dopings, the role of the Cr-dopant is clearly visible as its inclusion in each NiAg cluster transforms instantly the lower dimensional structures of the host NiAg clusters to a symmetric icosahedral structure for all the Cr-doped NiAg clusters. Moreover, the energy difference between these two morphologies is quite appreciable. This structural transition is mainly guided by the smaller size and higher cohesive energy of the Cr atom as it fits well in the central site of the optimized structure. It also helps to neutralize any strain in the optimized structures arising from the size mismatch between the constituent Ni and Ag atoms of the host NiAg clusters. Note that such structural transition from a rather open structural pattern to a compact one was also found in the case of a monometallic Co$_{13}$ cluster by V-doping as well as Mn doping.$^{42-44}$ The optimized structures of the Cd-doped NiAg clusters are less symmetric open structures with the overall appearance of few pentagonal motifs, and each surface atom of the icosahedral structure of the Cr-doped clusters is a part of five pentagons due to its fivefold structural symmetry. Furthermore, the Ni-atoms on the surface of the optimized structure for each Cr-doped NiAg cluster remain colonized and are relatively closer to the central Cr-atom compared to the surface Ag atoms mainly due to the stronger bond of Ni atoms with the Cr dopant and the smaller atomic size of Ni than that of Ag.

Figure 1 also shows the variation of the total magnetic moment with the Ni-content for either type of doped NiAg cluster. In both cases, the magnetic moment is primarily contributed by the constituent Ni atoms. Therefore, the total magnetic moment for the clusters usually increases monotonically with the increase in the Ni content. In each doped cluster of either system, the Ni-atom centered magnetic moments are ferromagnetically coupled. In the case of Cr-dopings, an appreciable contribution to the total magnetic moment also comes from the dopant Cr atom. So, the Cr-doped clusters possess relatively a larger net magnetic moment compared to the Cd-doped cluster for a similar Ni-content. On the other hand, the Ag-atom centered magnetic moments are very tiny and they are usually antiferromagnetically coupled with that of the constituent Ni atoms. Regarding the variation of the total magnetic moment for the Cd-doped NiAg clusters, it is seen from Fig. 1 that the variation is associated with two kinks corresponding to the CdNi$_{12}$Ag$_{10}$ and CdNi$_{7}$Ag$_{5}$ clusters. Our analysis of the atom-centered magnetic moments for the MES of each doped cluster indicates that the two constituent Ni atoms of the CdNi$_{12}$Ag$_{10}$ cluster are antiferromagnetically aligned, which results in nearly zero net magnetic moment. For the Ni-rich Cd-doped NiAg clusters starting from the CdNi$_{5}$Ag$_{5}$ cluster, the magnitude of the Ni-atom centered magnetic moment reduces slightly compared to its Ag-rich counterparts due to enhanced orbital hybridization of the constituting atoms. It is reflected by the second kink corresponding to the CdNi$_{7}$Ag$_{5}$ cluster.

In order to quantify the segregation vs mixing trend in the optimized structures, we have calculated a chemical order
B. Stability, mixing, and electronic properties

The stability of the doped NiAg clusters has been assessed by computing a mixing energy which measures the energy gain for the ternary cluster with respect to the segregated parts of the monoatomic fraction of the constituting species. The binary NiAg cluster with the dopant is equivalent to a ternary cluster. Therefore, the mixing energy for each doped NiAg cluster has been calculated using the following equation:  

\[ E_{\text{mix}} = E(Ni_{13}Ag_{12-n}D) - \frac{n}{13}E(Ni_{13}) - \frac{12-n}{13}E(Ag_{13}) - \frac{1}{13}E(D_{13}), \]  

where \( E(Ni_{13}Ag_{12-n}D) \) is the total energy for the optimized structure of the doped \( Ni_{13}Ag_{12-n}D \) cluster and \( E(Ni_{13}) \), \( E(Ag_{13}) \), as well as \( E(D_{13}) \) are the total energies of the pure monoatomic \( Ni_{13} \), \( Ag_{13} \), and \( D_{13} \) clusters, respectively. Note that all the terms on both sides of the above equation (1) have reference to the same cluster size. A negative value for the calculated mixing energy would indicate that the doping is energetically favorable, and the most negative value corresponds to the cluster possessing the highest mixing.

Our calculated mixing energies for the doped NiAg clusters have been plotted in Fig. 2 for all compositions. Note that our estimated \( E_{\text{mix}} \) values are negative for all compositions, which implies that the highest mixing is expected for both types of doped clusters, relatively more positive for the Cd-doped \( Ni_{13}Ag_{12-n} \) clusters. The mixing energy for each doped NiAg cluster has been calculated in the left panels. The inset in the left panels shows the variation of \( \Delta E \) as an efficient collective variable to understand chemical reordering as an efficient collective variable to understand chemical reordering. The composition possessing the highest mixing is usually termed the magic composition, and it corresponds to the \( Ni_{13}Ag_{8}Cd_{2}Cr_{2} \) cluster, respectively, for the present work. It is interesting to see that the obtained magic composition corresponds to a slightly Ag-rich cluster in the case of the Cd-doping and to an extremely Ni-rich cluster in the case of the Cr-doping, which is also normally expected from their parabolic and inverted parabolic nature of the mixing curves.

To compare the stability of a doped cluster with respect to its neighboring compositions, we have also calculated the second difference in energy, \( \Delta^2 E \), defined for the \( Ni_{13}Ag_{12-n}D \) cluster (\( D = Cr, Cd \)) as \( \Delta^2 E(Ni_{13}Ag_{12-n}D) = \frac{1}{2}[E(Ni_{11}Ag_{14-n}D) + E(Ni_{13-n}Ag_{13}D) - 2E(Ni_{13}Ag_{12-n}D)] \). A peak in the variation of \( \Delta^2 E \) indicates higher relative stability of that cluster compared to its neighboring clusters. If the system corresponding to the peak is also associated with the minimum in \( E_{\text{mix}} \), then a high stability of that system is further supported. Figure 2 also shows the plot of our calculated \( \Delta^2 E \) for both types of doped \( Ni_{13}Ag_{12-n} \) clusters. It is seen that the peaks in the variation of \( \Delta^2 E \) are associated with two Cd-doped clusters, namely, \( CdNi_{4}Ag_{9} \) and \( CdNi_{12}Ag_{1} \), and with two Cr-doped clusters, namely, \( CrNi_{12}Ag_{1} \) and \( CrNi_{4}Ag_{9} \). Note that the \( CdNi_{4}Ag_{9} \) cluster has also been predicted as the magic composition from the above analysis of mixing energy.

As the heteroatomic coordination number has been predicted as an efficient collective variable to understand chemical reordering for phase-segregated nanoalloys, estimation of the total number of nearest neighbor (NN) stronger mixed bonds would be a crude first step to understand the mixing trend for the alloyed clusters.
For the present systems, it is to be noted that the Ni–Ag bonds are stronger than the Ni–Cd as well as Ag–Cd NN bonds in the case of the Cd-doped NiAg clusters. Similarly, the Ni–Cr NN mixed bonds are stronger than the Ni–Ag and Cr–Ag NN bonds for the Cr-doped NiAg clusters. Figure 2 also shows the variation of the stronger NN mixed bonds for both the doped NiAg clusters with the varying Ni-content. Interestingly, this variation is also associated with a peak corresponding to the Ni$_4$Ag$_6$Cd cluster for the Cd-doped clusters and a peak at the Ni$_{12}$Cr cluster in the case of the Cr-doped NiAg clusters. It implies that the peak in the variation for the number of the stronger NN mixed bonds also corresponds to the magic composition of the respective doped system.

In order to have an overall impression about the mixing trend for the two classes of the doped NiAg clusters with respect to the undoped NiAg clusters, we have compared the mixing energy of the three systems in Fig. 3 using the bar-diagram for every common Ni-content. This plot clearly indicates that both types of dopings enhance the mixing trend for some specific range of compositions or throughout the whole range of compositions. While the Cd-doping enhances the mixing trend for the Ag-rich NiAg clusters, the Cr-doping enhances the mixing trend for all compositions of the NiAg clusters. However, the enhanced mixing trend for the Cr-doped NiAg clusters is relatively much larger in the case of the Ni-rich NiAg clusters. Therefore, the plot of Fig. 3 indicates clearly that the Cr-doping in the binary NiAg clusters would be more preferable to Cd-doping. Therefore, the plot of Fig. 3 indicates clearly that the Cr-doping in the binary NiAg clusters would be more preferable to Cd-doping. Therefore, the plot of Fig. 3 indicates clearly that the Cr-doping in the binary NiAg clusters would be more preferable to Cd-doping.

Hybridization of the valence orbitals of the constituting atoms plays an important role in deciding the adopted structural pattern as well as stability. In order to gain an understanding of the role of hybridization, we have calculated a $kl$ hybridization index,

$$h_{kl} = \sum_{n=1}^{13} \sum_{m=1}^{occ} w^{(n)}_{k} w^{(m)}_{l},$$

where $k$ and $l$ are orbital indices—$s$, $p$, and $d$, and $w_{kl}^{(n)}$ is the projection of $i$th Kohn-Sham orbital onto the $j$th spherical harmonic centered at atom $i$, integrated over a sphere of specified radius. The spin index is implicit in the summation. We have calculated the total hybridization index, $h = hsp + hsd + hpd$, for the undoped and doped Ni$_x$Ag$_{12-x}$ clusters. Our estimated values for the undoped as well as doped NiAg clusters are plotted in Fig. 4. The electronic configuration of a constituting Ni atom is characterized by filled 3$d$ as well as 4$d$ orbitals and a less than half-filled 5$s$ orbital. Similarly, for the NiAg clusters, the $pd$ hybridization also increases slightly. On the other hand, a Cr atom is characterized by filled 3$p$, 4$s$ orbitals and a less than half-filled 3$d$ orbital. Therefore, both the $sd$ and $pd$ hybridizations are large in the case of the Cr-doped NiAg clusters. It results in a much larger total hybridization index compared to that of the undoped and Cd-doped NiAg clusters containing the same Ni content. This large hybridization index for the Cr-doped clusters with a significant contribution from the $pd$ hybridization also favors its compact icosahedral structure. For visual impression about the orbital hybridization, the charge density plot corresponding to the top five occupied orbitals including the highest occupied orbital (HOMO) for the magic composition of each system is also shown in Fig. 4. From the

![FIG. 3. Comparison of mixing energy for the three classes of cluster systems: undoped (middle violet bars), Cd-doped (left magenta bars), and Cr-doped (right green bars) Ni$_x$Ag$_{12-x}$ clusters corresponding to a fixed Ni-content.](image)

![FIG. 4. Plot of the total hybridization index for all compositions (left panel) and charge density (right panel) corresponding to the top five occupied levels including the HOMO for the magic composition of the three systems. The isovalue for the charge density plot is fixed at 0.03 E$^-$/Å$^3$.](image)
orbital plot, one can clearly see that it is more delocalized for the Cr-doped clusters, while it is the least delocalized for the pure NiAg clusters.

To assess the merit of the dopings in the binary clusters compared to the same doping in the related monometallic Ni$_{13}$ and Ag$_{13}$ clusters, we have further redefined the mixing energy of the doped Ni$_{13}$Ag$_{13-n}$ clusters with the help of the following formulation:

$$E_{m}^{DB} = E(Ni_{13}Ag_{12-n}D) - \frac{n}{12}E(Ni_{12}D) - \frac{12-n}{12}E(Ag_{12}D),$$

where $E(Ni_{12}D)$ and $E(Ag_{12}D)$ are the energies of the doped monometallic Ni$_{13}$ and Ag$_{13}$ clusters, respectively. Note that the value of $E_{m}^{DB}$ has been renormalized here to have a zero value corresponding to the doped monometallic Ni$_{13}$ and Ag$_{13}$ clusters. This new formulation of the mixing energy for the doped bimetallic clusters was used for the first time in our recent work.

It actually separates the spurious effect due to the binding energy of the dopant as well as the mixing of only Ni and Ag atoms in the presence of the dopant. Its negative value indicates enhanced mixing for the doped bimetallic Ni$_{13}$Ag$_{13-n}$ clusters, while its positive value implies that the doping in either the monometallic Ni$_{13}$ cluster or the monometallic Ag$_{13}$ cluster would have more mixing than that of the doped bimetallic Ni$_{13}$Ag$_{13-n}$ clusters.

Our estimated $E_{m}^{DB}$ values for both the Cd-doped and Cr-doped Ni$_{13}$Ag$_{13-n}$ clusters are plotted in Fig. 5. Interestingly, our calculated $E_{m}^{DB}$ have negative values for the Cd-doped NiAg clusters, in contrast to its positive values in the case of the Cr-doped NiAg cluster for all compositions except at the end points. Furthermore, in the case of the Cd-doped NiAg clusters, it is seen that the Ag-rich clusters have relatively larger negative values of $E_{m}^{DB}$ compared to that of their Ni-rich counterparts. Thus, the Cd-doping in the Ag-rich NiAg clusters is rather more favorable. Interestingly, the CdNi$_{13}$Ag$_{13}$ cluster has the least $E_{m}^{DB}$ value among all the Cd-doped clusters, similar to our previous prediction from the variation of $E_{mix}$. On the other hand, the positive values of $E_{m}^{DB}$ for the Cr-doped NiAg clusters indicate that the Cr-doping in either the monometallic Ni$_{13}$ cluster or the monometallic Ag$_{13}$ cluster would have a larger mixing trend than the Cr-doping in the binary Ni$_{13}$Ag$_{13-n}$ clusters. Furthermore, between the Cr-doped Ni$_{13}$ and Ag$_{13}$ clusters, the Ni$_{13}$Cr cluster, however, has a better mixing trend, as shown in Fig. 2. Thereby, the Cr-doping in the pure Ni$_{13}$ cluster would have the best mixing trend out of all the Cr-doped Ni$_{13}$Ag$_{13-n}$ and CrAg$_{12}$ clusters.

Now, we can compare our results of the mixing trend for the Cd/Cr doped Ni$_{13}$Ag$_{13-n}$ clusters with that of our previous findings for Cd/Cr doped Cu$_{13}$Ag$_{13-n}$ clusters. In the case of Cd/Cr doped Cu$_{13}$Ag$_{13-n}$ clusters, we had also seen a similar mixing trend as we see in the present work for the Cd/Cr doped Ni$_{13}$Ag$_{13-n}$ clusters, i.e., the Cd-doping in binary CuAg clusters would have a better mixing trend, while the Cr-doping would be more preferable for the pure Cu$_{13}$ cluster. However, it is to be noted that the $E_{m}^{DB}$ value for the Cd-doped Cu$_{13}$Ag$_{13-n}$ clusters is more negative compared to that of the Cd-doped Ni$_{13}$Ag$_{13-n}$ clusters for a similar content of transition metal element Cu or Ni. Likewise, the $E_{m}^{DB}$ values for the Cr-doped Cu$_{13}$Ag$_{13-n}$ clusters are less positive compared to the $E_{m}^{DB}$ values for the Cr-doped Ni$_{13}$Ag$_{13-n}$ cluster having equal Ni and Cu contents. Therefore, our analysis of $E_{m}^{DB}$ clarifies that the Cd doping in the binary Cu$_{13}$Ag$_{13-n}$ clusters will have a better mixing trend than that of the Cd-doping in the binary Ni$_{13}$Ag$_{13-n}$ clusters. Furthermore, the Cr-doping would prefer to dope in their monometallic counterparts compared to the doping in either the binary Cu$_{13}$Ag$_{13-n}$ cluster or Ni$_{13}$Ag$_{13-n}$ cluster. Between the Cr-doping in the binary NiAg and CuAg clusters, although both are energetically not advantageous, it would comparatively favor for the Cu$_{13}$Ag$_{13-n}$ clusters than for the Ni$_{13}$Ag$_{13-n}$ clusters having equal Cu and Ni contents.

IV. SUMMARY AND CONCLUSIONS

An enhanced mixing trend for the binary Ni$_{13}$Ag$_{13-n}$ clusters has been achieved for all compositions through Cd/Cr doping. The magic composition of the highest mixing for the two classes of the doped clusters is an Ag-rich cluster in the case of Cd-doping and an Ni-rich cluster in the case of Cr-doping. Both the dopings induce enhanced orbital hybridization, which results in an increased mixing trend. While the Cd-doping in the binary Ni$_{13}$Ag$_{13-n}$ clusters is indeed favorable in all respect, the Cr-doping would be energetically even more favorable to dope in the monometallic Ni$_{13}$ cluster in comparison with the binary Ni$_{13}$Ag$_{13-n}$ clusters. The analysis of the present work gives valuable insights into the mixing trend of the ternary nanoclusters, and it could also be generalized for quaternary nanoalloys.

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