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Structures, stabilities and magnetic moment of small copper-nickel clusters

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This paper obtains the lowest-energy geometric structures and the electronic and magnetic properties of small $CuNi_N$ clusters by using all-electron density functional theory. The calculated results reveal that the Cu atom prefers to occupy the apical site when $N \leq 9$ and for the clusters with $N = 10$, the Cu atom starts to encapsulate in the cage. The $CuNi_7$ and $CuNi_9$ are magic clusters. The magnetism correlates closely with the symmetry of the clusters. For these clusters, the charge tends to transfer from the nickel atoms to the copper atoms. It finds that the doping of Cu atom decreases the stability of pure Ni_N clusters.

Keywords: first-principles calculations, density functional for molecules, copper-nickel clusters
PACC: 3120A, 3640B, 2110K

1. Introduction

The knowledge of the composition and degree of order in an alloy near its spatial boundaries (surfaces or interfaces) is important in many physical, chemical, and metallurgical phenomena: magnetic properties,[1−3] catalytic activity, corrosive behaviour, etc. The detailed knowledge of the atomic structure of clusters, and the dependence of structure on size, are intriguing issues. Segregation at surfaces in alloys and compounds plays a significant role in many processes.[4−6] Yang *et al*[4] found that the spin and orbital magnetic moments of nickel atoms increase at the surface and decrease at the interface. Based on embedded-atom method in conjunction with Monte–Carlo computer simulation, Foiles[5] calculated Ni–Cu alloys and showed that the composition varies non-monotonically near the surface with the surface layer enriched in Cu while the near-surface layers enriched in Ni, and Brown *et al*[6] found that Ni segregates in Ni–Al film.

Among the 30 kinds of pure transition-metal clusters, nickel clusters have been intensively studied with attention focusing on their geometric structures and their important magnetic properties.[7−23] Reuse *et al*[20] systematically studied Ni_N (N = 2–6, 8, 13) clusters using an approach based on a linear combination of atomic orbitals and molecular orbitals within the density functional formalism. Menon *et al*[21] obtained the optimized geometries of Ni_N (N = 2–10) clusters using the tight-binding approximation in molecular dynamics. Grigoryan *et al*[22] systematically studied the energetics, structure, growth, and stability of Ni_N (N = 2–150) clusters by a combination of the embedded-atom method in the version of Daw, Baskes and Foiles, the variable metric/quasi-Newton method, and the Aufbau/Abbau method. Michaelian[23] studied the geometries and binding energies of nickel, silver and gold clusters with n-body Gupta potential. Some studies have also been carried out in bimetallic clusters. Montejano–Carrezale *et al*[24] studied the Cu–Ni, Cu–Pd clusters and found that Cu segregates to the surface in the Cu–Ni and Cu–Pd clusters. Vlasta[25] studied the silver-gold clusters on the density functional theory (DFT). Calleja *et al*[26] obtained the optimized geometries of nickel–aluminium clusters. Rexeret *et al*[27] also studied nickel–aluminium clusters. In our previous works,[28−33] we have studied the electronic structures of small Ni_N, Co_N, La_N, Fe_N (N = 2–13) and La_MNi_N (M, N = 2–6), Si_NNi (N = 1–14) clusters using first-principles calculations based on the DFT.

In this paper, we calculate geometric structures, electronic structures and magnetic moments for small

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copper-nickel clusters using all-electron DFT with the general gradient approximation (GGA) for exchange and correlation.

2. Theoretical method

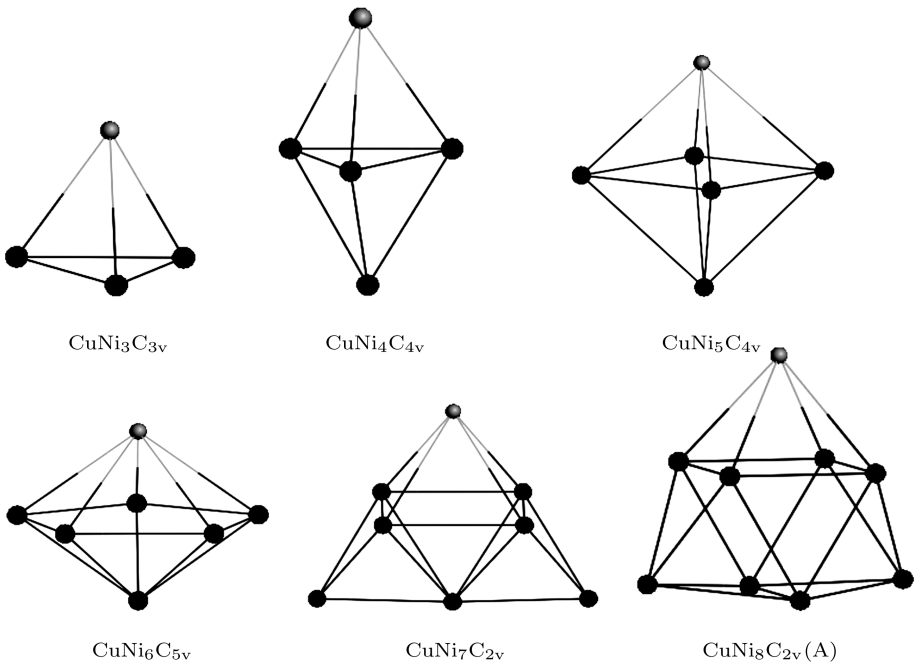
It is very important to choose suitable initial geometries in the study of stable structures using the energy minimum method. Fortunately for small clusters, the possible geometries are restricted. Initially the cluster geometries are constructed assuming a particular symmetry. We choose the initial geometries based mainly on previous studies of Ni_N clusters,[28] and included other seasonable geometries as appropriateness.

In the electronic structure calculations, the double numerical basis plus polarized functions[34] are chosen, for which, in general, the most accurate results can be obtained.[28−33] The accuracy of the present all-electron BLYP (the Becke exchange functional[35] and the Lee–Yang–Parr correlation functional[36]) computational scheme has been validated by benchmark calculations on the Ni_N (N = 2–13) clusters in a previous work.[28] The exchange-correlation interaction is treated within the GGA using the BLYP functional in this paper. For heavy elements, relativistic effects are important, so we perform all-electron spin-unrestricted calculations including relativistic effects.

In the optimizations, the convergence criteria are 1×10^{-4} Hartree/Bohr and 1×10^{-4} Å (1 Å = 0.1 nm) for the energy gradient and the atomic displacement, respectively. The charge density is found to converge to within 1×10^{-6} e/ Å^3, which corresponds to a total energy convergence of 1×10^{-5} eV.

3. Results and discussions

First of all, the ground-state structures of $CuNi_N$ (N = 2–12) clusters are obtained from our previous works.[28] Based on these results, a Cu atom is doped into the Ni_N clusters and geometric optimization is performed. Figure 1 shows the computational results of the lowest-energy structures and some other low-lying metastable isomers for copper–nickel clusters. For $CuNi_2$, the geometry obtained is an isosceles triangle with C_{2v} symmetry. The two Cu–Ni bonds are both 2.393 Å and the one Ni–Ni bond is 2.263 Å. This structure has a singlet HOMO (highest occupied molecular orbital) state. For $CuNi_3$, we have investigated the tetrahedron structure. After structural optimization, C_{3v} is found to be the most stable structure. The local spin moment of the nickel atoms is negative. For $CuNi_4$, the calculations have found that the ground state is a trigonal bipyramid. We have tried two structures C_{4v} and C_{3v}, and found that the lowest-energy structure for $CuNi_4$ is a C_{4v} geometry with the Cu atom at the vertex. This structure has a



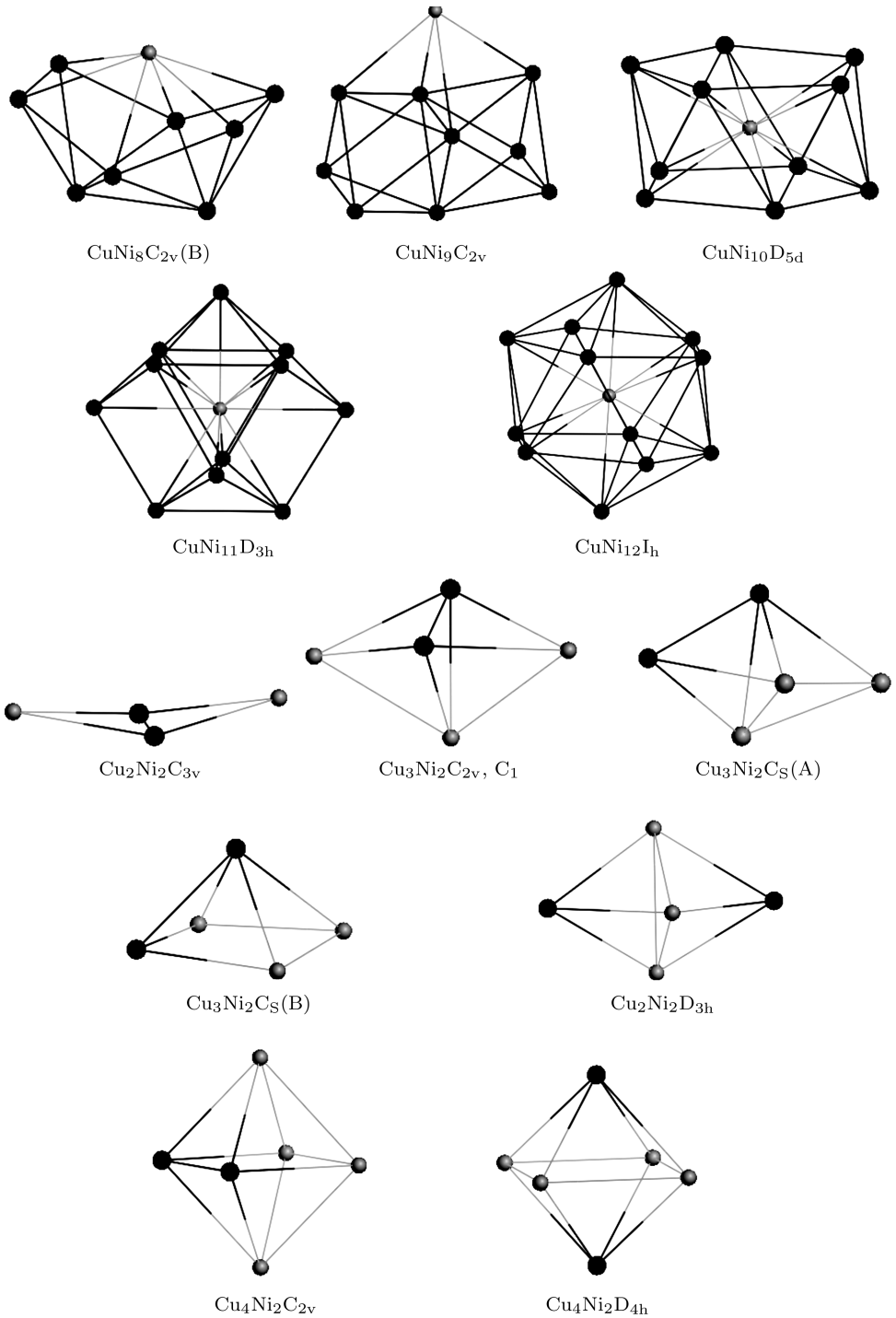


Fig.1. The structural sketches of $CuNi_N$ (N = 3–12) and Cu_NNi_2 (N = 2–4) clusters. Dark balls indicate Ni atoms and light ones Cu atoms.

singlet HOMO state. In the case of $CuNi_5$, two configurations (C_{5v} and C_{4v}) have been calculated. The configuration is a tetragonal bipyramid. The most stable structure is C_{4v} with a singlet HOMO state. The vertex site is preferable to the central site for the Cu atom for the lowest energy structure of $CuNi_5$ clusters. For $CuNi_6$, we have tried four structures (C_{5v}, C_{3v}, D_{3h} and C_S). The C_{5v} structure is the most stable, and the HOMO state is a singlet. Its configuration is a pentagonal bipyramid. For $CuNi_7$, the bi-capped octahedron has a singlet HOMO state which is consistent with the results obtained in Ref.[28] for pure Ni_8

cluster. For $CuNi_8$, we have tried two lowest-energy structures. The lowest energy structure obtained is a capped square prism with C_{2v}(A) symmetry as shown in Fig.1. The binding energy per atom of the C_{2v}(B) structure is 0.07 eV higher than that of the C_{2v}(A) structure, which may be regarded as an isomer for $CuNi_8$ cluster. For $CuNi_9$, the ground-state structure is obtained by adding a Cu atom into the apical site of the capped tetragonal bipyramid with C_{2v} symmetry. It has the lowest binding energy and a singlet HOMO state. Starting from $N > 9$, we find that the $CuNi_N$ clusters begin to adopt cagelike structures with Cu atoms encapsulated in the interior site. The ground-state structure of the $CuNi_{10}$ cluster is a D_{5d} symmetry. In the case of $CuNi_{11}$, the D_{3h} structure is the most stable and has the lowest energy. For $CuNi_{12}$, the I_h structure is a regular icosahedron with a central Cu atom. All these calculated lowest-energy structures for $CuNi_N$ ($N = 2$–12) clusters show that the Cu atom prefers to occupy the apical site when $N \leq 9$ and for the clusters with $N = 10$, the Cu atom completely falls into the interior site forming Cu-encapsulate Ni cage.

Table 1 lists the atomic charges in unit of e, where e is the charge of the electron, and the atomic magnetic moments of the Cu and Ni atoms. The results show that the charge tends to transfer from the Ni atoms to the Cu atoms in the mixed clusters. In the $CuNi_N$ ($N = 2$–12) cluster the local spin moment of the vertex nickel is different from those of the middle nickel atoms. The results again show that charge tends to transfer from the middle nickel atoms to the apical nickel atoms in these clusters except in the case of the apical nickel atom of the $CuNi_6$ cluster.

Table 1. The atomic charges (in unit of e) and the atomic magnetic moments of the Cu and Ni atoms in $CuNi_N$ clusters (* denotes the vertex nickel and the number in the column denotes the number of the vertex nickels).

Cluster	Ni (e)	Cu (e)	Ni/μ_B	Cu/μ_B
$CuNi_2$	0.040	–0.080	0.864	0.076
$CuNi_3$	0.036	–0.107	–0.855	–0.136
$CuNi_4$	0.122	–0.241	0.759	0.038
	*–0.125		0.989	
$CuNi_5$	0.027	–0.102	1.276	0.238
	*–0.008		*1.254	
$CuNi_6$	0.005	–0.072	1.020	0.098
	*0.045			
$CuNi_7$	0.052	–0.157	–1.025	0.009
	*–0.052(2)		*–0.835	
$CuNi_8$(A)	0.0377	–0.142	0.914	–0.070
	*–0.042(2)		*0.772	
$CuNi_8$(B)	0.013	–0.078	0.915	–0.039
	* 0.007(4)		* 0.847	
$CuNi_9$	0.051	–0.149	–0.792	0.081
	*–0.026(4)		*–0.760	
$CuNi_{10}$	0.010	–0.102	0.775	–0.111
$CuNi_{11}$	0.013	–0.146	0.674	–0.119
$CuNi_{12}$	0.016	–0.195	0.656	–0.117

Figure 2 illustrates the second derivative of the binding energy for $CuNi_N$ and Ni_N ($N = 2-12$) clusters, $\Delta_2 E = E_b(N+1) - 2E_b(N) + E_b(N-1)$, as a function of cluster size, here $E_b(N)$ is the obtained binding energy of the lowest-energy structures, which is defined as the difference in the total energy between the interacting atom system and all the free atom system. The binding energy per atom of $CuNi_N$ and pure

Ni_N (N = 2–12) clusters is also plotted in Fig.3 for comparison. It is clear that the binding energy monotonically descends with the increase of atom-numbers with the exception of the $CuNi_8$ and $CuNi_{10}$ clusters, at the same time the curve increases steadily. From the second derivative of the binding energy it can be seen clearly that $CuNi_7$ and $CuNi_9$ are magic clusters and should be abundant in the mass spectrum. It also can be seen that the corresponding binding energy per atom of $CuNi_N$ (N = 2–12) clusters is smaller than that of pure Ni_N (N = 2–13) clusters. Thus, the doping of Cu atom decreases the stability of pure Ni_N clusters.

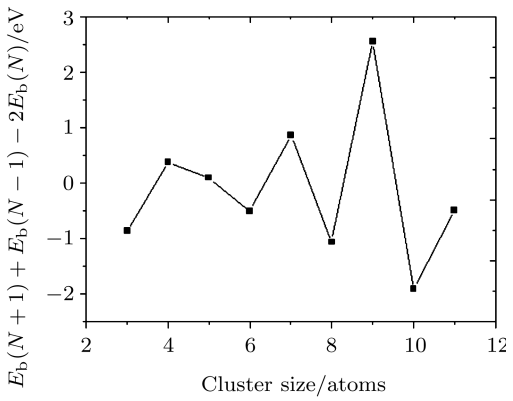


Fig.2. The second derivative of binding energy for $CuNi_N$ (N = 2–12) clusters as a function of the cluster size N.

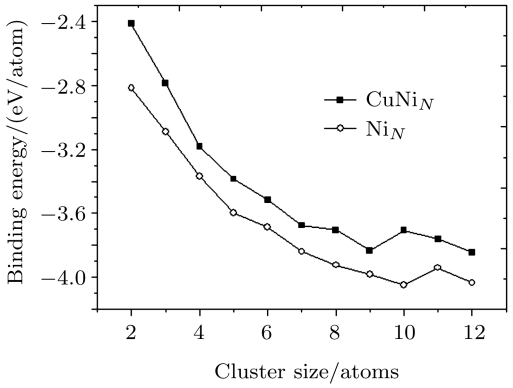


Fig.3. The binding energy per atom of $CuNi_N$ and pure Ni_N (N = 2–12) clusters as a function of the clusters N.

We have also calculated formation energy of $CuNi_N$ (N = 2–12) clusters which can be defined as $E_f(N) = E_b(N) - E_b(N+1)$. The understanding of the variations in the formation energy properties of clusters is important for catalysis and can provide a good way to show the relative local stability of small clusters.[31] Figure 4 shows the behaviour of the formation energy as a function of clusters size. Therefore,

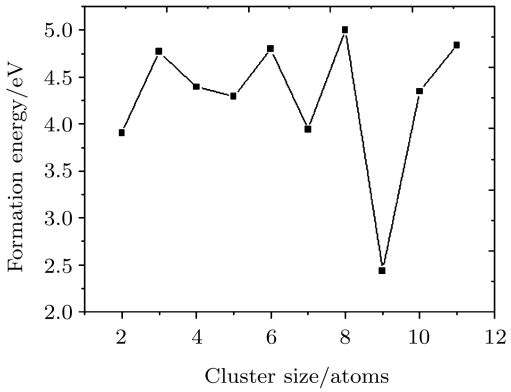


Fig.4. Formation energy of $CuNi_N$ ($N = 2-12$) clusters as a function of the cluster size.

if the addition of an atom to a nonmagic cluster makes it a magic one, the formation energy is large, such as N = 6 and 8 here. However, for magic clusters the formation energy is particularly small. We can see this in N = 7 and 9 clusters. This behaviour of clusters can play a very important role in tailoring catalysts for a particular reaction.

The magnetic moments per atom of the $CuNi_N$ (N = 2–12) clusters have been compared with those of Ni_N (N = 2–12) clusters in order to show the effects of adding a single atom of the other species. Figure 5 shows the results. For the spin moment of Ni_{13}, Xie *et al* obtained $0.615\mu_B$/atom. In the present study for $CuNi_N$ cluster, it is $0.60\mu_B$/atom. The mean spin moments of the $CuNi_N$ clusters decrease monotonically with size and which is similar with those for the pure Ni_N clusters. The results also indicate that the addition of a Cu atom reduces the magnetic moment per atom of the $CuNi_N$ (N = 2 –12) clusters in comparison with those for Ni_N (N = 2–13) clusters.

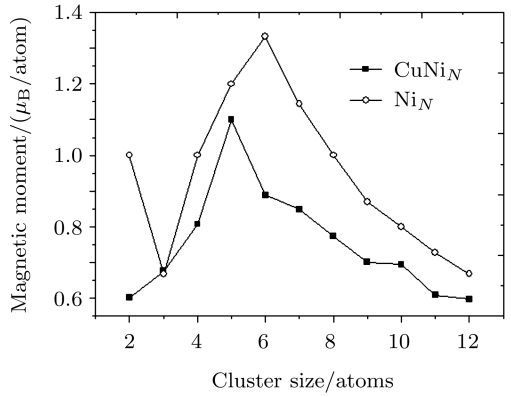


Fig.5. The spin moment for $CuNi_N$ and Ni_N (N = 2–12) clusters as a function of cluster size.

The Cu_NNi_2 (N = 2–4) clusters have also been calculated. Results of the structures are shown in Fig.1. The ground-state structure of Cu_2Ni_2 can be obtained as a butterfly structure with C_{2v} symmetry. The four Cu–Ni bonds are 2.426 Å and the one Ni–Ni bond is 2.235 Å. For Cu_3Ni_2, there exist five low-lying isomers with C_{2V}, C_1, C_S(A), C_S(B), and D_{3h} symmetries. The C_{2v}, C_1 isomers are considered as the lowest-energy configuration and have the same spin moments. From the viewpoint of binding energy, it is found that the isomers with the Cu atoms at the vertex (C_{2v} and C_1) are lower than that of the isomer with Cu atoms near the centre (D_{3h}). The binding energy of the C_S(A) is 0.015 eV higher than that of the C_1 structure, which may be regarded as a third isomer. The D_{3h} structure has the highest binding energy. Therefore, the vertex site is preferable to the central site for the Cu atom for the lowest energy structure of Cu_3Ni_2 clusters. In addition, the total spin in C_S(B) is larger than that of other symmetries. For Cu_4Ni_2, two structures (D_{4h} and C_{2v} structures) have been tried. The results show that the C_{2v} structure is more stable with the Cu atom at the vertex. In the Cu_NNi_2 (N = 2–4) clusters, the Cu atoms incline to occupy the apical sites. The magnetism correlates closely with the symmetry of the clusters. The calculated results are summarized in Table 2. As mentioned above, for the copper–nickel clusters, charge transfers from the Ni atoms to the Cu atoms.

Table 2. Calculated results for different structures of Cu_NNi_2 (N = 2–4) clusters. The table lists the symmetry, binding energy E_b (in eV), the energy gaps ΔE (in eV) between the LUMO and HOMO, the total spin moment μ_s (in μ_B).

	Sym	E_b/eV	ΔE	μ_s
Cu_2Ni_2	C_{2v}	–2.346	0.181	2.048
Cu_3Ni_2	C_{2v}	–2.23522	0.481	1.491
	C_1	–2.23182	0.443	1.461
	C_S(A)	–2.21679	0.427	1.684
	C_S(B)	–2.20956	0.171	2.56
	D_{3h}	–2.16878	0.366	1.073
Cu_4Ni_2	C_{2v}	–2.20212	0.212	3.184
	D_{4h}	–2.17486	0.156	3.33

4. Conclusions

The geometric structures, electronic structures and magnetism of small copper–nickel clusters have been calculated by using first-principles calculations based on all electrons DFT. The results indicate that in the lowest-energy configurations, the Cu atom prefers to occupy the apical site for smaller clusters with $N \leq 9$. Starting from $N = 10$, we find that the Cu atom completely falls into the interior site, forming Cu-encapsulated Ni cages. Furthermore, we have also discussed the size-dependent physical properties of the binding energy, atomic charge of the doped Cu atom, and the magnetic moment. The binding energy monotonically descends with the increase of atom-numbers and the second derivative of the binding energy indicates that $N = 7$ and 9 are magic clusters in $CuNi_N$ clusters. The calculation of formation energy further verifies this fact. It is found that the charge generally tends to transfer from the nickel atoms to the copper atoms in copper–nickel clusters except apical nickel atoms. The results indicate that the addition of a Cu atom reduces the magnetic moment per atom of the Ni in $CuNi_N$ (N = 2–12) clusters. It is also found that the doping of Cu atom decreases the stability of pure Ni_N clusters. In the copper–nickel clusters, the magnetism correlates closely with the symmetry of the clusters.

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