Sakarya University Journal of Science 24(3), 501-510, 2020

Alloying Effect on the Local Atomic Pressures of Nanoclusters

Songül TARAN[*1]

Abstract

In this study, simulations were performed to investigate local atomic pressures of icosahedral nanoclusters with 55 atoms. Before analyzing the local atomic pressures, the best chemical ordering structures were obtained using Monte Carlo Basin-Hopping algorithm within Gupta potential. Binary and ternary alloying effect on the local atomic pressures of mono, binary and ternary nanoclusters formed by Cu, Ag and Pt atoms was investigated in detail. It was obtained that adding one atom of second alloying metal in pure nanoclusters and also third alloying metal in binary nanoalloys can change the local atomic pressure due to locating tendency in the icosahedral structure. Also, it was observed that adding a smaller atom at the central site of the icosahedral structure exhibits decreasing of core stress.

Keywords: nanocluster, alloying, simulation, atomic pressure

1. INTRODUCTION

Nanoclusters occupy a very important place, since they are the building blocks of nanosicence [1]. Nanoclusters are aggregates of ~10 to 10^6 atoms or molecules within a size range of 1-100 nm [2]. Nanoclusters may consist of identical atoms, molecules and two or more different type of atoms [3]. Nanoclusters are well suited for several applications ranging from catalysis to optoelectronics, magnetism, optics and biomedicine [4]. Therefore, understanding of structural properties of nanoclusters is very important issue to fabricate and control nano materials.

Nanocluster structures can be classified due to geometric shape and chemical ordering [5]. Nanoclusters can present both crystalline and noncrystalline geometric structures with several chemical ordering [6]. Noncrystalline structures exist at nanosize with icosahedra and decahedra [7]. Since the addition of different type atom of alloying metal to nanoclusters can lead to structural variations, alloying of icosahedral nanoclusters organized in concentric atomic layers are gaining increasing attention especially

---

[*] Corresponding Author:songultaran@duzce.edu.tr
[1] Düzce University, Department of Physics, Düzce, Turkey, ORCID ID:0000-0001-8115-2169

for catalysis. Also, it is well known that catalytic activity is related to surface area, so icosahedral core-shell nanoalloys can be used effectively for catalytic applications due to their large surface-volume ratio.

In icosahedral nanoparticles, interatomic distances are non-optimal. With alloying of icosahedral nanoclusters, strain effects become more important due to size mismatch of the different type atoms [8]. It is still unclear how the alloying or introduction different type atom to nanocluster effects the preferential chemical ordering [9]. In this study, alloying effect on the local atomic pressures was investigated by substitution of only one different type atom of the second alloying metal in the pure monometallic clusters and also by substitution of one different type atom of the third alloying metal in the binary clusters. Local atomic pressure is quite important when analyzing the chemical ordering in binary and multimetallic nanoalloys where size mismatch occurs between the metal atoms. As it is well known that the element with larger atomic size prefers to locate on nanoalloy surface while small elements prefer to locate in core. Thus, with alloying of icosahedral nanoclusters, the stability of icosahedral structures can be explained through the strain induced by the size difference between the atoms.

Interest in nanoalloys formed with group 10 and group 11 transition metals arises as they can vary the structure and also catalytic activity. Thus, in this study 55-atom nanoclusters formed by Cu, Ag and Pt atoms were analyzed. The choice reason of this size is that 55 is a geometric magic number for icosahedral structures which have quasi-spherical shape and close-packed surface at small sizes. Also, icosahedral geometric structure with high symmetry is especially interesting for core-shell segregated behaviour of nanoalloys.

In literature, melting properties of Cu_{55} and Ag_{55} monometallic nanoclusters were studied in some studies [10], [11]. Moreover, structures of $Ag_{54}Cu_1$ [11], [12] and $Cu_{13}Ag_{42}$ [13] bimetallic nanoclusters were examined. Since there is not sufficient data about structural properties of mono, binary and ternary compositions formed by Cu, Ag and Pt atoms, alloying effect on the structural properties nanoclusters were detailed investigated by analyzing the local atomic pressures of the systems. The best chemical ordering structures were obtained using Monte Carlo Basin-Hopping algorithm within Gupta potential.

2. SIMULATION METHODS

The interatomic interactions of the nanoclusters were modeled by using Gupta many body potential energy function [14], [15]. Gupta potential has been widely used in several studies [16]–[23]. Gupta potential energy of nanoclusters is obtained by summing over all N atoms of the repulsive pair term (V_i^r) and the attractive many body (V_i^m):

$$V = \sum_i^N (V_i^r - V_i^m) \quad (1)$$

$$V_i^r = \sum_{j\neq i}^N A(a,b) exp\left[-p(a,b)\left(\frac{r_{ij}-r_0(a,b)}{r_0(a,b)}\right)\right] \quad (2)$$

$$V_i^m = \left(\sum_{j\neq i}^N \xi^2(a,b) exp\left[-2q(a,b)\left(\frac{r_{ij}-r_0(a,b)}{r_0(a,b)}\right)\right]\right)^{\frac{1}{2}} \quad (3)$$

The Gupta potential parameters used in this study were taken from the studies [24], [25] and were given in Table 1. Also, chemical ordering searches were performed by using Monte Carlo-Basin-Hopping algorithm [26]. Local relaxations were carried out for the chemical ordering optimization. For each nanocluster, searches of 2.0×10^6 Monte Carlo steps were made and the atomic labels were permuted randomly in the Basin-Hopping steps.

Table 1. The Gupta potential parameters for nanoclusters

	A (eV)	**ξ (eV)**	**p**	**q**	**r_0 (Å)**
Cu-Cu	0.0855	1.224	10.96	2.278	2.556
Ag-Ag	0.1031	1.1895	10.85	3.18	2.89
Pt-Pt	0.2975	2.695	10.612	4.004	2.7747
Cu-Ag	0.098	1.2274	10.700	2.805	2.7224
Cu-Pt	0.16	1.82	10.786	3.141	2.666
Ag-Pt	0.175	1.79	10.73	3.59	2.833

3. RESULTS AND DISCUSSION

In this study, local atomic pressures of 55-atom monometallic Cu, Ag and Pt nanoclusters were investigated. Besides, binary and ternary alloying effect on the local atomic pressures was investigated.

The local pressure P_i acting on atom i is proportional to the trace of the tensor given as follows [6], [8], [27]:

$$P_i = -\frac{1}{3}Tr(\boldsymbol{\sigma_i}) \quad (4)$$

where $\boldsymbol{\sigma_i}$ is atomic stres tensor. P_i can assume positive and negative values. $P_i > 0$ indicates compressive stress on atom i and $P_i < 0$ indicates tensile stress on atom i. If $P_i = 0$, it indicates the absence of stres [8].

Fig.1 shows the local atomic pressure for 55-atom icosahedral Cu-Ag-Pt nanoclusters. In the figure, the best chemical ordering structure, side view, cross-section view and pressure scale are given for each nanocluster.

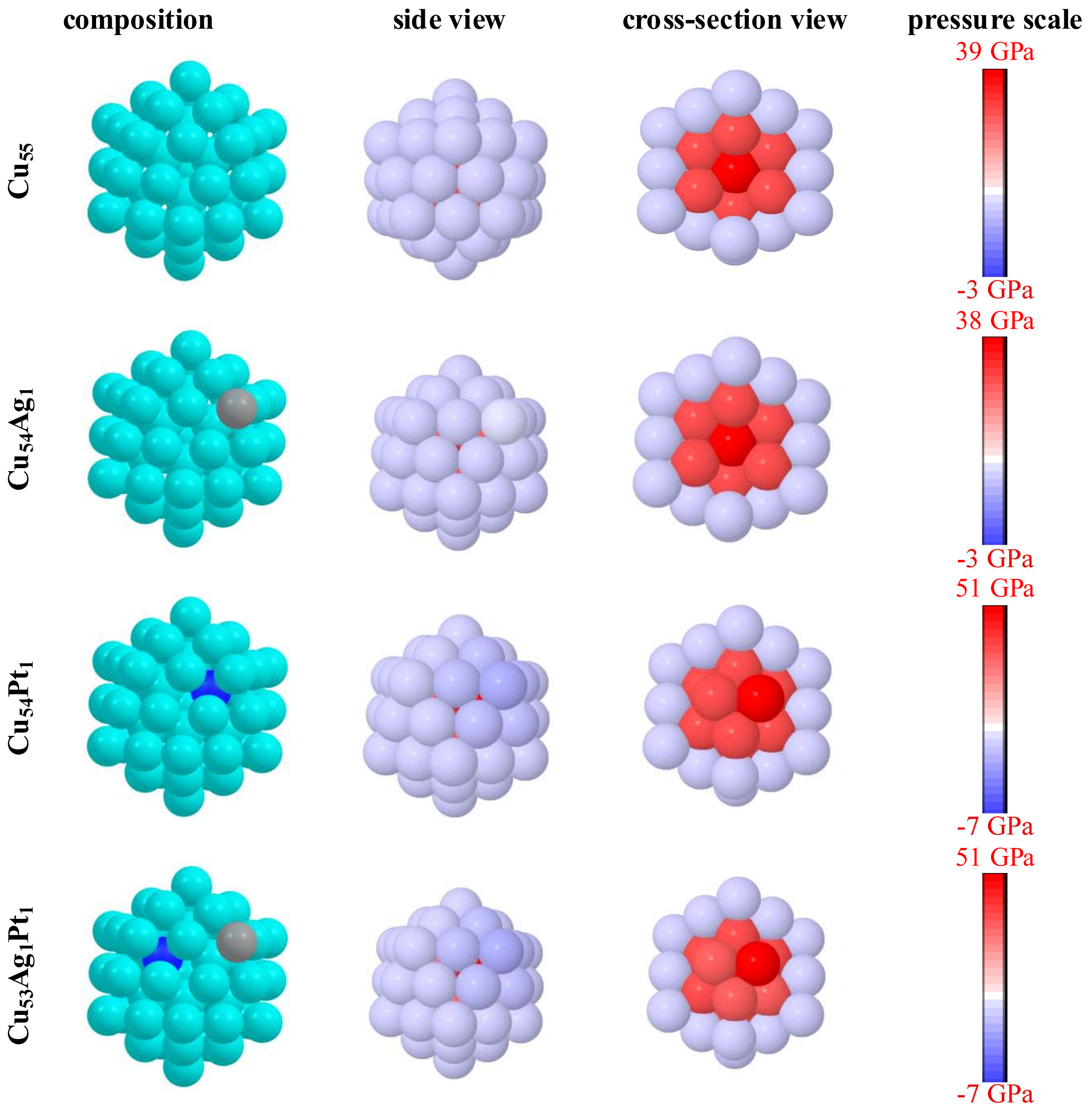

Figure 1. Local atomic pressure for icosahedral Cu-based nanoclusters

The central site is heavily compressed in pure Cu icosahedral nanocluster, so the pressure is strongly positive. The subshell atoms of the icosahedral structure have also positive pressure values lower than the central site. The shell atoms of the structure present negative local pressure values.

With the addition of one Ag atom, Ag atom prefers to locate on surface in $Cu_{54}Ag_1$ binary nanoalloy due to lower surface and cohesive energy of Ag atom. The vertex Ag atom presents negative pressure and the pressure color of Ag atom is a bit lighter than surface Cu atoms. However, with the addition of one Pt atom in pure Cu cluster, single Pt atom prefers to locate at subshell of the $Cu_{54}Pt_1$ binary nanoalloy structure due to higher surface and cohesive energy. With the locating in subshell, the pressure of the central Cu atom shows a bit decrease. Besides, the shell Cu atoms exhibit higher negative pressure values. Single Pt atom also has strongly positive pressure.

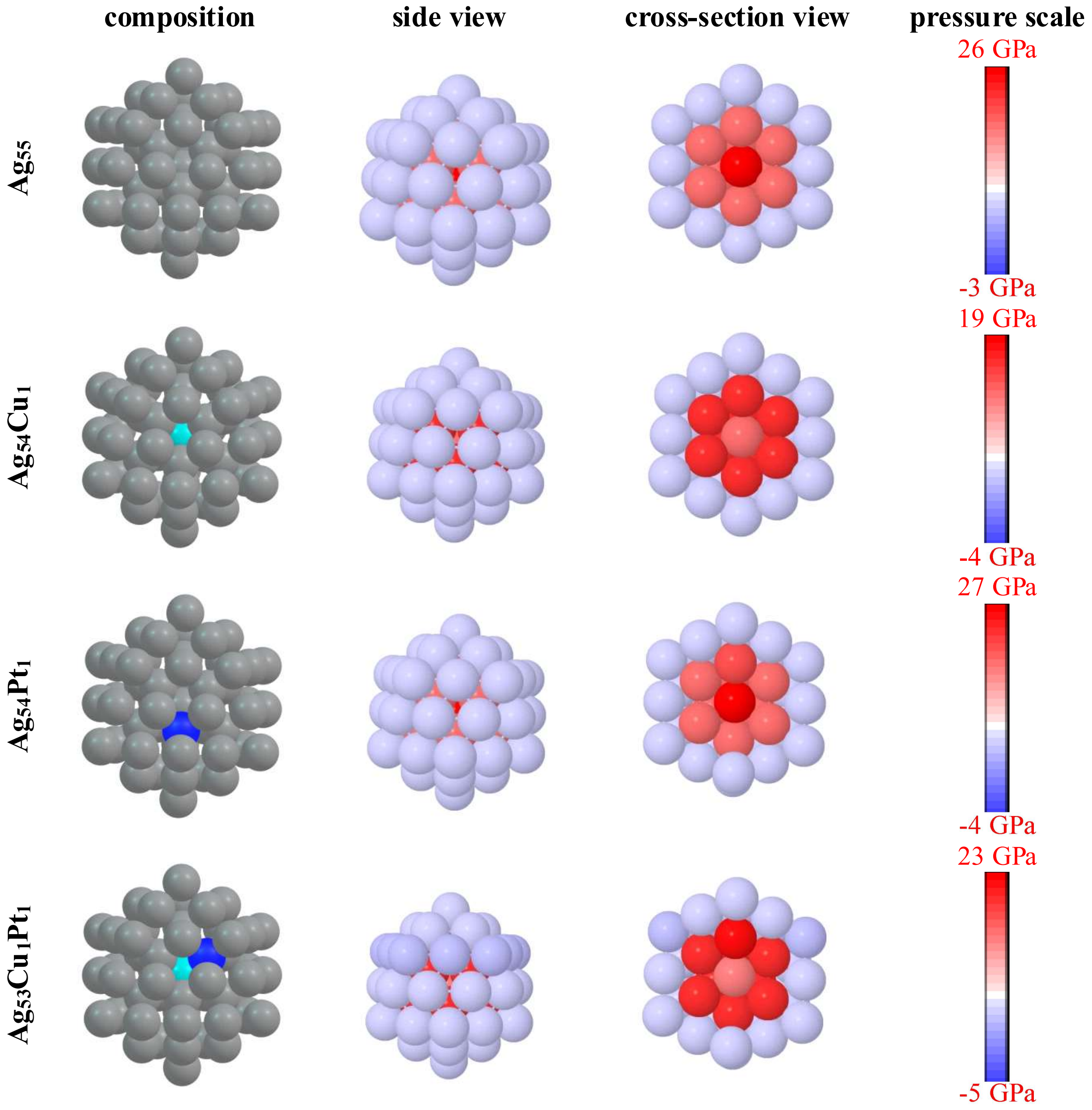

Figure.2. Local atomic pressure for icosahedral Ag-based nanoclusters

For $Cu_{53}Ag_1Pt_1$ ternary nanoalloy, single Ag and Pt atoms prefer to locate on shell and subshell of the icosahedral structure, respectively. The pressure scale shows similarity with $Cu_{54}Pt_1$, although it was observed that some increase and decrease of the pressure values of shell and subshell Cu atoms.

Fig.2 shows the local atomic pressure for 55-atom icosahedral pure Ag nanocluster and binary and ternary nanoalloys formed by doping one atom. For pure Ag nanocluster, local pressure values of core and shell atoms are positive and negative, respectively. With the addition of Cu atom, Cu atom preferentially placed at the central site in $Ag_{54}Cu_1$ nanoalloy. Pressure value of central site decreases and also, the largest positive pressure value of the structure considerably decreases. Besides, subshell Ag atoms have higher positive value, as can be seen in cross-section view of $Ag_{54}Cu_1$ and shell Ag atoms present a bit lower negative pressure. However, with the doping of one Pt atom, single Pt atom prefers to locate on subshell of $Ag_{54}Pt_1$ and central Ag atom has more positive pressure value than single Pt atom.

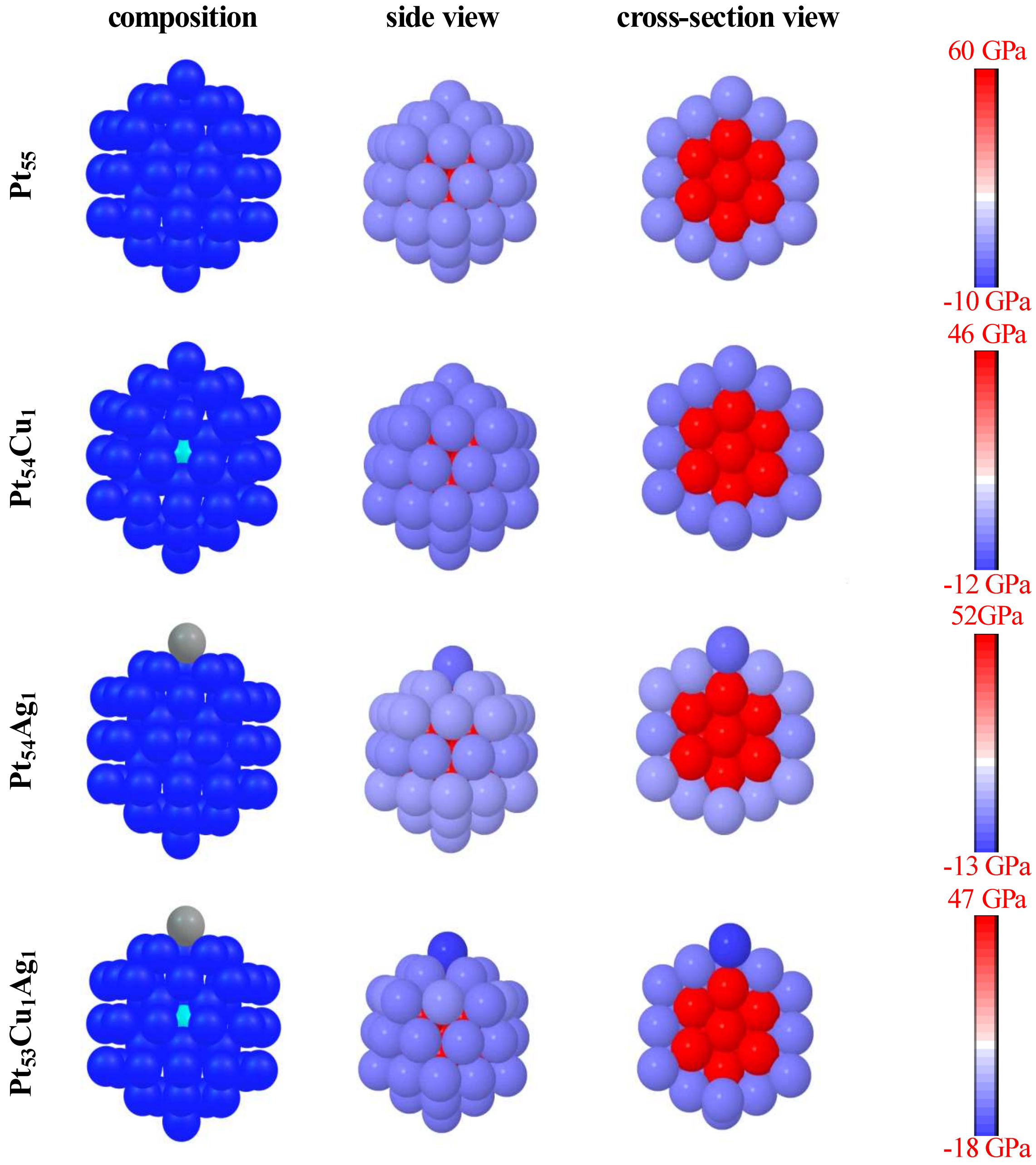

Figure.3. Local atomic pressure for icosahedral Pt-based nanoclusters

For $Ag_{53}Cu_1Pt_1$ ternary nanoalloy, central site presents again lower positive pressure value due to central Cu atom and shell Ag atoms present more negative pressure values.

Fig.3 shows the local atomic pressure for 55-atom icosahedral Pt-based nanoclusters. Pure Pt nanocluster has a central site atom which is heavily compressed. The pressure value of central site is strongly positive. With the substitution of one Cu atom, single Cu atom locates on central site and for $Pt_{54}Cu_1$ binary nanoalloy the most positive pressure value of core atoms decreases and the most negative pressure value of shell atoms increases. In the case of adding one Ag atom to pure cluster, single Ag atom prefers to locate on surface of the structure and it can be seen from the figure that vertex single Ag atom presents more negative pressure value. For $Pt_{53}Cu_1Ag_1$ ternary nanoalloy, single Cu atom is central atom and single Ag atom is vertex atom of surface. When compared to pure and binary nanoclusters, ternary nanoalloy presents much higher negative pressure value.

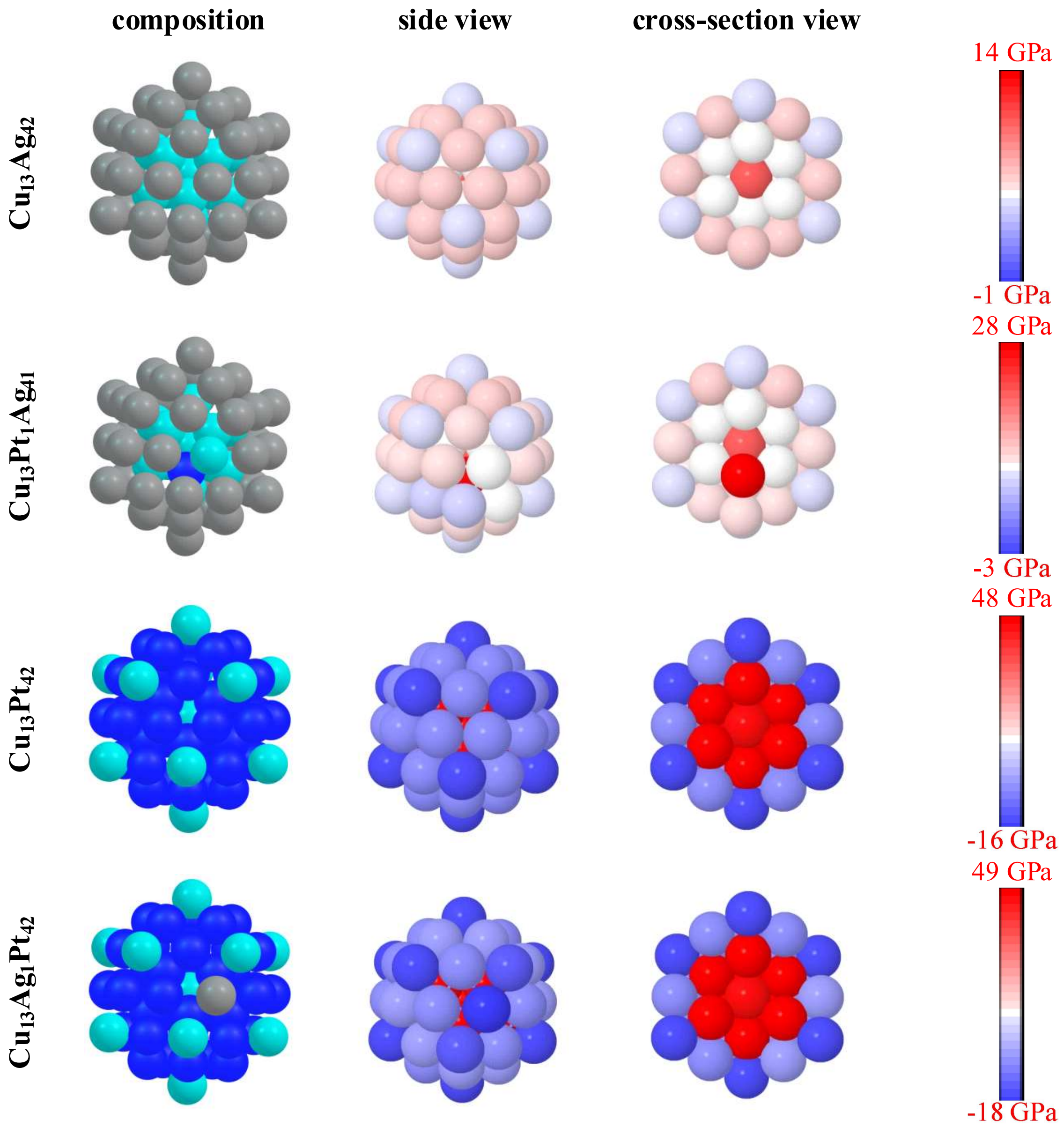

Figure 4. Local atomic pressure for $Cu_{13}Ag_{42}$, $Cu_{13}Pt_1Ag_{41}$, $Cu_{13}Pt_{42}$ and $Cu_{13}Ag_1Pt_{42}$ nanoalloys

Fig.4 shows the local atomic pressure for some chosen binary nanoalloys and ternary nanoalloys formed by doping one atom to chosen binary nanoalloys. $Cu_{13}Ag_{42}$ binary core-shell nanoalloy has 13 Cu core atoms and 42 Ag surface atoms. The local pressure of central Cu atom is positive, however other 12 Cu subshell atoms exhibit negative pressure which are closer to zero. While pressure values of 12 Ag vertex atoms are negative, other 30 Ag shell atoms present positive pressure values. In order to analyze the ternary alloying effect on local pressure values, one Pt atom was introduced to $Cu_{13}Ag_{42}$ binary nanoalloy and it was obtained that central Cu atom becomes more compressive by locating of Pt atom on subshell and reposition of one Cu atom on shell. As for $Cu_{13}Ag_{42}$ all subshell atoms are negative, single Pt atom and one Cu atom in subshell present positive pressure values for $Cu_{13}Pt_1Ag_{41}$ ternary nanoalloy. Also, Pt atom presents the more positive value. In shell of ternary nanoalloy, two Ag atoms exhibit pressure values which are close to 0 shown by white color. The negative pressure values of the shell atoms become more negative.

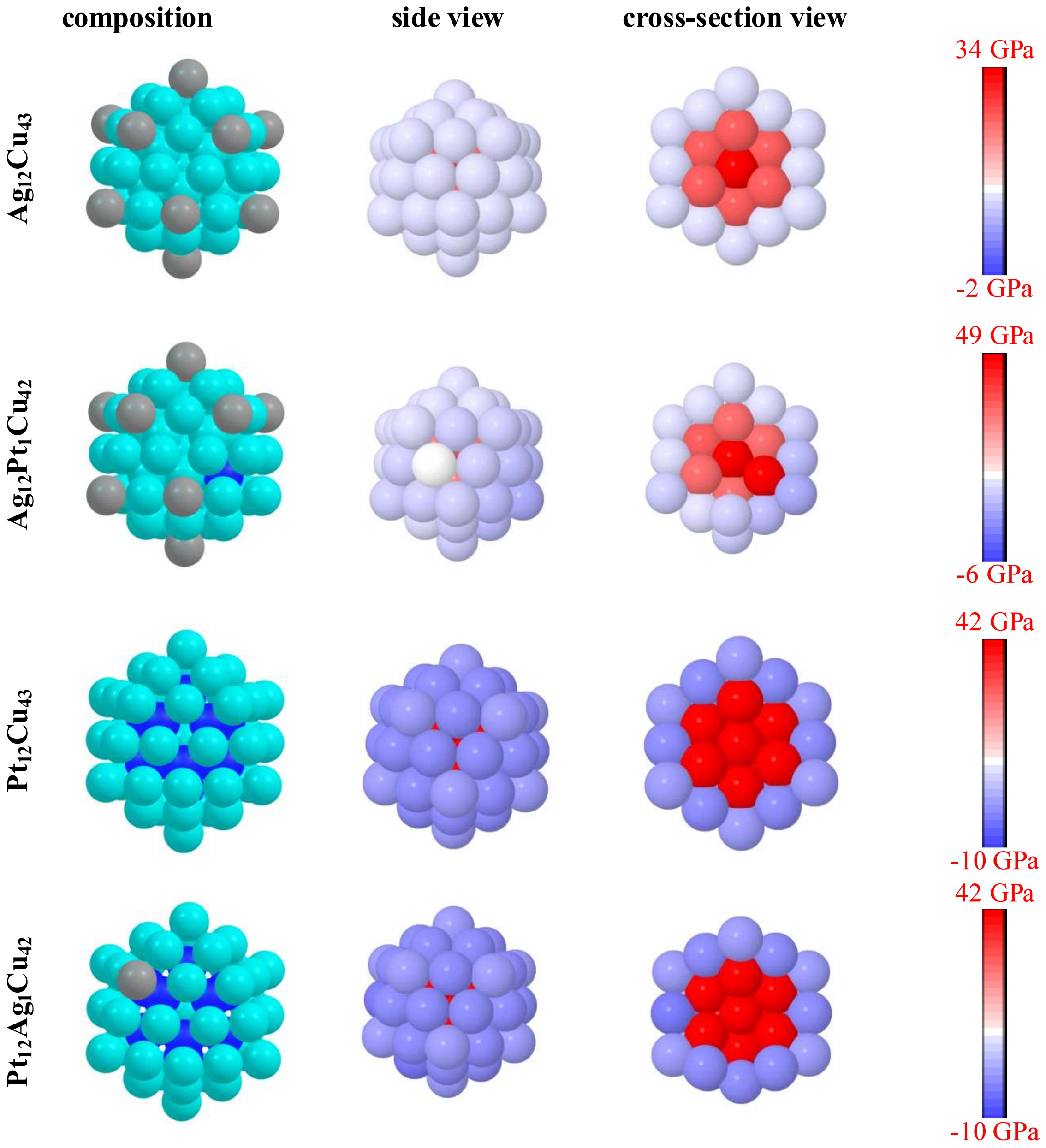

Figure 5. Local atomic pressure for $Ag_{12}Cu_{43}$, $Ag_{12}Pt_1Cu_{42}$, $Pt_{12}Cu_{43}$ and $Pt_{12}Ag_1Cu_{42}$ nanoalloys

In $Cu_{13}Pt_{42}$ binary nanoalloy, one Cu atom occupies the central site and remaining 12 Cu atoms occupy the vertex atoms of the shell. Central Cu atom has a positive pressure value however, 12 vertex Cu atoms have negative pressure. Besides, 12 Pt atoms occupy the subshell and remaining 30 Pt atoms locate on shell. 12 subshell Pt atoms have positive pressure values however, shell Pt atoms have negative values. It can be said that positive local pressure increases with the distance in the core region. In shell region the pressure of vertex atoms is more negative than others. With the introduction of one Ag atom, single Ag atom locates on surface in ternary $Cu_{13}Ag_1Pt_{42}$ nanoalloy and has the more negative pressure value of the shell. Also, with the introduction of one Ag atom more negative and positive pressures appear.

Fig.5 shows the local atomic pressure for $Ag_{12}Cu_{43}$, $Ag_{12}Pt_1Cu_{42}$, $Pt_{12}Cu_{43}$ and $Pt_{12}Ag_1Cu_{42}$ nanoalloys. For binary $Ag_{12}Cu_{43}$ nanoalloy, 12 Ag atoms prefer to locate on surface vertex and local pressures of vertex atoms are negative. The pressure of the Cu atom at central site is also positive and on average decreases with the distance from the center. However, for $Ag_{12}Pt_1Cu_{42}$ nanoalloy all of the Ag atoms are not at vertex of the surface and pressure value of one Ag atom is much closer to 0. The pressure of the Cu atoms at surface is between -2 GPa and -6 GPa. The pressure of the single Pt atom is higher than the central site. It can be concluded that positive and negative local pressure values increase with the addition of one Pt atom to binary $Ag_{12}Cu_{43}$ nanoalloy.

$Pt_{12}Cu_{43}$ binary nanoalloy exhibits a classical three-shell onion-like structure. There is a Cu atom located in the central site of the icosahedral structure with the 12 Pt atoms occupying the whole subshell and the remaining 42 Cu atoms occupy the third shell. The pressure of the central site is more positive than subshell Pt atoms. All surface Cu atoms have negative pressure. For $Pt_{12}Ag_1Cu_{42}$, the doped Ag atom locates on surface and has a negative pressure value. The pressure scale shows similarity with $Pt_{12}Cu_{43}$, although it was observed that some increase and decrease of the local atomic pressure values of the structure.

As a result, if an atom feels a negative pressure, it means it is suffering tensile strain and if an atom feels a positive pressure, the strain is compressive. It can be concluded that doping one atom of second alloying metal in pure nanoclusters and also third alloying metal in binary nanoalloys can change the local atomic pressure due to elemental properties of the doped atom.

4. CONCLUSIONS

In this study, simulations were performed to analyze alloying effect on chemical ordering and structural properties of nanoclusters. 55-atom nanoclusters consist of Cu, Ag and Pt atoms were chosen to study. The best chemical ordering structures were obtained and Cu, Ag and Pt atoms preferred to locate in accordance with their elemental properties such as surface, cohesive and atomic radius. Our results show that doping one atom of second alloying metal in pure nanoclusters and also third alloying metal in binary nanoalloys can change the local atomic pressure due to elemental properties of the doped atom. It can be concluded that doping a smaller atom at the central site of the icosahedral structure exhibits decreasing of core stress and also relaxation of the strained icosahedral structure.

Acknowledgments

The author thanks to Dr. Haydar Arslan for providing the atomic pressure code.

REFERENCES

[1] F. Baletto and R. Ferrando, “Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects,” *Rev. Mod. Phys.*, vol. 77, no. 1, pp. 371–423, 2005.

[2] R. Ismail, “Theoretical studies of free and supported nanoalloy clusters,” 2013.

[3] R. Johnson, *Atomic and Molecular Clusters*. 2014.

[4] R. Ferrando, J. Jellinek, and R. L. Johnston, "Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles," *Chem. Rev.*, vol. 108, no. 3, pp. 845–910, 2008.

[5] R. Ferrando, "Determining the equilibrium structures of nanoalloys by computational methods," *J. Nanoparticle Res.*, vol. 20, p. 179, 2018.

[6] R. Ferrando, *Structure and properties of nanoalloys*. Elsevier, 2016.

[7] T. P. Martin, "Shells of atoms," *Phys. Rep.*, vol. 273, pp. 199–241, 1996.

[8] R. Ferrando, "Symmetry breaking and morphological instabilities in core-shell metallic nanoparticles," *J. Phys. Condens. Matter*, vol. 27, p. 013003, 2015.

[9] D. Bochicchio and R. Ferrando, "Morphological instability of core-shell metallic nanoparticles," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 87, no. 16, p. 165435, 2013.

[10] T. X. Li, Y. L. Ji, S. W. Yu, and G. H. Wang, "Melting properties of noble metal clusters," *Solid State Commun.*, vol. 116, no. 10, pp. 547–550, 2000.

[11] C. Mottet, G. Rossi, F. Baletto, and R. Ferrando, "Single impurity effect on the melting of nanoclusters," *Phys. Rev. Lett.*, vol. 95, no. 3, p. 035501, 2005.

[12] D. Cheng and D. Cao, "Ternary alloying effect on the melting of metal clusters," *Eur. Phys. J. B*, vol. 66, no. 1, pp. 17–23, 2008.

[13] M. Zhang and R. Fournier, "Structure of 55-atom bimetallic clusters," *J. Mol. Struct. THEOCHEM*, vol. 762, no. 1–3, pp. 49–56, 2006.

[14] R. P. Gupta, "Lattice relaxation at a metal surface," *Phys. Rev. B*, vol. 23, no. 12, p. 626, 1981.

[15] V. Rosato, M. Guillope, and B. Legrand, "Thermodynamical and structural properties of f.c.c. transition metals using a simple tight-binding model," *Philos. Mag. A*, vol. 59, no. 2, pp. 321–336, 1989.

[16] S. Taran, A. K. Garip, and H. Arslan, "Theoretical study of the structures and chemical ordering of CoPd nanoalloys supported on MgO(001)," *Int. J. Mod. Phys. C*, vol. 27, no. 12, p. 1650146, 2016.

[17] H. Arslan, A. K. Garip, and S. Taran, "A molecular dynamics study: structural and thermal evolution of 147 atom ComAun nanoalloys," *J. Nanoparticle Res.*, vol. 21, no. 6, p. 130, 2019.

[18] H. Arslan, A. K. Garip, and R. L. Johnston, "Theoretical study of the structures and chemical ordering of cobalt–palladium nanoclusters," *Phys. Chem. Chem. Phys.*, vol. 17, no. 42, pp. 28311–28321, 2015.

[19] S. Taran, "Composition effect on melting behaviors of Cu-Au-Pt trimetallic nanoalloys," *Comput. Theor. Chem.*, vol. 1166, p. 112576, 2019.

[20] H. Akbarzadeh, M. Abbaspour, and E. Mehrjouei, "Effect of systematic addition of the third component on the melting characteristics and structural evolution of binary alloy nanoclusters," *J. Mol. Liq.*, vol. 249, pp. 412–419, 2018.

[21] G. Rossi and R. Ferrando, "Combining shape-changing with exchange moves in the optimization of nanoalloys," *Comput. Theor. Chem.*, vol. 1107, pp. 66–73, 2017.

[22] X. Wu, G. Wu, Y. Chen, and Y. Qiao, "Structural optimization of Cu - Ag - Au trimetallic clusters by adaptive immune optimization algorithm," *J. Phys. Chem. A*, vol. 115, no. 46, pp. 13316–13323, 2011.

[23] Z. Zhao, M. Li, D. Cheng, and J. Zhu, "Understanding the structural properties and thermal stabilities of Au-Pd-Pt trimetallic clusters," *Chem. Phys.*, vol. 441,

pp. 152–158, 2014.

[24] D. J. Borbón-González, A. Fortunelli, G. Barcaro, L. Sementa, R. L. Johnston, and A. Posada-Amarillas, “Global minimum Pt13M20 (M = Ag, Au, Cu, Pd) dodecahedral core-shell clusters,” *J. Phys. Chem. A*, vol. 117, no. 51, pp. 14261–14266, 2013.

[25] D. Cheng, X. Liu, D. Cao, W. Wang, and S. Huang, “Surface segregation of Ag-Cu-Au trimetallic clusters,” *Nanotechnology*, vol. 18, no. 47, p. 475702, 2007.

[26] D. J. Wales and J. P. K. Doye, “Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms,” *J. Phys. Chem. A*, vol. 101, no. 28, pp. 5111–5116, 1997.

[27] R. Ferrando, “Stress-driven structural transitions in bimetallic nanoparticles,” *Front. Nanosci.*, vol. 12, pp. 189–204, 2018.